Characterising Pesticide Runoff from Soil on Cotton Farms using a Rainfall Simulator

A thesis submitted to the
Faculty of Agriculture, Food and Natural Resources
University of Sydney
for the Degree of Doctor of Philosophy

By
David Mark Silburn

September 2003
Statement of Originality

Unless indicated otherwise, the results presented in this thesis are from original works of the author.

D. Mark Silburn
September 2003.
ACKNOWLEDGEMENTS

The scale of work undertaken was only possible because of cooperation between the field studies (under my direct supervision) and the analytical laboratory (directed by Bruce Simpson), and activities undertaken by related projects. Experimental work was funded by the Department of Natural Resources and Mines (NR&M) and Land and Water Australia (LWA), Cotton Research and Development Corporation (CRDC) and Murray Darling Basin Commission (MBDC), under the 'Minimising the Impact of Pesticides on the Riverine Environment Program', and DuPont Ag. Products (Jondaryan study).

Spraying was conducted at Gatton, Emerald and Warren by staff from C-PAS (Centre for Pesticide Application and Safety, University of Queensland; Nicolas Woods, Gary Dorr, Robert Battaglia) and at Jondaryan by Mr Geoff Cornwell (Du Pont, Toowoomba). Pesticide analysis on water, soil and crop residue samples were performed by Robert Lee, Kelvin Spann, Leslie Ruddle, Bill Osbourne, Phil Hargreaves and Bruce Simpson (Pesticides Laboratory, Indooroopilly, NR&M), and Mary Hodge and staff of Queensland Health Scientific Services (Jondaryan study). Helen Beasley and Shuo Wang performed pesticide analyses by ELISA Immunoassay.

A number of people made sterling contributions to the various field studies, including Dr. Robin Connolly ('Horsepower'), Jim Bourke ('Mr Rainfall Simulator'), Ralph deVoil ('KingRalf'), Steve Glanville ('The original simulator'), Keith Goodings (“An Oxy’ll fix that”), Graham Welsh, Graeme Wockner ('Mr. Meticulous'), with Irene Jacobson and Jeff Mitchell doing a great job in ‘the lab of no fixed address’ (all from NR&M). Staff operating the field studies also provided essential assistance in setting up field experiments, at Warren NSW (Ivan Kennedy, Steve Kimber, Lyndal Hugo, Paco Sanchez-Bayo, University of Sydney), and at Emerald Qld (Evan Thomas, Bob Noble, NR&M).

I am also indebted to Jenny Foley (NR&M) for undertaking statistical analysis, with guidance from Kerry Bell (QDPI), Lisette Bourke (CSIRO) for help in compiling the manuscript, and Andrew Biggs (NR&M) and David McKenzie for soils information. AUSCOTT Farms (Dave Anthony, Stefan Henggeler, Chris Hogendyke, Harvey Gaynor), the Hopson family (Emerald) and the Armstrong family (Jondaryan) provided access to their farms, provided water, field preparation, insights into what is involved in cotton farming and put up with us in good humour.

The following people provided valuable comments on the manuscript: Dr. David Freebairn for encouragement to “keep going”, Bruce Simpson “No one has a monopoly on understanding pesticide behaviour”, Dr Lyndal Hugo, Dr Rob Loch, Dr Peter Hairsine, unnamed and brave referees of the two chapters published in Australian Journal of Soil Research, and in particular Prof. Ivan Kennedy.

I would like to thank my colleagues at NR&M, APSRU, CRC For Catchment Hydrology and the Australian Cotton CRC for putting up with my ‘absences’ from project activities (and not inviting me to lots of meetings!), in particular Dr Chris Chilcott, Philippa Tolmie, Ralph deVoil, Iain Drever, Don Peglar, Jenny Foley and Jyo Yee Yet, who operated our projects so well over the last few years. I thank my family for their understanding at a time when they have had their own hardships to deal with and for my mother’s sterling advise ‘wind it up, just wind it up’.

I would particularly like to thank Professor Ivan Kennedy and Dr David Freebairn for their advice, encouragement and patience.
PUBLICATIONS

Publications from this thesis and related work:


Finlayson B and Silburn DM (1996). Soil, nutrient and pesticide movements from different land use practices and subsequent transport by rivers and streams. *In* ‘Downstream Effects of Land Use’. (Eds HM Hunter, AG Eyles, GE Rayment.) pp. 129-140. (Dept. of Natural Resources: Brisbane)


ABSTRACT

This study considered runoff of pesticides from cotton fields using a rainfall simulator. The Australian cotton industry is based on clay soils on low sloping land and uses a hill-furrow surface geometry. These conditions are unlike those in many studies of pesticide dissipation, sorption and runoff and there has been little previous research into hydrology, erosion and pesticide runoff in the industry. Of particular interest was to characterise runoff of different pesticides, clarify the underlying factors controlling pesticide runoff, and investigate management practices to reduce runoff of pesticides with contrasting chemical properties, for the conditions found in the cotton industry.

Runoff behaviour of different pesticides has often been studied independently. Separating the inherent behaviour of the pesticide and the conditions of the study, and comparing pesticides, is difficult. Runoff concentrations depend on the hydrology and erosion of each site, and particularly on the timing of runoff events after spraying. These factors can be controlled and/or measured using a rainfall simulator. Furthermore, multi-residue pesticide analysis now allows study of a number of pesticides simultaneously, so that their behaviour can be compared directly for the same site conditions and management options.

Review of the literature indicated that a large variation in pesticide runoff is related to application rate, formulation and placement, and dissipation, and that only a shallow soil surface layer contributes pesticides to runoff. In this study, the analysis was simplified by only considering placement on the soil surface (i.e. not on plant foliage) of liquid/emulsified formulations and soil-incorporated sprays. A simple conceptual framework was used to compare and integrate data from simulated rainfall studies of pesticides used in the cotton industry and contrast them with data in the literature. By comparing pesticide runoff to the concentration in the soil surface at the start of rain, one set of factors, those that occur before the rainfall event - application and dissipation, were separated from those that occur during the rainfall event – leaching and runoff extraction.

To complete the picture of how pesticides get from the spray nozzle to the edge of a field in runoff, four main areas were considered - dissipation, runoff extraction, sediment-water partitioning and management. Dissipation data were collected at four sites across the cotton growing areas and runoff data at three of these sites, on soils with medium to high clay content. Some 14 pesticides were studied, including the insecticide endosulfan (α- and β-isomers and the breakdown product endosulfan sulfate) at all sites.

Dissipation studies concentrated on the 3-6 weeks after application, when concentrations are highest, and on the soil surface layer that contributes pesticides to runoff. For practical reasons, soil concentrations were measured in the 0-25mm soil depth. While the major emphasis was on dissipation of endosulfan from soil and crop residues, several organophosphate (OP) insecticides
(chlorpyrifos, dimethoate and profenofos) and a range of herbicides (fluometuron, metolachlor, prometryn, diuron, pendimethalin, pyrithiobac sodium) were also studied.

Dissipation in the 0-25mm soil depth followed first-order exponential decay, with one phase, for most pesticides. However, large initial losses occurred for several of the insecticides studied: 35-55% for endosulfan, but only when applied at higher temperatures, most likely due to volatilisation. Initial losses of 50-75% occurred for the OP’s, dimethoate (inconsistently), chlorpyrifos and profenofos.

Dissipation half-lives in the 0-25mm soil depth (after initial losses) were 6-20 days for endosulfan (total of α-, β- and sulfate), 8-13 days for organophosphates, and 13-32 days for herbicides. α-endosulfan consistently dissipated more rapidly than β-endosulfan, but the two isomers were affected differently by site and/or climatic factors. Dissipation of endosulfan was similar for ULV and EC formulations, for bare and covered soil and for band and blanket sprays, but was somewhat slower after two applications. Only small amounts of endosulfan sulfate formed in dry soils, while more formed in temporarily wet soil, contributing about half the total endosulfan remaining after 30 days.

Dissipation in surface 0-25mm soil was more rapid than in 0-50mm soil, but this varied from no effect for the rapidly dissipated OP’s to 1.6 times faster for endosulfan, and varied according to Koc for the herbicides. Herbicides with lower Koc dissipated faster in the surface layer than those with higher Koc, due to greater downward movement. Downward movement decreased the apparent half-life in the 0-25mm soil and increased the apparent half-life in 0-50mm soil. Half-lives in 0-25mm soil were considerably lower than published ‘selected’ values. Dissipation of endosulfan was consistent with studies in other warmer climates. The shallow depth of soil studied (which enhanced downward movement) and application on the surface contributed to this more rapid dissipation. The results are consistent with observations that “runoff available residues” dissipate more rapidly than generally expected for bulk soil.

Endosulfan dissipated rapidly (e.g. 75-90%) from crop residue cover (wheat or cotton trash) within the first day after spraying, apparently a result of volatilisation. Half-lives for endosulfan on crop residues after the initial loss were similar to those in bare and covered soils. The data indicate that a benefit of retaining crop residues on the soil surface, in addition to reducing runoff and sediment losses, is that it intercepts and dissipates the endosulfan more rapidly than when sprayed onto soil.

Runoff extraction was investigated, in a simple empirical analysis, by comparing concentration in soil (mg/kg) before rain and event average concentration in runoff (μg/L), using data from three rainfall simulator studies in cotton fields, for 14 pesticides, and from the literature. The ratio of runoff to soil concentrations, or the linear regression slope fitted through the origin, was termed the runoff extraction ratio (ER0). The pesticides varied widely in solubility (0.003-700,000mg/L) and ranged from strongly (DDE, Kd~15,000) to weakly sorbed (fluometuron, dimethoate, pyrithiobac sodium, Kd <30).
Runoff extraction behaviour from bare soil was remarkably consistent for pesticides of widely different properties. Total concentrations in runoff of each pesticide were closely related to concentrations in the soil (0-25mm) before rain, generally with a similar relationship for all pesticides and sites, over four orders of magnitude range in concentrations. As a first approximation, concentration in runoff (μg/L) = 28 times concentration in soil (mg/kg), (or $E_{RO} = 28$). Runoff extraction was also somewhat similar for dissolved N and P, and organic N.

$E_{RO}$ values were not related to partition coefficients ($K_P$) measure in runoff. However, runoff extraction did decrease with time after spraying and was lower for aged DDE and trifluralin at one site. This is considered to relate to lower concentrations in the surface few mm of soil (c.f. 0-25mm soil) over time. $E_{RO}$ values were similar for the slopes studied (0.2-4%), for long and short plots, and for banded and blanket spray plots. Runoff extraction was reduced where cover reduces sediment concentration. Runoff extraction was significantly lower for a weakly sorbed pesticide (dimethoate) in only one instance and not for a range of other weakly sorbed pesticides at the other sites.

Concentrations in the water and sediment phases in runoff, and in sediment (mg/kg), were also linearly related to soil concentrations for pesticides of similar $K_P$, but extraction in two phases varied according to normal partitioning (Eqn 5-5). The sediment concentration in runoff (10-60 g/L from bare plots) had a secondary effect on $E_{RO}$, and only affected $E_{RO}$ when sediment concentration was low (i.e. with cover). This is because higher sediment concentrations were associated with lower concentrations in the sediment (mg/kg), due to greater desorption and decreasing physical enrichment.

Less physical enrichment (due to size-selective sediment sorting) occurred than observed on coarser textured soil (e.g. enrichment ratio up to 8), with enrichment ratios mostly less than 1.0 (due to desorption) and no greater than 2.0. For all pesticides, the concentration in sediment (mg/kg) was within a factor of about two of the soil concentration adjusted for desorption using the normal partitioning equation. Organic carbon and clay were also only slightly enriched in sediment, despite considerable deposition in the furrows. This is because the soils eroded as aggregates (due to low sand and high clay content), and because coarser sediment had greater concentrations of sorbed pesticides than finer sediment, the opposite of what is normally expected (e.g. where coarser sediment is sand).

The notable similarity of runoff extraction ratio for all pesticides in the rainfall simulator studies was probably because (a) the main factor that limit runoff of weakly sorbed chemicals, i.e. leaching from the runoff mixing zone, was ineffective because of low infiltration and ponding of infiltrated water in the shallow tilled layer in the bottom of furrows, (b) sediment concentrations were high enough to ensure transport of strongly sorbed pesticides, and (c) all pesticides had some transport in both the water and sediment phases, diluting the response to sediment load. The concentration of pesticide extracted from soil into runoff appears to be determined by the soil concentration, with, in the absence of significant leaching and with sufficient sediment transport, little differentiation between pesticides of different partition properties. This is partly because, on any plot, the same mass of soil
and the same volume of water are involved in mixing, independent of the chemical being considered, and because factors that increase extraction of solutes also tend to increase detachment of sediment.

Analysis of published runoff data for a range of pesticides in US croplands indicated similar average runoff extraction to the rainfall simulator studies in Australian cotton fields. However, runoff extraction was higher for much more erosive conditions (e.g. cultivated 10-15% slopes) and lower for low erosion conditions (furrow irrigation on low sloping fields in California). Runoff extraction was similar for this latter case (i.e. $E_{RO}=30$) once adjusted to a higher sediment concentration.

Analysis of the rainfall simulator and published data presents a conceptual framework where the major drivers of pesticide runoff were separated between (a) application rate and dissipation, described by soil concentration at the start of rain, which accounts for five orders of magnitude differences in runoff concentrations, and (b) runoff extraction during the rainfall event, which varied over a limited range. The first of these factors causes most of the difference in runoff between pesticides.

Partition coefficients in runoff ($K_p$) were not affected by cover and wheel traffic treatments even though these treatments had large effects on pesticide runoff concentrations. $K_p$ values increased with time after spraying, rapidly in the first few days and more slowly over the next few weeks, for all pesticides. $K_p$ values were greater than soil sorption $K_d$ values, increasingly so for pesticides of lower sorption. Thus pesticides normally considered weakly sorbed were much more sorbed in sediment than expected, particularly at longer times. Conversely, moderately/strongly sorbed pesticides, such as endosulfan, were less sorbed than expected in the first day or so.

Partitioning appeared to be influenced by both time of contact with soil and time of mixing (during rain). The results are conceptually consistent with a two-compartment, bi-phasic (fast-slow) sorption model, with the soil in the runoff-mixing layer under rainfall being a continuous dilution system. The ‘slow’ phase, due to diffusion into less accessible soil domains, leads to increasing partition coefficients with greater time of contact. The short time of mixing means that the water phase is mainly interacting with the ‘fast’ or most accessible fraction, while the ‘slow’ fraction remains in the sediment phase.

Percentages in the water phase in runoff, for 14 pesticides, roughly followed a published relationship with solubility, and an empirical relationship with soil sorption $K_{oc}$ values, but only for erosive conditions. These relationships do not reflect the full range in responses that occur due to the likely range of concentrations and organic carbon content of sediment, or the increase in $K_p$ with time. Because of lower $K_p$ values soon after spraying, less soluble pesticides had 20-45% in water. Conversely, a few days/weeks after spraying, more soluble pesticides had only 60-80% in water. Thus all pesticides tended to have a ‘foot in each camp’ and some potential for management using erosion control practices.

It is an over simplification to expect ‘percent in water’ to be a characteristic of a pesticide. So long as sediment concentration and $K_p$ can be estimated, the percentage in the water phase can be...
calculated quite simply from first principles (Eqn 5-5) and behaviour for relevant field conditions can be assessed. This equation was used to show that reported values of percentage in the water phase for endosulfan that appeared to conflict (20-95%) and the values from the rainfall simulator plots (15-45%) are explained by differences in sediment concentration and organic carbon in the studies. A wide range of percentages in water (10-95%) will occur for pesticides with $K_p$ of 5-500 (or solubilities $\sim$1-100), such as endosulfan, for the range of sediment concentrations and organic carbon that might occur in the environment.

Improved practices are needed to minimise soil erosion, and related agrochemical transport, from cotton fields during rain. The most influential practice used in other agricultural industries, that is, retaining crop residues as surface cover, is rarely practiced in the Australian cotton industry. Therefore two options available to cotton growers, namely retention of surface cover and controlling wheel traffic, were evaluated using simulated rain on a well-aggregated black Vertosol. Increasing cover (0-60%) resulted in decreasing runoff, soil loss and sediment concentration. Runoff and soil loss were reduced by an order of magnitude with about 50% cover and by a small amount with no-traffic. Cover and no traffic combined gave least runoff and soil loss.

Pesticide transport in runoff was also reduced strongly by retaining on-ground cover and somewhat reduced by avoiding prior wheel traffic. With 45-60% cover, concentrations were reduced 5-fold for $\alpha$-, $\beta$- and total endosulfan; halved for endosulfan sulfate, trifluralin and DDE, and unchanged for prometryn. Cover had more effect on endosulfan because cover intercepted and dissipated the sprayed endosulfan, reducing concentrations in surface soil. Cover greatly reduced total pesticide losses (g/ha) because cover reduced runoff and soil loss considerably. With 45-60% cover, total losses were reduced by 90-98%. No-traffic gave 40% lower losses, and enhanced the effect of cover, but did not prevent large pesticide losses from bare plots. Cover provided more control of more soil-sorbed pesticides (endosulfan, trifluralin and DDE). Control of the less sorbed prometryn was largely due to cover reducing runoff.

An examination of the practical requirements for maintaining effective cover in cotton farming systems indicated that most of the perceived conflicts with insect, weed and irrigation management could be overcome, although further study is needed.

Many of these results have only been possible because of the use of the rainfall simulator, multi-residue pesticide analysis and the availability of sufficient resources. Such opportunities are rare in field research. By allowing an intensive regime of runoff sampling at controlled times after pesticide applications, the study has yielded data with more significance, enabling the conclusions made above regarding the relative behaviour of individual pesticides and their extraction from soil in runoff. The author acknowledges the contributions made by others to this study, but all of the experimental work and the data reported in this thesis were under his control.
# ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>alpha (generally referring to alpha isomer of endosulfan)</td>
</tr>
<tr>
<td>β</td>
<td>beta (generally referring to beta isomer of endosulfan)</td>
</tr>
<tr>
<td>μ</td>
<td>micro ($10^{-6}$)</td>
</tr>
<tr>
<td>m</td>
<td>milli ($10^{-3}$)</td>
</tr>
<tr>
<td>K</td>
<td>kilo ($10^3$)</td>
</tr>
<tr>
<td>M</td>
<td>mega ($10^6$)</td>
</tr>
<tr>
<td>cm</td>
<td>centimetres</td>
</tr>
<tr>
<td>d</td>
<td>days</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>g.a.i.</td>
<td>grams active ingredient</td>
</tr>
<tr>
<td>ha</td>
<td>hectares</td>
</tr>
<tr>
<td>hr</td>
<td>hours</td>
</tr>
<tr>
<td>L</td>
<td>litre</td>
</tr>
<tr>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>mm</td>
<td>millimetres</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>CEC</td>
<td>cation exchange capacity of soil</td>
</tr>
<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
</tr>
<tr>
<td>DL</td>
<td>detection limit of pesticides analysis</td>
</tr>
<tr>
<td>DSS</td>
<td>days since spraying</td>
</tr>
<tr>
<td>EC</td>
<td>emulsified concentrate pesticide/ water based high volume formulation</td>
</tr>
<tr>
<td>ECD</td>
<td>Electron Capture Detector</td>
</tr>
<tr>
<td>ELISA</td>
<td>enzyme-linked immuno-sorbent assay</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance (Pressure) Liquid Chromatography</td>
</tr>
<tr>
<td>KD</td>
<td>linear distribution coefficient for partitioning in soil-water (L/kg)</td>
</tr>
<tr>
<td>KOC</td>
<td>linear distribution coefficient for partitioning in soil organic carbon-water (L/kg)</td>
</tr>
<tr>
<td>KP</td>
<td>linear distribution coefficient for partitioning in (runoff) sediment-water (L/kg)</td>
</tr>
<tr>
<td>KH</td>
<td>Henry coefficient for distribution between vapour-water</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>OC</td>
<td>organic carbon content of soil (%)</td>
</tr>
<tr>
<td>OM</td>
<td>organic matter content of soil (%) (approximately 1.72 time OC)</td>
</tr>
<tr>
<td>OP</td>
<td>organophosphate (class of pesticide)</td>
</tr>
<tr>
<td>SOL</td>
<td>solubility in water of a pesticide (mass/volume)</td>
</tr>
<tr>
<td>T1/2</td>
<td>half-life of first-order decay (days)</td>
</tr>
<tr>
<td>ULV</td>
<td>ultra low volume pesticide formulation</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>NSW</td>
<td>New South Wales</td>
</tr>
<tr>
<td>Qld</td>
<td>Queensland</td>
</tr>
<tr>
<td>CNWRWQP</td>
<td>Central and North-West Regions Water Quality Program (NSW)</td>
</tr>
<tr>
<td>CRDC</td>
<td>Cotton Research and Development Corporation (Australia)</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organisation (Australia)</td>
</tr>
<tr>
<td>NR&amp;M</td>
<td>Department of Natural Resources and Mines (Qld)</td>
</tr>
<tr>
<td>DLWC</td>
<td>Department of Land and Water Conservation (NSW)</td>
</tr>
<tr>
<td>LWA</td>
<td>Land and Water Australia (formally LWRRDC)</td>
</tr>
<tr>
<td>LWRRDC</td>
<td>Land and Water Resources Research and Development Corporation (Australia)</td>
</tr>
<tr>
<td>MDBC</td>
<td>Murray Darling Basin Commission (Australia)</td>
</tr>
</tbody>
</table>

Mathematical symbols are defined in the text.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>STATEMENT OF ORIGINALITY</td>
<td>I</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>II</td>
</tr>
<tr>
<td>PUBLICATIONS</td>
<td>III</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>V</td>
</tr>
<tr>
<td>ABBREVIATIONS</td>
<td>X</td>
</tr>
<tr>
<td><strong>CHAPTER 1. LITERATURE REVIEW</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.2 AUSTRALIAN COTTON PRODUCTION SYSTEMS</td>
<td>1</td>
</tr>
<tr>
<td>1.2.1 Pesticide use and environmental risks</td>
<td>1</td>
</tr>
<tr>
<td>1.2.2 Infiltration, runoff and soil erosion in cotton fields</td>
<td>3</td>
</tr>
<tr>
<td>1.3 PESTICIDE PROCESSES RELATED TO RUNOFF TRANSPORT</td>
<td>6</td>
</tr>
<tr>
<td>1.3.1 Pesticide processes in the soil</td>
<td>7</td>
</tr>
<tr>
<td>1.4 FACTORS AFFECTING PESTICIDE RUNOFF</td>
<td>17</td>
</tr>
<tr>
<td>1.4.1 Pesticide runoff processes in a cropping system</td>
<td>18</td>
</tr>
<tr>
<td>1.4.2 Pesticide runoff from soil during an event</td>
<td>24</td>
</tr>
<tr>
<td>1.4.3 Sediment-water partitioning</td>
<td>34</td>
</tr>
<tr>
<td>1.5 MANAGEMENT OF PESTICIDES IN RUNOFF</td>
<td>37</td>
</tr>
<tr>
<td>1.5.1 Conservation cropping and stubble retention</td>
<td>38</td>
</tr>
<tr>
<td>1.5.2 Tillage (incorporation of pesticides)</td>
<td>43</td>
</tr>
<tr>
<td>1.5.3 Controlled traffic</td>
<td>44</td>
</tr>
<tr>
<td>1.5.4 Pesticide application rate and method</td>
<td>44</td>
</tr>
<tr>
<td>1.5.5 Pesticide use in different farming systems</td>
<td>45</td>
</tr>
<tr>
<td>1.5.6 Requirements of management practices for controlling pesticide runoff from irrigated cotton</td>
<td>45</td>
</tr>
<tr>
<td>1.6 USE OF RAINFALL SIMULATORS TO STUDY PESTICIDE RUNOFF</td>
<td>46</td>
</tr>
<tr>
<td>1.6.1 Benefits and limitations</td>
<td>46</td>
</tr>
<tr>
<td>1.6.2 ‘Validation’ of rainfall simulators against natural rainfall and larger scales</td>
<td>47</td>
</tr>
<tr>
<td>1.7 AIMS AND SCOPE OF STUDY</td>
<td>48</td>
</tr>
<tr>
<td>1.7.1 Current situation</td>
<td>48</td>
</tr>
<tr>
<td>1.7.2 Aims</td>
<td>49</td>
</tr>
<tr>
<td>1.7.3 Scope of this study</td>
<td>49</td>
</tr>
</tbody>
</table>
### CHAPTER 2. GENERAL METHODS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 EXPERIMENTAL OUTLINE AND DESIGN</td>
<td>50</td>
</tr>
<tr>
<td>2.2 LOCATIONS AND SOILS</td>
<td>52</td>
</tr>
<tr>
<td>2.3 HILL-FURROW GEOMETRY AND PLOT CONDITIONS</td>
<td>53</td>
</tr>
<tr>
<td>2.4 RAINFALL SIMULATOR</td>
<td>54</td>
</tr>
<tr>
<td>2.4.1 Runoff and sediment measurements</td>
<td>55</td>
</tr>
<tr>
<td>2.5 PESTICIDE TREATMENTS AND ANALYSIS</td>
<td>56</td>
</tr>
<tr>
<td>2.5.1 Pesticides studied and their properties</td>
<td>56</td>
</tr>
<tr>
<td>2.5.2 Pesticide application</td>
<td>57</td>
</tr>
<tr>
<td>2.5.3 Sampling for pesticide analysis</td>
<td>58</td>
</tr>
<tr>
<td>2.5.4 Pesticide analysis</td>
<td>59</td>
</tr>
<tr>
<td>2.6 DATA PRESENTATION</td>
<td>61</td>
</tr>
<tr>
<td>2.6.1 Runoff, sediment and soil loss</td>
<td>61</td>
</tr>
<tr>
<td>2.6.2 Pesticide data presentation</td>
<td>62</td>
</tr>
<tr>
<td>2.6.3 Statistical analysis</td>
<td>63</td>
</tr>
</tbody>
</table>

### CHAPTER 3. DISSIPATION OF PESTICIDES IN SURFACE SOIL AND CROP RESIDUES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 INTRODUCTION</td>
<td>64</td>
</tr>
<tr>
<td>3.1.1 Depth and conditions of the runoff mixing layer</td>
<td>64</td>
</tr>
<tr>
<td>3.2 PESTICIDE DISSIPATION</td>
<td>65</td>
</tr>
<tr>
<td>3.2.1 Endosulfan</td>
<td>65</td>
</tr>
<tr>
<td>3.2.2 Scope and aims of this chapter</td>
<td>68</td>
</tr>
<tr>
<td>3.3 METHODS</td>
<td>69</td>
</tr>
<tr>
<td>3.3.1 Experimental outline and design</td>
<td>69</td>
</tr>
<tr>
<td>3.3.2 Calculation of half-lives and initial loss</td>
<td>70</td>
</tr>
<tr>
<td>3.4 RESULTS AND DISCUSSION</td>
<td>71</td>
</tr>
<tr>
<td>3.5 PART A. ENDOSULFAN DISSIPATION FROM SURFACE SOIL</td>
<td>71</td>
</tr>
<tr>
<td>3.5.2 Effects of rainfall on dissipation</td>
<td>76</td>
</tr>
<tr>
<td>3.5.3 Effects of soil depth</td>
<td>78</td>
</tr>
<tr>
<td>3.5.4 Summary of endosulfan half-lives in surface soil</td>
<td>81</td>
</tr>
<tr>
<td>3.6 PART B. ENDOSULFAN DISSIPATION FROM CROP RESIDUES</td>
<td>84</td>
</tr>
<tr>
<td>3.6.2 Discussion</td>
<td>88</td>
</tr>
<tr>
<td>3.7 PART C. OTHER PESTICIDES</td>
<td>91</td>
</tr>
<tr>
<td>3.7.1 Organophosphates</td>
<td>91</td>
</tr>
<tr>
<td>3.7.2 Herbicides</td>
<td>95</td>
</tr>
<tr>
<td>3.7.3 Comparison of soil concentrations (runoff potential) between pesticides</td>
<td>98</td>
</tr>
<tr>
<td>3.8 CONCLUSIONS</td>
<td>100</td>
</tr>
<tr>
<td>3.8.1 Endosulfan in soil</td>
<td>101</td>
</tr>
<tr>
<td>3.8.2 Endosulfan on crop residues</td>
<td>102</td>
</tr>
<tr>
<td>3.8.3 Consequences for pesticide runoff</td>
<td>103</td>
</tr>
</tbody>
</table>
CHAPTER 5. PESTICIDE DISTRIBUTION IN WATER AND SEDIMENT

5.1 INTRODUCTION

5.1.1 Relating pesticide partitioning in runoff and soil sorption

5.2 CONCEPTUAL FRAMEWORK

5.2.1 Pesticide distribution in runoff

5.2.2 Partition coefficients observed in runoff studies

5.2.3 Aims

5.3 METHODS

5.3.1 Data sources

5.4 RESULTS AND DISCUSSION

5.5 PART A. PERCENT OF PESTICIDE LOSSES IN THE WATER PHASE

5.5.2 Endosulfan runoff in the water phase

5.5.3 Comparison between pesticides and with other data

5.6 PART B. SEDIMENT-WATER PARTITION COEFFICIENTS $K_F$ AND $K_{OC}$

5.6.2 Comparison between sites

5.6.3 Comparison with published sorption data

5.7 DISCUSSION

5.7.1 Models for change in partitioning with time after spraying

5.8 CONCLUSION
CHAPTER 6. MANAGEMENT PRACTICES FOR CONTROL OF RUNOFF LOSSES FROM
COTTON FURROWS UNDER STORM RAINFALL. I. RUNOFF AND SEDIMENT
ON A BLACK VERTOSOL...................................................................................................194

6.1 INTRODUCTION........................................................................................................194
6.2 METHODS ..................................................................................................................196
   6.2.1 Location and soil .................................................................................................196
   6.2.2 Experimental rationale and design ......................................................................196
   6.2.3 Rainfall simulator and runoff and sediment measurements.................................198
   6.2.4 Rainfall wet surface and sediment sizes measurements .........................................198
6.3 RESULTS AND DISCUSSION ....................................................................................199
   6.3.1 Effects of cover and wheel traffic on runoff .........................................................199
   6.3.2 Effects of cover and wheel traffic on soil loss ......................................................202
   6.3.3 Effects of cover and wheel traffic on sediment concentration ...............................202
   6.3.4 Effects of cover for a range of storm sizes ..........................................................203
   6.3.5 Sediment sizes in soil surface and in runoff .........................................................203
   6.3.6 Effects of treatments on sediment sizes ..............................................................205
6.4 GENERAL DISCUSSION ............................................................................................207
   6.4.1 Observed processes of sediment generation and deposition in hill-furrow systems 207
   6.4.2 Large storms and small plots in context ..............................................................209
   6.4.3 Implications of sediment sizes for off-site management options .............................210
   6.4.4 Optimal cover placement ....................................................................................210
   6.4.5 Practical requirements of effective cover retention in cotton .................................211
6.5 CONCLUSION.............................................................................................................212

CHAPTER 7. MANAGEMENT PRACTICES FOR CONTROL OF RUNOFF LOSSES FROM
COTTON FURROWS UNDER STORM RAINFALL. II. TRANSPORT OF
PESTICIDES IN RUNOFF..................................................................................................213

7.1 INTRODUCTION........................................................................................................213
   7.1.1 Requirements for managing runoff of pesticides from irrigated cotton ................214
7.2 METHODS ..................................................................................................................215
   7.2.1 Location and soils ...............................................................................................215
   7.2.2 Hill-furrow geometry, rainfall simulator and plot conditions .................................215
   7.2.3 Experimental design ..........................................................................................215
   7.2.4 Pesticides ..........................................................................................................217
7.3 RESULTS AND DISCUSSION ....................................................................................219
   7.3.1 Effects of cover and wheel traffic on pesticide transport .......................................219
   7.3.2 Effect of cover on concentrations of pesticides in soil and runoff .........................226
   7.3.3 Effects of treatments on transport in sediment or water phase ..............................227
   7.3.4 Interactions between cover, sediment sizes and pesticide transport .....................230
   7.3.5 Comparison between pesticides ........................................................................233
   7.3.6 Management of pesticide runoff from cotton fields ..........................................233
CHAPTER 1.
LITERATURE REVIEW
CHAPTER 1. LITERATURE REVIEW

1.1 Introduction

Pesticides include a range of chemicals with diverse environmental effects and of variable properties and toxicity. The risk they present to the surrounding environment is related to the extent to which they may be transported from sites of application. A major mechanism for transport is in surface runoff of water and sediment. This study specifically focuses on pesticide runoff from cotton fields, the relationship between pesticide runoff to pesticide and soil properties, and practices that farmers can use to manage pesticide runoff. The review of literature considers factors influencing pesticide transport in runoff from agricultural lands, examining in detail previous experimental studies.

1.2 Australian cotton production systems

In 1998-99 cotton (*Gossypium hirsutum* L.) was grown on some 550,000 ha in inland New South Wales and Queensland, with 82% of the area irrigated, predominantly by flood irrigation in furrows (Cotton Yearbook 1999). Major cotton growing areas are in:
- New South Wales (NSW), in the Macintyre, Gwydir, Namoi and Macquarie valleys, with smaller areas near Bourke, the Lachlan valley and Murrumbidgee Irrigation Area - about 70% of total area.
- Queensland (Qld), on the Darling Downs, Lower Balonne (near St. George), Emerald, Dawson valley, with smaller areas in the Lockyer and South Burnett near Murgon - some 30% of total area.
- Northern Australia. New development of cotton is occurring in northern Qld (e.g. Richmond), Northern Territory (e.g. Katherine) and northern Western Australia (Ord River Irrigation Area).

Production now exceeds three Mbales and almost one Mtonnes of cottonseed, with gross value of production of $1400M (Cotton Yearbook 1999).

Cotton is grown mainly on cracking clay soils (grey, black and brown Vertosols) although some cotton is grown on a wider range of soils. Irrigation development is mostly on alluvial or colluvial soils in flat valley floors and floodplains (Yule 1997). Cotton has a summer growing season and is grown as a row crop (e.g. 1m rows). Soil compaction was a major problem for the industry and led to wide adoption of controlled traffic systems which limit the furrows used for wheel traffic, retaining raised beds 1-2 m wide from season to season (McGarry 1994). Under furrow irrigation, cotton is planted into the top of hills (beds) separated by furrows used for irrigation and wheel traffic. This hill-furrow geometry and the generally low land slopes lead to a particular set of erosion/sediment transport conditions, which are discussed in a later section. Similarly, the widely used practice of maintaining soil bare of crop residues, and the resulting effects on runoff and erosion, are discussed in detail below.

1.2.1 Pesticide use and environmental risks

(a) Pesticide use in the cotton industry

Some 29 insecticides, 22 herbicides and 9 conditioner/defoliant compounds were in common use on cotton farms as at 1991 (Barrett et al. 1991). At that time, 7-11 insecticide applications were made on average each year, though this varies from year to year due to different insect pressures. Generally, at least two to three herbicides are applied, e.g. two pre-emergent residual herbicides and a knockdown herbicide. Insecticides are applied in stages through the season as part of an Insecticide Resistance
Management Strategy, with endosulfan dominating in Stage I, synthetic pyrethroids in Stage II and organophosphates in Stage III. Some insecticides are applied multiple times in a season. For example, endosulfan may be applied up to seven times at reasonably high rates (e.g. 750 gai/ha) within a short period of the season\textsuperscript{A}. The pesticides (and relative amounts) used in the cotton industry have changed over time, due to changing regulations/registrations, insect resistance, new products etc. For example, use of endrin and DDT was phased out during the 1970’s and 1980’s respectively, while use of endosulfan and pyrethroids increased (Barrett \textit{et al.} 1991).

(b) Environmental risks of pesticides in the cotton industry

Petersen and Batley (1992) assessed environmental risk of pesticides commonly used in the cotton industry, using simple risk factor models (using mass applied, toxicity to fish, dissipation rate and sediment-water partitioning). Endosulfan had the highest risk ranking, due to a combination of high usage and high toxicity, followed by cypermethrin, due to its persistence and high toxicity. Herbicides had a lower risk ranking, due to lower mammalian toxicity.

Given the levels of pesticide usage in cotton production, considerable transport of pesticides can occur in runoff and sediment from cotton fields (Connolly \textit{et al.} 1998, Kennedy \textit{et al.} 1998, Simpson \textit{et al.} 1998), and may contribute to contamination of inland waterways (Muschal and Cooper 1998). Simpson \textit{et al.} (1998) determined that the early part of the growing season was the period of major potential risk for pesticide transport in runoff, because of hydrologic and erosion factors outlined in Section 1.2.2(b), and because soil concentrations of herbicides and insecticides, particularly endosulfan, were elevated due to recent applications. The highest risk period for the more water-soluble herbicides (e.g. prometryn, fluometuron and diuron) was the first 4-6 weeks after application. The risk period for endosulfan was extended by repeated applications resulting in a short-term build-up in the soil and partial conversion to endosulfan sulfate which is slightly more persistent (Kennedy \textit{et al.} 1998). This period may typically extend for some 8-12 weeks after planting, with six applications of endosulfan not atypical. Thus it is highly likely that, when storm rainfall occurs during this period, an endosulfan application was made some time in the previous two weeks.

(c) Pesticides in northern Murray-Darling rivers

Monitoring of water quality in inland rivers where cotton is grown regularly detect a range of pesticides. In 1995-96, endosulfan, atrazine, profenofos, chlorpyrifos, prometryn, metolachlor, pendimethalin, fluometuron and simazine were detected in rivers in northern inland NSW, mostly in the Nov-Mar period (DLWC 1996). Among the herbicides, atrazine was the most widely detected pesticide in the DLWC study, although it is not used in cotton farming (Kookana \textit{et al.} 1998). This is due to widespread use of atrazine in other summer crops and its persistence once in water bodies. Connolly and Waters (NR&M pers. comm.) found that atrazine had a half-life of 150-300 days in the water column in farm dams on the Darling Downs and in the Chinchilla weir on the Condamine River during a period of low flow. Endosulfan was detected regularly within areas of irrigated agriculture in all rivers in the DLWC study area from 1991-1996 (>0.01 μg/L in 75% of water samples in Nov-Mar and 14% of samples outside Nov-Mar). These levels exceeded the current water quality guideline concentration for protection of aquatic ecosystems (0.01 μg/L) but never exceeded the current health guideline value (40 μg/L) although 32% of samples exceeded a health action guideline of 0.05 μg/L.

1.1.1 \begin{flushright}
\textsuperscript{A} Use of endosulfan has since been restricted to three sprays per season.
\end{flushright}
Results are more or less similar from monitoring in the Qld Condamine catchment (CBWC 1999). Sampling at three sites along the Condamine River (1993 to 1997) tested monthly for 20 pesticides of the 144 or so pesticides registered for use in the catchment (based on the audit of Rayment and Simpson 1993). Of these 20 pesticides, nine were detected at one or more sites - in decreasing order of occurrence: atrazine, metolachlor, endosulfan, prometryn, fluometuron, methomyl, diuron, pendimethalin, and dimethoate. The variety, concentration and peak concentrations of pesticides increased with time during the sampling period, probably due to increases in flows, summer crop planting opportunities and pesticide usage due to increased rainfall. Atrazine was detected in 69%, 85% and 91% of samples (increasing with distance downstream) and was often above (NHMRC & ARMCANZ 1996) drinking water guidelines (0.5 μg/L). Concentrations were highest during summer months but were not necessarily absent during winter months. Metolachlor was rarely detected prior to March 1995, but was frequently detected during summer months once summer cropping and application increased. Endosulfan was frequently detected at all three sites, increasingly downstream, and frequently exceeded drinking water guidelines (0.05 μg/L). Other herbicides (prometryn, fluometuron, diuron, pendimethalin) were detected in 7-15% of samples at the two downstream sites, typically in summer, and never exceeded drinking water guidelines.

The pesticides detected in these rivers include compounds either not used in cotton production (e.g. atrazine) or not exclusively used in cotton. Many of the herbicides and some of the insecticides are used in other agricultural industries, particularly grain cropping, and in urban and infrastructure (roads, railways etc) settings, in the catchments. Lock (1998), in a ‘one-off’ sampling of storm flows in Gowrie Creek and its tributaries through Toowoomba, found consistent detections of the triazine herbicides atrazine and simazine at up to 2 μg/L, and the OP insecticides chlorpyrifos (up to 0.29 μg/L) and diazinon (up to 0.09 μg/L). The herbicides are presumably used for weed control around infrastructure. Various forms of DDT and derivatives (total 0.23 μg/L) were detected downstream of the sewerage treatment plant and the refuse dump, but not above them.

Concentrations of pesticides detected in these rivers are small (e.g. 0.1-10 μg/L) compared with concentrations measured from plots and small catchments (up to 200 μg/L for higher usage compounds soon after application). Only a small proportion of the total amount of high usage compounds, such as endosulfan, used in the catchment need enter the river to create the observed low concentrations, especially if it is persistent in the water column and/or bottom sediments. To achieve the higher concentrations detected (i.e. atrazine at 10 μg/L), considerable runoff with concentrations in the order of 10-100 μg/L must be entering the river, given that considerable dilution, and some degradation, sediment deposition, filtering etc., must occur (Willis et al. 1987, Finlayson and Silburn 1996).

1.2.2 Infiltration, runoff and soil erosion in cotton fields

Because pesticide transport in runoff is dependent on runoff and associated sediment movement, an understanding of runoff and erosion from cotton fields is relevant.

(a) Infiltration

Many soils, and in particular cracking clays, have a surface composed of aggregates rather than primary particles. Under rainfall these aggregates only partially break down, initially due to slaking upon wetting with some gradual ongoing breakdown due to raindrop impacts (Loch and Foley 1994). In the absence of cover, raindrop impacts form a surface seal by compaction and rearrangement of particles (both aggregates and primary particles) in a surface layer 3-10 mm thick (Loch 1989, Moss
As rainfall progresses the hydraulic conductivity of the seal decreases and infiltration rate declines (Silburn and Foley 1994). When infiltration rate falls below the rainfall rate (time to ponding) and surface storage capacity is filled, runoff commences.

On bare cultivated soil, surface seals persist between tillage events and become progressively less conductive with cumulative rainfall, even through wetting and drying cycles (Connolly et al. in press). Self-mulching or cracking disrupts the seal during drying, but it return to its previous state when wet by the next rain. Cover prevents surface sealing by intercepting raindrops and adsorbing the energy; steady-state seal conductivity decreases considerably with the proportion of soil exposed to rainfall (Connolly et al. in press). Crop canopy cover appears much less effective in preventing surface sealing than surface cover, due to formation of destructive large diameter drops on the leaves.

If the wetting front advance is slow due to low soil moisture deficit and/or low hydraulic conductivity in the sub-seal soil, ponding and runoff may occur before surface sealing limits infiltration. Furthermore, many soils have less conductive layers under the surface (e.g. B-horizon or a compacted plough pan). Once the wetting front reached this layer, ponding can occur on the restrictive layer, fill the remaining air-filled porosity back up to the surface and cause a further reduction in infiltration rate, or cause runoff if it is not already occurring due to surface sealing (Silburn et al. 1990, Silburn and Connolly 1995). Ponding on restrictive layers is often the cause of runoff from covered soil where cover prevents/reduces surface sealing (Silburn and Connolly 1995, Connolly et al. 1997, Connolly et al. in press). Where there is sufficient slope, water ponded above the restrictive layer will flow laterally and may emerge downslope (exfiltration) to contribute to runoff (a process called shallow interflow). The occurrence and contribution to total runoff of shallow interflow is poorly defined.

These infiltration/runoff processes lead to several mechanisms for extraction of chemicals from soil into runoff: (a) raindrop interaction with pore water in the surface soil, (b) mixing of water and chemical in the soil above the restrictive layer because downward leaching is limited, contributing to a above and (c) via shallow interflow. Also the proportion of water that infiltrates before runoff commences is important in leaching desorbed chemicals out of the surface soil.

(b) Soil erosion by water

In the current cotton production system, the potential for soil erosion by water in the summer cropping season is enhanced by summer dominant rainfall, occurrence of high intensity thunderstorms, frequent irrigation leaving the soil wet and causing erosion directly, and management practices that leave the soil bare. Furrow irrigated cotton is generally grown on low sloping lands (<1%) which is expected to reduce the erosion potential (Yule 1997). However, cotton under furrow irrigation is grown in a hill-furrow system, similar to ridge-till in the United States (Stein et al. 1986); while the coarse scale topography of a field may be virtually flat much of its fine scale surface has steep slopes (e.g. 50% on the sides of the hills). These conditions may alter the dominance of various erosion processes and notions of effects of slope on soil erosion, and the effectiveness of control practices.

Carroll et al. (1995) determined that the critical period for soil erosion from irrigated cotton in the Emerald Irrigation Area (EIA) was early in the growing season, from pre-plant irrigation to canopy closure. During this period there is a high risk of runoff and soil erosion, due to low cover levels, low soil moisture deficits, unconsolidated soil and occurrence of intense storms.
In a review of available data from Australian cotton studies, Silburn et al. (1998) concluded that runoff of 100–200 mm/year was typical from cotton furrows and fields. Annual soil losses averaged about 10 t/ha (2–26 t/ha) and are higher than expected given the low slopes, partly due to direct and indirect effects of irrigation (Table 1.1). This soil erosion leads to sedimentation of farm drains and off-farm drainage networks, requiring expensive ‘de-silting’ (Connolly et al. 1999). While there is a perception that soil erosion is not a significant problem in cotton farming, the amounts of runoff are reasonably large compared with dryland cropping and soil movement is large considering the low slopes (Freebairn et al. 1996). These large fluxes of water and sediment predispose irrigated cotton to pesticide runoff, but this water is often recycled within the farm, particularly during irrigation.

Table 1.1. Summary of mean annual runoff and soil loss measured from irrigated cotton field taildrains, with conventional management practices.

<table>
<thead>
<tr>
<th>Location</th>
<th>No. Site-years</th>
<th>Annual Runoff (mm)</th>
<th>Annual Soil loss (t/ha)</th>
<th>Sediment Concentration (g/L)</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rain</td>
<td>Irrigation</td>
<td>Total</td>
<td>% by rain</td>
</tr>
<tr>
<td>Eira Irrigation Area (EIA) Qld</td>
<td></td>
<td>11</td>
<td>87</td>
<td>83</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>(range)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Macquarie Valley (Warren) NSW</td>
<td></td>
<td>2</td>
<td>156</td>
<td>433</td>
<td>590</td>
</tr>
<tr>
<td>Nevertire</td>
<td></td>
<td>1</td>
<td>n.d.</td>
<td>75</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ewenmar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


However, runoff and soil loss data from irrigated cotton are limited, with most data from the Emerald Irrigation Area (EIA) and some indicative data from Macquarie Valley, NSW (Table 1.1). Studies in the EIA during 1986-1996 (Carroll et al. 1991, Simpson et al. 1995, 1996) indicate that irrigated farming has a higher runoff potential (c.f. dryland) as irrigation maintains a higher soil water status. Runoff was typically 100-200 mm (or 1-2 ML/ha) per cotton growing season. The proportion of runoff from rainfall (c.f. irrigation tailwater) was highly variable from year to year, from 0% to 80%. Tailwater runoff makes a considerable contribution to soil loss, e.g. 8 t/ha in 94/95 from six irrigations. Thus irrigation management can make a large difference to soil loss. Soil losses were greater for storms early in the season when the crop gives less cover and soil is less consolidated. Runoff and soil loss from taildrain outlets were similar to those from furrows. More recent studies (Waters 2001) measured greater soil losses than during the 1986-1996 period reviewed above (which included some very dry years), increasing the estimated mean annual soil loss to about 10 t/ha (Table 1.1).

Studies in the Macquarie Valley NSW indicate that soil loss was 10-12 t/ha per season from fields with slopes of 1:1500 or 0.07 %. That is, soil losses were greater than on the steeper slopes in the EIA (0.5-1.5%). This is based on monitoring from only one year, in two fields, of contrasting soils and behaviour (Silburn 1995). On a grey cracking clay (at Ewenmar, Holden 1995), soil loss was 11 t/ha from irrigation alone (six irrigations, no rainfall runoff) with irrigation inflow stopped when outflow occurred on one or more furrow. This resulted in 2-2.6 hours of tailwater per irrigation and 75 mm of runoff for the season, less than in any year/site in the EIA monitoring. In contrast, on a hardsetting red-brown soil (near Nevertire, Kennedy et al. 1995) soil loss was 10 t/ha, from six irrigations and one...
major rainfall runoff events. However, 742 mm or 7.4 ML/ha of water ran-off from the field (i.e. at taildrain outlet) or 84 mm of tailwater per irrigation. In 1995/96 near Nevertire, Kennedy et al. (1996) recorded 436 mm of runoff (365 mm irrigation, 71 mm storms) from Field 20, confirming the high runoff amounts being generated under some irrigation management programs.

A wide range in runoff was measured at these sites, indicating irrigators may have different strategies in mind. For instance, they may irrigate for long times, generating large tailwater volumes (e.g. up to 1 ML/ha per irrigation), to achieve wetting on soils with poor infiltration (e.g. the hardsetting red-brown soil). While the water may be recycled, the soil loss from the field is increased considerably. Much of this soil is deposited in the taildrains and the remainder in channels and storages.

Studies of erosion control practices in the EIA found that soil loss was 5-10 times less on furrows of 0.5% slope compared with 1-1.5% slope. Soil loss from cotton planted into a wheat cover crop was only 12% of that from conventional cotton. In contrast, retaining cotton trash, reduced tillage and use of unanchored stubble were not effective in reducing soil loss during irrigation on these self-mulching soils. Self-mulching provides sufficient loose surface soil to allow considerable erosion in the absence of tillage. Unanchored trash is often washed away during irrigation. On a grey cracking clay in NSW (Holden 1995), soil loss from irrigation was halved when no-till chemical weed control (without substantial cover) was used rather than two inter-row cultivations. This soil may be more hardsetting than the EIA soils, thus gained some benefit from no-tillage even though there was little cover.

1.3 Pesticide processes related to runoff transport

Pesticides may be applied to the soil (particularly herbicides), or over the plant canopy (particularly insecticides) and be deposited on the plant canopy and on soil depending on the proportion of canopy cover. For insecticides used early in the crop season, such as endosulfan in cotton, a large proportion of the pesticide intended to treat the plant in fact ends up on the soil. Where crop residues are present on the soil surface (e.g. in conservation farming systems) a proportion of the pesticide applied to the soil, or arriving below the plant canopy, will be intercepted by the crop residues. Thus there are three ‘pools’ of pesticides (plant foliage, crop residues and soil) that may be increased by applications and continuously decreased by dissipation, including washoff from plants and crop residues and leaching in the soil during rainfall events (Fig. 1.1). Pesticides transported in runoff are sourced from these pools during rainfall events and are proportional to concentrations in these pools.

Dissipation of a pesticide from the surface pools (soil, crop canopy and crop residues) after application is an important determinant of runoff potential, as runoff potential is strongly related to pesticide concentration on rain-impacted surfaces (Section 1.4.1(c)). Losses may be due to volatilisation, biological or chemical degradation, washoff from crop canopy or residues by rain, and diffusion or leaching deeper into the soil. Because pesticides in runoff are generally sourced from surfaces that are exposed to environmental extremes and to potential volatilisation, dissipation rates influencing pesticide runoff are likely to be more rapid than for the entire mass of material or expected based on conventional estimates of persistence (Leonard 1990). This is reinforced by movement of pesticides into compartments where they are no longer (easily) extracted into runoff e.g. lipophilic compounds into waxy leaf surface (Willis and McDowell 1987, Willis et al. 1980).

This thesis investigates pesticide runoff from soil. Pesticide processes on plant canopies, while important, are not considered here. Therefore processes involved in pesticide behaviour in soil and their consequences to the runoff transport of pesticides, are discussed below.
Fig. 1.1. Water balance and pesticide processes in a crop and soil. Adapted from Leonard et al. 1987.

1.3.1 Pesticide processes in the soil

(a) Soil sorption (soil-water partitioning)

In a soil-water system, a pesticide will have greater or lesser affinity for the solid (soil mineral and organic matter (OM)) phase, which is referred to as sorption. Adsorption refers here in a general sense to transfer from the water phase (and from spray formulations) to the soil phase, while desorption refers to transfer from soil to water phase. The soil-organic matter composition, and reactions and bonding mechanisms involved, are reviewed elsewhere (e.g. Bailey and White 1964, Hamaker and Thompson 1972, Weber 1972, Koskinen and Harper 1990) and will not be discussed in detail here. Rather pesticide sorption in the soil-water system is considered here and in later sections in terms of the resultant partitioning that may impact on pesticide behaviour in soil and thereby on transport in runoff.

Adsorption-desorption processes in soil-pesticide systems are complex, due to the variety of bonding mechanisms possible, the complex composition of the soil-organic matter matrix (Koskinen and Harper 1990) and the heterogeneous nature of soil and pore-water domains (e.g. mobile/immobile regions, Brusseau and Rao 1989). Adsorption-desorption may be non-linear, non-singular, not completely reversible and not necessarily instantaneous, i.e. non-ideal. Brusseau and Rao (1989) comprehensively review the impact of such non-ideal behaviour on organic contaminant transport in porous media. Whether non-ideal behaviour significantly affects the outcome (e.g. environmental risk) depends on whether uncertainty about sorption is outweighed by uncertainty about other specifications of the system (Pionke and DeAngelis 1980) and appears to depend very much on the specific conditions and the pesticide. As shown elsewhere in this thesis, quite large differences in partition coefficients (e.g. >an order of magnitude) may be required for large changes in behaviour such as leaching and sediment-water distribution. Models that assume linear-equilibrium sorption often give adequate predictions (Leonard 1990). In other cases, particularly leaching studies (Brusseau and Rao 1989, Li et al. 1999, Truman et al. 1998a) more complex sorption models (e.g. two-compartments) perform better in reproducing results of a specific experimental study. Also sorption is usually measured in laboratory
studies with high solution-soil ratio and vigorous shaking which may disrupt soil aggregates, and may not be directly applicable to field behaviour (McDowell et al. 1981, Kookana et al. 1998).

Sorption depends on temperature (Bailey and White 1964, Talbert and Fletchall 1965), properties of the pesticide, concentration of pesticide and properties of the soil and the water, as discussed below.

**Pesticide properties.** Solubility and sorption can vary up to 8 orders of magnitude between pesticides, much greater than differences between, say soil types, for a given pesticide. For example, Kookana et al. (1998) found sorption coefficients (K_D) of 0.5-5 for atrazine in 68 Australian soils, with 80% of the variation accounted for by differences in soil organic carbon. Some pesticides are normally always positively (cationic) or negatively (anionic) charged and generally have very strong and very weak sorption, respectively, while other pesticides (referred to as acidic or basic) are capable of forming charged ions and their sorption depends on soil pH (Wauchope et al. 1992). For most other (non-ionic) pesticides, sorption tends to be a ‘hydrophobic’ process ‘in which non-polar chemicals attempt to escape the polar environment of water and enter the less-polar environment of soil organic matter’ (Wauchope et al. 1992) and their sorption tends to depend on soil organic matter (Karickhoff 1981), subject to the other factors described below. Sorption tends to be positively correlated with persistence (see dissipation section below) and, for non-ionic pesticides, negatively correlated with solubility (Wauchope et al. 1992, Weber 1994) and positively correlated with octanol-water partition coefficient (K_{OW}) (Briggs 1981, Kookana et al. 1998). Wauchope et al. (1992) and Weber (1972, 1994) give comprehensive reviews of properties and behaviour of a wide variety of pesticides in soils. Pesticide properties are discussed further below in relation sorption and soil properties.

**Effects of concentration.** At low concentrations of adsorbate, which is often the case with pesticides in soils, there can be a simple linear relationship (isotherm) between concentrations in the water and soil phases (Hamaker and Thompson 1972, Green and Karickhoff 1990). Karickhoff (1981) found for hydrophobic compounds at low concentrations (aqueous phase concentration < half the solubility) sorption isotherms were linear and reversible. Hamaker and Thompson (1972) conducted an extensive literature review and found for the Freundlich isotherm (non-linear with water phase concentration to the power 1/n), the value of 1/n was commonly close to 1 (0.75-0.95). Rao and Davidson (1980) suggest that for many modelling purposes a linear isotherm with a constant slope of K_D would adequately describe most data. Karickhoff et al. (1979) found linear isotherms with no hysteresis for hydrophobic compounds in water-sediment systems. Pesticide distribution between water and soil phases can be described with a simple (linear isotherm) partitioning coefficient (K_D), as:

\[
K_D = \frac{C'_s}{C_w}
\]

Eqn. 1-1

where C'_s (mg/kg) is concentration in soil and C_w (mg/L) is concentration in water, and K_D has units of L/kg (Leonard et al. 1987). This assumes ideal behavior i.e. instantaneous equilibrium, linearity, reversibility and singularity.

**Effects of soil properties.** For non-ionic pesticides, sorption tends to be directly related to soil organic matter (Bailey and White 1964, Briggs 1981, Karickhoff 1981, Chiou 1990). To account for sorption dependence on soil organic matter and to transfer sorption estimates between soils of differing organic matter content, sorption is often normalised using the partitioning coefficient K_{OC}, as:

\[
K_{OC} = \frac{K_D}{OC} \quad \text{or} \quad K_{OC} = \frac{C'_{OC}}{C_w}
\]

Eqn. 1-2
where \( OC \) = fraction of organic carbon in soil, \( C'_{OC} \) = concentration of pesticide per unit mass of OC. This involves further assumptions that sorption is dominated by organic components of the soil and these are invariant in sorption capacity (within and between soils etc) (Green and Karickoff 1990).

Karickhoff (1981) found high correlation coefficients (>0.9) between \( K_D \) and OC, for 5 polycyclic hydrocarbons, for a wide variety of US soils and sediments. A zero intercept at very low OC indicated little contribution of sorption to inorganic material. Linear increases in \( K_D \) with OC content with high correlation were found for 24 non-ionised organic chemicals (mainly substituted ureas and anilides) in 17 diverse Australian soils (Briggs 1981), and for various hydrophobic compounds (Karickhoff et al. 1979) and endosulfan (Peterson and Batley 1993) in water-sediment systems. A review by Kookana et al. (1998) confirms that sorption of non-ionic compounds is directly related to organic matter for Australian soils. Chiou (1990) considered that, compared with OC, soil minerals are a poor adsorbate for non-ionic compounds as the water competes for sorption sites.

However, when a broad range of pesticides are considered (including ionised or ionisable compounds), sorption is generally found to relate to varying degrees to OM or OC, clay content, CEC, surface area and pH (Bailey and White 1964, s-triazines - Talbert and Fletchall 1965, fenamiphos, linuron, simazine and diquat - Singh et al. 1989, metolachlor in soils of low OC - Crisanto et al. 1995, atrazine - Novak et al. 1997). OC is often the soil property most correlated with measured sorption (Talbert and Fletchall 1965, Singh et al. 1989, Gerritse et al. 1996, Crisanto et al. 1995, Novak et al. 1997), but not exclusively. For example, adsorption of prometryn and prometone related more to clay content than OM in 25 soils, while adsorption of atrazine, simazine and propazine related more to OM than clay (Talbert and Fletchall (1965). The soil properties are often significantly correlated among themselves, making interpretation more difficult.

Most of the compounds listed in the previous paragraph are ionic (e.g. diquat - strongly basic, s-triazines – basic) and their sorption is expected relate to surfaces other than OC, however three are non-ionic (metolachlor, fenamiphos, linuron). Bailey and White (1964) considered, based on physical properties of organic and mineral constituents, that: (a) organic matter has a high potential adsorption capacity for pesticides that can be adsorbed as cations and those adsorbed physically, (b) adsorption would vary somewhat between soils due to differences in organic matter composition, while (c) the clay minerals montmorillonite and vermiculite have a great capacity for physical adsorption, while other clay minerals had much less adsorption capacity. Talbert and Fletchall (1965) found adsorption for five s-triazines varied with clay type (kaolinite < illite < montmorillonite), but model organic materials were much more adsorptive than clays. Thus soil OC is likely to describe much of the variation in sorption between soils, but in soils with low OC content, contribution to sorption of other properties can be more significant, for instance, clay content (Seybold et al. 1994) or type of minerals (Gerritse et al. 1996).

For some pesticides and some entire classes of pesticides, sorption is not entirely (or not at all) attributed to OC, either due to pesticide (e.g. ionic/charge) properties or properties of the sorbing materials. Some pesticides with intrinsically different properties will respond quite differently to soil properties. Cationic pesticides such as parquat and diquat are readily adsorbed by clay minerals but only slightly adsorbed by charcoal (Weber 1972, 1994). Acidic compounds are only weakly adsorbed by soils, but can adsorb through anion exchange reactions and sorption is pH dependent (Weber 1972, 1994). However, some acidic compounds (organic As and P acids) are readily adsorbed to clays and some minerals (Weber 1994), e.g. “adsorption of glyphosate increases strongly with clay content and is not, or sometimes is negatively, correlated with organic carbon content” (Gerritse et al. 1996).
Even for non-ionic compounds (including many insecticides and some herbicides used in the cotton industry), caution should be applied in extrapolation of sorption estimates from overseas to cotton growing areas in Australian, due to the prevalence of soils of low OC (as low as 0.5%), higher pH (e.g. 7.7-8.7), high clay content (up to 85%) and swelling clays.

Properties of the water phase. Properties of the water, for instance pH and the presence of salts (Ferris and Haigh 1993), dissolved organic carbon (Baskaran et al. 1996) and other non-settling particles (Petersen and Batley 1991) can affect the apparent partitioning of pesticides. These properties (e.g. dissolved material) are often related to properties of the soil. Baskaran et al. (1996) found that dissolved OC added to the water phase increased the apparent solubility and mobility of atrazine and 2,4-D during leaching. The presence of very small size fractions (non-settling particles, micro-particles such as clay or macromolecules such as dissolved OC and humic acids), which are typically not removed from water by filtering (e.g. 0.45μm) or centrifuging used to separate the water phase, can alter the water chemistry (e.g. pH) and bind pesticides. Furthermore, the particles may have greater availability of sorption sites than organic carbon bound in a soil or sediment matrix. Means and Wijayaratanne (1982) found colloidal particles 10-35 time better as a sorptive substrate for linuron and atrazine (on an organic carbon basis) than sediment or soil organic matter. Sorption to colloids was dependent on the characteristics of the bulk water, such as pH and salinity. This enhances the water phase concentration and apparent solubility (Kookana et al. 1998), and decreases the apparent sorption coefficient, of hydrophobic compounds (Peterson and Batley 1991). Karickhoff and Brown (1978) found greater than 50% of paraquat remaining in the water phase was sorbed on particulates not removed by centrifugation. However, results of detailed studies of the influence of non-settling particles have been mixed, e.g. colloid association was found for linuron and atrazine (Means and Wijayaratanne 1982) but was minimal for endosulfan in natural river waters (Peterson and Batley 1991).

Desorption and effects of kinetics. Karickhoff (1980) found that both adsorption and desorption approached equilibrium in sediment suspensions in two phases, a rapid component which achieved about 50% of final sorption in minutes and a much slower component which continue until the arbitrary end of the study (<24 hr). The slower process was viewed as diffusion to sorption sites that are inaccessible directly to the bulk water. Novak et al. (1994) found adsorption of atrazine to aggregates of two Iowa soils was initially rapid followed by a period of slower sorption, with only minor differences in kinetics (and K_d) for aggregates of different sizes. Much of the final sorbed concentration (at 72 hr) was achieved at the first sampling time of 1 hr (e.g. sorption of 2.5-3 mg/kg occurred in 0-1 hr compared with 0.35-0.5 mg/kg in 1-27 hr).

In reality, "equilibrium is typically only apparent, and sorption and desorption involve a complex system of processes with fast and slow kinetics. Rather than being instantaneous, there are at least three time scales describing sorption-desorption responses to solution concentration changes" Wauchope et al. (in press). These three time scales describing sorption-desorption responses to solution concentration changes are (Wauchope et al. in press): (1) rapid, reversible diffusion and adhesion to "accessible" sites of soil surfaces near the soil/water interface, with a time scale of minutes, (2) slower exchange of pesticide between water and soil phases, that requires between hours and a day or two to approach equilibrium, and appears to be fully reversible, and (3) a very slow reaction, which is now generally referred to as "aging", with a time frame of weeks to months, which stores intact pesticide molecules, that may be freed by subsequent processes.
Models that assume instantaneous linear-equilibrium sorption often give adequate predictions (Leonard 1990). However, more complex sorption models (e.g. two-compartment models which result in two phases of sorption) often perform better in reproducing results of specific experiments, particularly leaching studies (Boesten and Van Der Pas 1983, Brusseau and Rao 1989, Li et al. 1999) but also in the few cases where they have been applied to pesticide runoff (Truman et al. 1998a). Soil physical non-equilibrium (mobile-immobile water domains) and chemical non-equilibrium (fast-slow phases) appear to be closely linked, and result in apparent sorption hysteresis (Brusseau and Rao 1989, Pignetello 1989).

Effects of aging. Leonard and Wauchope (1980) noted that in some field situations the apparent sorption coefficient in soil increased with time during a growing season, that is, pesticides appear to become more difficult to desorb with time of contact in soil. Boesten and Van Der Pas (1983) found that desorption coefficients measured 56 days after application of cyanazine and metribuzin to soil were 2-3 times those from laboratory slurry adsorption studies. After 121 days, desorption coefficients were 6 times and 8 times laboratory values, for cyanazine and metribuzin, respectively. Pesticide models that do not account for this behaviour will tend to over predict leaching (Boesten and Van Der Pas 1983). Leonard (1990) suggests a possible explanation is “pesticide diffusion into the soil organic matter particles with subsequent desorption becoming kinetically inhibited”. Diffusion will tend to transfer pesticides into any region of the soil where there is some degree of attraction (or lack of repulsion) and there is a gradient (i.e. lower concentration), including into the interior of organic macromolecules and aggregates and regions of immobile water (Brusseau and Rao 1989). The aging process influences pesticide behaviour relating to runoff, with aged pesticides tending to have higher sorption coefficients, longer half-lives in soil and as ‘runoff available’ residues, although to varying degrees (Leonard 1990).


\[ K_D(t) = K_{D1} + S(t^{0.5}) \]  

where \( K_D(t) \) is the \( K_D \) value at time \( t \) (days), \( K_{D1} = K_D \) on the first day, \( S \) = slope of the \( K_D \)-time dependence. According to an empirically determined rule \( S = 0.1.K_{D1} \) (Walker and Barnes 1981).

Models that include two sorbed compartments (labile and non-labile) (Kookana et al. 1991, Truman et al. 1998a, Li et al. 1999) and/or physical non-equilibrium (Brusseau and Rao 1989) result in increased \( K_{Dn} \), and increased persistence, with time. Improved predictions of runoff and long-term persistence of atrazine were obtained using the two-compartment model GLEAMS-TC (Truman et al. 1998a). Sorption is considered further in the context of water-sediment partitioning in Chapter 5.

(b) Dissipation from soil

Of most interest here is dissipation from the soil surface layer that interacts with runoff and erosion, 2-20mm thick under rainfall (Ahuja et al. 1981, Sharpley 1985) or the depth of the tilled layer where rilling occurs (the effective depth of interaction is discussed elsewhere). Pesticides in this soil surface layer may dissipate more rapidly than expected based on conventional estimates of persistence, due to a combination of volatilisation, photolysis and leaching, and their exposure to environmental extremes (Wauchope and Leonard 1980, Leonard 1990), although persistence may be greater in surface soil where OC is higher than in subsoil (Malone et al. 1999).

Dissipation involves losses by volatilisation, degradation or transformation (chemical, biological or photochemical) and, for more mobile pesticides, leaching or diffusion into the soil.
Degradation/transformation can be due to abiotic and biotic processes, which both alter the chemical structure of the pesticide causing oxidation, reduction, hydrolysis or other reactions, and it is often difficult to distinguish their relative contribution in a complex system such as soil (Scheunert 1992). A range of factors affects pesticide resistance or susceptibility to the various dissipation processes, and ultimately the potential for runoff transport. These include chemical properties (structure, toxicity, solubility and concentration), application (efficiency, formulation, dose) and soil, environmental and management factors (moisture, temperature, pH, microorganisms) that interact in a complex manner, and are summarised by Leonard (1990) and Ferris and Haigh (1993). From the point of view of soil dissipation, applications above a plant canopy or crop residues and gross inefficiency or error in application (e.g. drift) represent a large difference in the amount of pesticide input and have a large effect on the starting point for calculating dissipation (Walker 1976).

Dissipation rates vary widely between pesticides due to difference in chemical structure, both directly (e.g. stability of bonds in the structure, Scheunert 1992) and via secondary mechanisms such as sorption. Thus there is an association between dissipation and sorption (Wauchope et al. in press), with a significant positive correlation between field half-lives and KOC for all active ingredients in the database by Hornsby et al. (1996). Wauchope et al. (in press) consider pesticide molecules adsorbed to soil surfaces will in general be unavailable for microbial ingestion and degradation. Also a significant proportion of soil pore volume and soil solution is inaccessible to microorganisms such as bacteria due to small pore sizes (e.g. 50% of pore volume <1 μm) (Alexander and Scow 1989).

Dissipation rates can vary between soils due to factors that affect rates of chemical reactions and microbial activity. Walker et al. (1983) found dissipation rates for simazine in a wide range of soils were negatively correlated with organic carbon, clay content and pH. Degradation by abiotic chemical processes such as hydrolysis is dependent on pH. For instance, endosulfan degrades more rapidly in sterile soils of higher pH (Kuar et al. 1998). Dissipation rates can also vary depending on the presence or absence of particular microbes that degrade a particular pesticide or group of related pesticides. For example, Sparling et al. (1998) found that mineralisation of atrazine was associated with numbers of atrazine-degrading microbes and cation exchange capacity of the soil. Mineralisation was very low in subsoils, except for one that had an unusually high number of atrazine-degrading microbes.

(c) **Time course of dissipation**

After a pesticide is applied to soil under field conditions, a series of overlapping dissipation processes may occur (Nash 1980): (a) considerable losses can occur during application and in the following few minutes, due to drift and volatilisation of the pesticide before it has sorbed into the soil-water system, (b) volatilisation from the soil-water system can occur over a few hours for pesticides that degrade rapidly or for several months for more persistent pesticides, (c) penetration, adsorption and/or leaching, and (d) chemical and biological degradation (discussed above). The rates of each of these processes can vary with moisture content and/or temperature. However, as a first approximation pesticide concentration in the soil declines exponentially with time and follows a first-order equation though the processes involved may not be first-order kinetics, decay or reaction (Nash 1980). Pesticide dissipation is often represented by a first-order equation (Haigh and Ferris 1991, Wauchope et al 1992):

\[
C_t = C_{t1} e^{-k(t-t_1)}
\]

\[
t_{1/2} = \ln 2/k = 0.693/k
\]

Eqn. 1-4
where \( C_{t2} \) and \( C_{t1} \) are the concentration of the pesticide at times \( t2 \) and \( t1 \) (days) and \( k \) is the time constant with units of days\(^{-1}\). The half-life \( t_{1/2} \) is defined as the time required for the pesticide to undergo dissipation and/or degradation to half its initial concentration. \( t_{1/2} \) is independent of the initial time and concentration, and concentration would halve with each successive half-life elapsed.

Unfortunately, use of a single half-life is simplistic; due to the variety of dissipation mechanisms of varying rapidity (time course) experienced by pesticides after application, often with a large initial loss due to volatilisation (Nash 1980). An initial single half-life may apply for only a few hours to several half-lives and then the compound exhibits gradually increasing persistence as more rapidly degraded fractions (e.g. residues on the soil surface) are lost (Wauchope et al. 1992). Thus multiple phases of dissipation from soil are not uncommon in field studies (Scheunert 1992). Timme et al. (1986) (cited by Scheunert 1992) found that, for 420 experimental series of soil dissipation data, 35% followed first-order kinetics, 35% followed 'first-order square root kinetics' and 10% followed '1.5 order square root kinetics'. Multi-phase dissipation is also likely where total residues are summed for related compounds (e.g. the \( \alpha \) and \( \beta \)-isomers of endosulfan) with different dissipation rates or include more stable metabolites (e.g. total endosulfan including the sulfate).

Even where microbial degradation dominates, for complex systems such as soil it is unreasonable to always expect a simple rate law, as degradation may be limited by availability of the pesticide, or availability, activity and adaptation of the microorganisms (Torstensson 1987). Models of pesticide fate and transport that do not account for these processes (i.e. \( t_{1/2} \) increasing with time) will overestimate longterm pesticide degradation in soil and underestimate sediment-transported pesticides losses in runoff (Truman et al. 1998a). More complete models that include two compartments of soil pesticide (labile and non-labile) and/or effects of temperature and soil moisture on dissipation may overcome this problem (Haigh and Ferris 1991, Truman et al. 1998a) but require more effort to parameterise.

Dissipation rates can vary through time and with soil depth, due to changes in conditions such as soil moisture content and temperature, because chemical reactions and microbes have preferred ranges in these conditions. Haigh and Ferris (1991) and Sparling et al. (1998) found that degradation of atrazine was a function of soil water content and temperature, with continuous reduction in degradation rates with lower moisture content and with lower temperature. Walker et al. (1983) obtained similar results for simazine. However, as shown by Walker et al. (1983), a model that adjusts dissipation for moisture content and temperature based on laboratory studies may still underestimate dissipation in the field, where surface loss processes (e.g. volatilisation and photochemical degradation) contribute.

It should be noted that losses/gains from surface soil by volatilisation, leaching/advection and diffusion, discussed below, are generally lumped together, with losses by chemical and biological degradation, in dissipation data where pesticide concentrations are measured over time in the field.

(d) Volatilisation

Volatilisation involves the direct physical loss of a pesticide from the soil surface to the overlying air in gaseous form. Since the background vapour pressures of all pesticides in the atmosphere are extremely low, pesticides will evaporate as if in a vacuum, and the overall gradient in vapour pressure is established by the vapour pressure of the pesticide on the surface (Taylor and Spencer 1990). Thus loss through volatilisation can be a major contributor to dissipation from the soil surface for more volatile compounds, e.g. volatilisation losses of 80-90% have been measured within a few days after application (Taylor and Spencer 1990). Volatilisation is controlled primarily by environmental factors (soil moisture content, temperature, surface roughness and wind velocity) and pesticide properties (volatility,
sorption) and distribution within the soil. Taylor and Spencer (1990) regard the main controlling factors as vapour pressure of the pesticide, distribution of the residues and the soil moisture status.

Volatilisation rate is expected to increase with temperature and soil moisture content. Burkhard and Guth (1981) found that volatilisation rates from soil increased 3.5+/-0.75 times with a 10°C increase in temperature, on average for five pesticides, consistent with literature values of a 4-fold change for other pesticides. However, the relationship is non-linear and no simple correlation with temperature can be expected in the field (Taylor and Spencer 1990). Surface soil temperature increases rapidly once soil dries below a certain point, with the two factors working against each other.

The highest volatilisation rates are observed where a pesticide is applied to moist soil, while volatilisation rates are low for very dry soil because many chemicals are very strongly adsorbed by dry surfaces (Graham-Bryce 1981). However, this could only be expected under the driest conditions as even air-dry soil contains a few percent of water (Graham-Bryce 1981). Burkhard and Guth (1981) state the “literature data (Spencer et al. 1969) showed that soil moisture does not affect the volatility of a pesticide from soil as long as the amount of soil water is enough to form a monomolecular layer in the soil.” Thus volatilisation rate remains constant over a wide range in moisture contents and decline rapidly at relatively low moisture content (Taylor and Spencer 1990). For trifluralin, volatilisation was still at a maximum (plateau) rate at 0.06g/g and declined to near zero at 0.02-0.04g/g. For dieldrin, the decline occurred over an even narrower moisture range (see Fig. 7-7 & 7-8, Taylor and Spencer 1990). However, except for immediately after recent surface applications, the rate of volatilisation is likely to be limited by the rate of transport of the pesticide to the soil surface (Graham-Bryce 1981). This probably occurs by advection with upward moving (evaporating) water, which slows rapidly as the soil surface dries. In dry soil, upward transport depends on vapour diffusion, which with some exceptions is slow. Thus, volatilisation is greatly reduced by incorporation of the pesticide deeper into the soil.

Taylor and Spencer (1990) describe volatilisation as involving two distinct processes, which are fundamentally different and are controlled by different chemical and environmental factors; (a) firstly, evaporation of pesticide molecules from the soil into the air, involving a change in phase from solution into vapour, (b) vapour dispersion into the atmosphere, where the vertical flux at any height equals the diffusivity coefficient times the gradient in vapour pressure. Vapour dispersion occurs through a laminar boundary layer at the soil-air interface, involving molecular diffusion. Above the boundary layer, turbulent or eddy diffusion processes dominate (Taylor and Spencer 1990). The diffusion coefficient for eddy flux is much larger than that for molecular diffusion so that, except when the atmosphere is exceptionally stable, dispersal of pesticide vapour in the turbulent zone is relatively rapid.

Volatilisation of pesticides from soil is often represented by relating gaseous and soil solution phase concentrations, where the Henry’s coefficient $K_H$ equals the ratio of concentrations in these phases (Gerritse et al. 1991) or the modified Henry’s coefficient $K_{H*}$ (ratio of saturated vapour density and aqueous solubility) (Wagenet and Rao 1990, Gerritse et al. 1991). Using the Henry’s coefficient to represent the evaporation process and assuming the vapour concentration at some height equals zero (and implying the flux through the boundary layer is more limiting than in the turbulent zone), at the soil-air interface $(z=0)$, the diffusion mass flux of volatilisation $J(z,t)$ (Mass Length$^{-2}$ Time$^{-1}$) is:

$$J(0,t) = D_0 K_{H*} C_w(0,t)/h$$

Eqn. 1-5

where $D_0 =$ molecular diffusion coefficient (L$^2$/T), $C_w =$ concentration in water phase in the soil surface and $h = boundary$ layer thickness above the soil surface (L) (Wagenet and Rao 1990). This equation
indicates the dependence of volatilisation on pesticide volatility (via $K_H^*$) and on sorption and soil moisture content, via $C_w$, so that (a) a strongly soil-sorbed compound (high $K_D$) will maintain low concentrations in water and inhibit volatilisation via the aqueous pathway inferred in Eqn. 1-5, contributing to the observed association between dissipation and sorption described above, (b) volatilisation generally decreases as the soil dries (Gerritse et al. 1991). The equation reduces to a pseudo-first-order equation if $D_0$, $K_H^*$, $h$ and moisture content (and $K_D$) are constant, which would rarely occur under field conditions. Also, there may be significant differences in volatilisation for recent application to the surface of the soil compared with a pesticide thoroughly mixed/diffused into the soil and having attained equilibrium adsorption.

Volatilisation operates similarly to evaporation of water from the soil (i.e. with an initial high rate limited by evaporative potential while the soil surface is moist after rain, followed by a continuously reducing rate as the soil dries, limited by delivery of water to the surface and the soil hydraulic properties). Availability is represented in the volatilisation equation above by $C_w$, which is determined by the concentration in the soil surface and the sorption coefficient, decreasing with dissipation (and as the soil dries) and increasing with new applications. At some time after application, particularly for soil-incorporated pesticides, volatilisation is limited by the rate of upward movement of pesticide in the soil via water evaporation-induced advection and diffusion (in liquid and gaseous phases, see below) (Taylor and Spencer 1990). Volatilisation controlled by both advection and diffusion will almost cease when the soil surface becomes very dry. Due to the complexity of these processes, volatilisation is often lumped with application inefficiency and degradation into ‘apparent dissipation’.

(e) Diffusion and advection

Movement of pesticides in soil is usually assumed to result from three processes (Wagenet and Rao 1990): (i) diffusion in the water phase in response to a concentration gradient, (ii) diffusion in the gas phase in response to a gradient in gas-phase concentration, and (iii) advection (mass flow, convection) due to movement of the bulk fluid (water or gas) in which the pesticide is dissolved, with water phase transport generally considered much more important. Movement in the water phase will depend on the degree to which the pesticide is desorbed (i.e. will be much more rapid for pesticides of low $K_D$ and almost negligible for pesticide of high $K_D$) while movement in the gas phase depends on the volatility of the pesticide (i.e. preference for gas phase rather than water or solid phases).

The contribution of diffusion to dissipation from the soil surface layer is probably small compared with losses due to volatilisation, degradation and advection via leaching. However, diffusion is probably important over longer times in (a) movement of surface applied pesticides into the surface soil layer, creating lower concentrations in the surface few mm of soil and a more uniform concentration gradient with depth, (b) movement of pesticides into soil aggregates, contributing to slowing in dissipation rates and increased sorption coefficients at longer times discussed elsewhere, (c) movement of pesticides horizontally creating more uniform spatial concentrations at longer times (Kimber et al. 1994), and (d) movement of pesticides upwards in the soil to re-supply surface volatilisation losses, where concentration at the surface is lower then in deeper layers. Still, the upward advective transport of pesticide with evaporation-induced upward movement of water is probably more important than, and may prevent or distort, upward movement by diffusion (Taylor and Spencer 1990).

Diffusion flux is the product of the concentration gradient with soil depth ($\delta C_w/\delta z$) and the effective diffusion coefficient ($D_p[\theta]$), where $\theta$ is volumetric moisture content (Wagenet and Rao 1990). Kemper and van Schaik (1966) found that $D_p[\theta]$ can be estimated as [$D_0\exp[b\theta]$], where $D_0$
is the diffusion coefficient in a pure liquid phase and a and b are empirical coefficients with values of 0.005-0.01 and 10, respectively (Wagenet and Rao 1990). Thus diffusion flux in the liquid phase is approximately a function of \[\exp[10 \theta]\], which increases from 1.65 at \(\theta=0.05\), 7.4 at \(\theta=0.2\), 20 at \(\theta=0.3\), 148 at \(\theta=0.5\). Thus the flux of solute moved by diffusion is much greater with increasing moisture content and is slow in dry soil. Since effective diffusion coefficients are a complex function of diffusion pathways through solid, liquid and gas phase, and these change with water content, soil pore structure and temperature, calculation of diffusion rates relies on experimental study of the chosen combination of pesticide and soil.

(f) Leaching

Leaching of pesticides from the surface soil layer has two functional effects on pesticide runoff, firstly by contributing to dissipation over time, and secondly by affecting concentrations in the soil during runoff events; it is these possible effects of leaching on runoff that are of interest here (i.e. rather than possible accessions to groundwater). According to the advection-dispersion equation (Wagenet and Rao 1990, Kookana et al. 1991), solute leaching flux (M L^{-2}T^{-1}) is the sum of advection (q C_w) and dispersion fluxes \([-\theta D_m(q) (\delta C_w/\delta z)]\), the product of the concentration gradient with soil depth \((\delta C_w/\delta z)\) and the mechanical dispersion coefficient \((D_m[q], L^2T^{-1})\), where q is soil water flux \((L T^{-1})\) and \(\theta\) is volumetric moisture content. Leaching flux potential is greatest when the soil is saturated when q and \(\theta\) are maximised and in soil with higher infiltration rates (i.e. greater q).

Solute leaching only operates on the desorbed component of pesticides \((C_w)\), which is related to the total mass of pesticide in the soil volume \((C^* M L^{-3})\) (Haigh and Ferris 1991) or in the soil mass \((C'_TOT, M M^{-1})\), assuming linear partitioning with Eqn. 1-1, as:

\[
C_w = \frac{C^*}{(\theta + BD K_D)} = \frac{C'_TOT BD}{(\theta + BD K_D)}
\]

Eqn. 1-6

where BD is soil bulk density \((M L^{-3})\). Thus \(C_w\) and potential leaching flux decreases greatly as \(K_D\) increases over the eight order of magnitude range (e.g. 0.1-10^6) of different pesticides. BD is large compared with \(\theta\), so \(C_w\) approaches \(C'_TOT / K_D\) as \(K_D\) increases. For \(K_D=100\), \(C_w \approx 0.01.C'_TOT\), that is, only a small proportion of pesticide is involved in the leaching process.

For leaching to contribute significantly to dissipation of pesticides from the soil surface, soil water flux must be reasonably large and \(K_D\) must be small. Briggs (1981) suggests that, for 250mm of rainfall (i.e. a large flux), no significant leaching would occur with \(K_D\geq100\) (L kg^{-1}), little leaching below 50mm at \(K_D=10\), and \(K_D=1\) or less is required for significant leaching below 50mm depth. This is consistent with observations of endosulfan \((K_D 100-400)\) largely remaining in the soil surface (e.g. 0-50mm) even under irrigation (Kathpal et al. 1997, Kennedy et al. 1998). Even relatively mobile pesticides, such as picloram \((K_D 0.1-1)\), have been observed to concentrate in the surface 150mm of a heavy clay soil under dryland cropping (Marley 1980), probably because total flux below this depth was not too large in a dryland situation. Similarly, Walker and Blacklow (1995) found most surface-applied simazine and atrazine remained in the surface 0-25mm on an acid sand that received 76-105mm of rain during 100 days after application, despite 8-9 rains that were estimated to wet the soil to 300mm. Increase in \(K_D\) through time was considered to have contributed to the limited leaching (SR Walker, pers. comm.). Briggs (1981) found the highest concentrations in the 0-25mm soil after 100mm of rain, for all eight pesticides studied on a sandy soil, even for the relatively mobile fenuron and simazine. Kookana et al. (1985) found a greater degree of leaching on a sandy soil with 900mm of rain and irrigation over 150 days, but six of the nine pesticides remained in the surface 100mm. This is not to
say that pesticides will not leach to considerable depth in soil given the right combination of high flux, low \( K_D \) and persistence.

Reduction in pesticide concentration due to leaching in a soil layer of depth \( D \) can be calculated using the approximate advection equation (Steenhuis and Walter 1980, Leonard et al. 1987):

\[
C_s'_{S2} = C_s'_{S1} \exp \left[ \frac{-(P - Q - AWS)}{D \left( K_D \left( BD / 1000 \right) + POR \right)} \right]
\]

where \( C_s'_{S1} \) and \( C_s'_{S2} \) = concentration in soil (mg/kg) before and after rain of \( P \) (mm) and runoff of \( Q \) (mm). \( AWS \) = available water storage in the soil layer (mm), \( D \) = soil layer depth (mm), \( K_D \) = sorption coefficient (L/kg), \( BD \) = bulk density (kg/m\(^3\)) and \( POR \) = soil porosity (v/v). (See Chapter 4).

(g) Complete and approximate pesticide/solute soil models

The abovementioned process components of dissipation, sorption, volatilisation, diffusion, advection and dispersion have been coupled via the mass conservation equation, and with various models of soil water flow, in various computer models of behaviour of pesticides (and other solutes) in soil. Examples are the PRZM model (Carsel et al. 1984), LEACHM (Wagenet and Hutson 1989, Wagenet and Rao 1990), RZWQM (Ahuja et al. 1993) and CREAMS/GLEAMS (Knisel 1980, 1993; Leonard et al. 1987). Most of these models concentrate on pesticide leaching (e.g. groundwater contamination risk assessment) rather than runoff processes, with the exception of GLEAMS, often with runoff and erosion represented simplistically (e.g. PRZM, RZWQM) or not at all (e.g. LEACHM). Review of such models is presented elsewhere (Wagenet and Rao 1990, Kookana et al. 1991) and is beyond the scope of this thesis.

1.4 Factors affecting pesticide runoff

Off-site movement in surface runoff is a major pathway for pesticide delivery into rivers in cotton growing areas (Raupach and Briggs 1998). Considerable effort has been devoted to quantifying the occurrence, concentrations and losses of particular pesticides in runoff, from small catchments or rainfall simulator plots. A considerable proportion of the literature, particularly from the USA, compares effects of treatments such as conservation tillage systems and is discussed in Section 1.5. However, it is also important to understand how these pesticide losses came about (Baker 1980) and such studies are rare. Few studies have separated out, quantitatively, the contribution to runoff losses of factors such as application rate, dissipation rate and extraction efficiency, and it is arguable that this may only be possible using a combination of measurement and modelling. Each study, of necessity, typically characterises behaviour of only a few compounds – how would any of the hundreds of other compounds behave? Of interest here are the processes involved in pesticides entering runoff at within-field scales, how they interact to produce a pesticide loss or concentration in runoff for a particular event and how these processes may differentiate between runoff of different pesticides.

Pesticide runoff from agricultural field or plot scale is influenced by (Leonard 1988, 1990):

- Hydrology – the amount, timing and rate of surface runoff, lateral flow and infiltration of rain water, which is influenced by the timing, amount and intensity of rainfall, soil moisture status (thus evapotranspiration), soil hydraulic properties, soil layering and management practices such as tillage, compaction and cover.

- Soil erosion and sediment transport, which is strongly related to hydrology, but is also modified by cover, soil properties, slope (angle, shape and length), flow hydraulics (particularly degree of flow
convergence e.g. rills) and roughness. The contribution of sediment to pesticide losses varies depending on the sorption properties of the pesticide (K_D).

- Pesticide application – the amount applied determines the initial amount of pesticide in the plant-soil system; the placement and method of application determines the distribution in the canopy, residue and soil surfaces and initial distribution in the soil; timing of application (and dissipation rate) relative to the timing of runoff strongly influences pesticide runoff (Wauchope 1978). Formulation is also considered important especially for events soon after application (Wauchope et al. 1995).

- Pesticide properties – the two most important properties affecting runoff (and leaching) losses are sorption (K_D) and persistence (half-life) (Baker 1980, Leonard et al. 1995), discussed above.

1.4.1 Pesticide runoff processes in a cropping system

Pesticide runoff, and particularly the difference between pesticides, is much easier to understand if viewed as two components: (i) the time course of pesticide concentrations in the plant-soil surfaces (i.e. dissipation, discussed above) between application and the critical runoff event, and (ii) the transfer or extraction of the pesticide into runoff during the event. Both the dissipation and extraction processes are affected by where the pesticide is located in the various surfaces and stores in the plant-soil system.

The cropping system as previously defined (Fig. 1.1) includes three ‘surfaces’ or stores, the plant canopy, crop residues on or near the soil surface and the soil, where pesticides may be stored, dissipated and contribute to runoff. Pesticides transported in runoff may be sourced from washoff from plant foliage and crop residues, and from soil by extraction into surface runoff (Fig. 1.1) or shallow interflow (Leonard 1990). Shallow interflow involves water that has infiltrated the soil surface but returns to the surface as exfiltration down-slope or into rills, furrows and surface depressions, and thus may return previously leached chemicals to runoff (Ahuja 1986). During rainfall, washoff from plant foliage and crop residues may add to the concentration in the soil or contribute directly to runoff. Prior to a runoff producing rainfall event, levels of pesticides in these source “pools” may be increased by applications and are more or less continuously decreased by dissipation (as described above), including washoff and leaching during non-runoff producing rainfall events. The net outcome determines the mass in each pool at the start of the runoff producing rainfall event and the potential for pesticide runoff.

(a) Seasonal pesticide runoff losses and patterns

Wauchope (1978) and Baker (1980) conducted extensive reviews of available data (mainly for non-irrigated cropland in the US) and proposed rule-of-thumb estimates of average or reasonably expected edge-of-field pesticide seasonal runoff losses. For water-soluble pesticides on cropland, suggested seasonal losses of 0.5% or less (note range 0.001-10%, Wauchope 1978) or ‘probably <1%’ (Baker 1980) of the amount applied were reasonably typical, if a runoff event does not occur within a couple of weeks after application. Up to three times this typical level (Wauchope 1978) or up to 5% (Baker 1980) were typical if a large, early runoff event occurred. However, annual runoff losses of up to 15% of the applied amount have been observed in catchment studies (Ritter et al. 1974, Baker and Johnson 1979, Baker 1980, Clausen et al. 1996). Where pesticides are applied annually (e.g. herbicides in corn), the bulk of runoff losses for the season were often produced in single storms, being the first (Ritter et al. 1974, Wauchope 1978, Glenn and Angle 1987, Isensee and Sadeghi 1993, Clausen et al. 1996) or the first one or two (Triplett et al. 1978) runoff events after application. With repeated applications, large losses are possible after each application.
Wauchope (1978) defined pesticide runoff events as:

- 'critical events' when runoff losses of 1-2% of the amount applied were not uncommon. Critical events are those occurring within 2 weeks of pesticide application with at least 10 mm of rainfall, 50% of which becomes runoff (i.e. 5 mm of runoff or more).
- 'catastrophic' events, where runoff losses exceed 2% of the application. These events, almost without exception are first events after application.

Note that losses of quite small proportions of applied amounts may represent environmentally hazardous loads or concentrations, depending on other factors such as toxicity. Considering losses as percent of applied amounts may be a hangover from older assessments of effects of runoff losses on herbicide efficacy. However it does normalise the data for differences in application rate and allow comparisons between pesticides.

Hall et al. (1972) found event average concentrations of atrazine in runoff sediment and water phases, and in total, decreased with each successive event during the season, but event losses depended on event runoff amount. Thus the largest runoff loss occurred during the sixth runoff event, midway through the corn-growing season. Following any one application, pesticide concentrations (event average) are also generally greatest in the first event after application and decline with time after application (Hall et al. 1972, 1983, Ritter et al. 1974, Triplett et al. 1978, Leonard et al. 1979, Isensee and Sadeghi 1993). The concentration in sediment (per kg of sediment) is also usually highest in the first runoff event after application (Hall et al. 1972, Leonard et al. 1979, McDowell et al. 1981, Willis et al. 1983, Malone et al. 1999). Similarly, the highest concentrations observed in runoff are associated with runoff that occurs soon after application for less sorbed pesticides (Willis et al. 1975, Glenn and Angle 1987, Isensee and Sadeghi 1993, Gaynor et al. 1995) or in the first large erosion event for more sorbed pesticides (Carroll et al. 1981). Isensee and Sadeghi (1993) measured event average water phase concentrations of 2000-3800 µg/L in runoff from small catchments for both atrazine and cyanazine in an event three days after application. Total pesticide losses and concentrations are evidently very dependent on how soon after application these first one or two runoff events occur. Thus large runoff events and their timing relative to pesticide application have a large influence on pesticide runoff.

The actual concentrations and losses in runoff that occur at any time after application increase in direct proportion to the rate applied (Hall et al. 1972, Hall 1974, Triplett et al. 1978, Wauchope and Leonard 1980). The dissipation rate of a pesticide, or its repeated application, is therefore very influential in determining the duration of the period when critical or catastrophic events might occur, and losses in subsequent events. The critical period is much shorter for a pesticide that dissipated rapidly, but is much longer for a persistent pesticide. For the least persistence pesticides on the most dissipation prone surface (e.g. plant canopy), the critical period may be less than one day. For the most persistent pesticides the critical period may effectively be a number of years. Simpson et al. (1998) determined that the period of major risk for endosulfan runoff from cotton was extended over several months by repeated (e.g. 6-8) applications resulting in a short term build up in the soil. When storm rainfall occurs during this period it is highly likely that an endosulfan application was made in the previous two weeks.

In addition to in-situ degradation of the pesticide, non-runoff producing rainfall events after application can reduce losses of more mobile pesticides in subsequent runoff events, due to washoff from crop residues and leaching into the soil (Baker and Johnson 1979, Wauchope and Leonard 1980, Hall et al. 1983, Gaynor et al. 1995).
For the simpler case of annually applied herbicides, event average concentrations in runoff generally decline 3-4 orders of magnitude within a year from US and Canadian cornfields (e.g. for atrazine, simazine, metolachlor) (Hall et al. 1972, 1983, Glenn and Angle 1987, Buttle 1990, Gaynor et al. 1995) and declined to below the limit of detection in 2-6 months in southern US cropping systems (diuron, linuron, fenac, trifluralin) (Willis et al. 1975). Pesticide runoff concentrations for a series of events decline approximately exponentially with time after application, for a wide range of pesticides (Triplett et al. 1978, Leonard et al. 1979, Edwards et al. 1980, Willis et al. 1983, Leonard 1988, 1990, Gaynor et al. 1995), similar to first-order soil dissipation curves (Fig. 1.2, Fig. 1.3).

However the actual relationship is often closer to a power function (log-concentration linearly related to log-days after application), e.g. for triazines (Hall et al. 1972, Hall 1974, Triplett et al. 1978) and glyphosate (Edwards et al. 1980), although an exponential relationship sometimes fits just as well (Buttle 1990, Gaynor et al. 1995). Gaynor et al. (1995) found that event average concentrations in runoff of atrazine, deethylatrazine (a metabolite of atrazine) and metolachlor each declined with days after application (Fig. 1.3), with log-concentration or log-log functions fitting the data equally well. Days after application described much of the variation in runoff concentration over four years and three tillage treatments. Power functions are observed because half-lives for runoff concentrations increased with time after application for a wide range of pesticides (Wauchope and Leonard 1980); the typical rate of increase in half-life results mathematically in concentrations decreasing with $(1-0.28\text{.days})^{-2.5}$ while a best-fit equation had a power of $(1-0.44\text{.days})^{-1.6}$. 

![Fig. 1.2. Event average concentrations in runoff from catchments with time after application (Source: Leonard et al. 1979).](image-url)

![Fig. 1.3. Event average metolachlor concentration (µg/L) in runoff from conventional tillage (CT), ridge-till (RT) and zero till (ZT) catchments over 4 years (Gaynor et al. 1995).](image-url)
The dissipation pattern observed in soil is generally reflected in runoff, and in sediment and water phases in runoff. Thus, Edwards et al. (1980) found that both soil and runoff concentrations of glyphosate declined as log-log functions of time after application, while Buttle (1990) found that metolachlor concentrations in soil and runoff declined exponentially with time after application. Interestingly, Triplett et al. (1978) found cumulative rainfall and cumulative heat units were not important in determining concentrations in runoff for atrazine and simazine, even though the amount of non-runoff producing rainfall between runoff events influences subsequent runoff (Hall et al. 1983).

Event average concentrations of sediment-sorbed pesticides are also strongly related to time after application, so long as sediment composition (OC etc) and enrichment ratio do not vary too much from event to event. Willis et al. (1983) found that event average concentrations of toxaphene (per kg of sediment), a highly sorbed compound, declined exponentially with days since application (first order) with one equation for four years of catchment data giving an $R^2=0.75$. Variation was large (e.g. 1.5 orders of magnitude) during the first 60 days due to differences in event sediment composition and sediment delivery/enrichment. McDowell et al. (1981) found a similar result for toxaphene after a single application, with less variation ($R^2=0.85$), on a nearby catchment. Malone et al. (1999) also found good relationships with exponentially decreasing concentrations of metribuzin in soil and in sediment with time after application, on steep plots where variations in sediment enrichment/composition appeared secondary. For these sediment-sorbed pesticides, concentration per L of runoff is influenced by the sediment concentration (kg/L) in each event. Thus Willis et al. (1987) found water phase concentrations of endosulfan and methoxychlor in runoff were highly related to time after application for a series of events over a 15-day period, but sediment phase concentrations were more related to event sediment and organic matter export.

Leonard (1988, 1990) noted that the half-life of runoff concentrations (or ‘runoff available residues’) tended to increase at longer times, consistent with the increase in half-lives in soil after the first 1-2 half-lives (Nash 1980, Wauchope et al. 1992) and with the tendency for soil sorption to increase with time of contact with soil (Leonard 1990). Wauchope et al. (1995) noted that ‘runoff half-lives’ are generally much shorter than the usual soil half-lives (supported by Ritter et al. 1974, McDowell et al. 1981, Willis et al. 1983, Buttle 1990, but not by Malone et al. 1999), indicating that the most runoff available residues (on soil and foliage surfaces) are more rapidly dissipated than those in the soil. Malone et al. (1999) found half-lives for metribuzin concentrations in sediment (~8days) were longer than in the bulk soil (0-15cm, 5.3 days), apparently due to greater OC in the soil surface.

Such simple pesticide runoff responses are less likely where a pesticide is applied multiple times, with new applications before the residues of pervious applications have dissipated significantly (e.g. Carroll et al. 1981). Where dissipation is reasonably rapid, runoff concentrations will still relate well to time after the last application. However, apparent dissipation may slow with successive applications (Malone et al. 1999), because older residues are more tightly bound and resistant to degradation and leaching. Kennedy et al. (2001) found endosulfan concentrations in runoff from furrow irrigation declined with time after spraying, both for a series of events on a single field (conc.=7.64-0.25x+0.002x^2, $R^2=0.89$ where x=days after application) and for 19 different cotton fields. They commented that ‘decline in endosulfan concentration in irrigation runoff is correlated with the declining residues in soil, which to a great extent are determined by the canopy cover at the time of application’.

While event average runoff concentrations are related to the time after a particular application, the concentration is also related to the application rate as indicated by the vertical displacement of
runoff concentrations in Fig. 1.2. Application rates may vary over an order of magnitude for various pesticides e.g. 'older' herbicides such as diuron, fluometuron and metolachlor may be applied at 10 times the rate of 'newer' herbicides such as pyrithiobac sodium (Silburn 1998). Greater application rate means proportionally greater runoff potential, all else being equal (Wauchope and Leonard 1980). Relating pesticide runoff to concentrations in the plant-soil system at the time of the runoff event captures the effect of both application amount and time after application.

(c) Pesticide runoff related to concentrations in the soil

It appears that concentration of pesticide in runoff should be closely related to concentrations of pesticide in the foliage, crop residue and soil pools when a runoff event occurs. However, studies where both factors have been measured to illustrate this relationship are rare. Spencer et al. (1985) found a strong correlation between pesticide concentrations in surface soil and in runoff from furrow irrigation in the US; pesticide concentrations in surface soil were a good indicator of expected pesticide concentrations in runoff. Leonard et al. (1979) found a strong relationship (R=0.93) between concentrations in runoff and concentrations in the soil surface (0-10mm), for four herbicides transported dominantly in the water phase (atrazine, cyanazine, diphenamid and propazine, all with K<sub>OC</sub> of 100-210), with no difference due to herbicide, watershed or year (Fig. 1.4).

\[ Y = 0.05 X^{1.2} \]
\[ R = 0.93 \]

Fig. 1.4. Relationship between concentration in 0-10 mm soil and in surface runoff from catchments, for four 'water transported' herbicides. (Source: Leonard et al. 1979, Leonard 1990).

The relationship between total (event average) concentration in runoff (water and sediment) (C<sub>T</sub> µg/L) and concentration in soil (0-10mm) (C<sub>soil</sub> mg/kg) was:

\[ C_T = 50 (C_{soil})^{1.2} \]

Eqn. 1-8

The coefficient of 50 was termed an "extraction coefficient" (Leonard et al. 1979). The exponent of 1.2 indicates that extraction is somewhat more efficient at higher soil concentrations and may reflect changing partitioning with time of herbicide contact with the soil. Higher concentrations in both soil and runoff were associated with more recent applications where extraction efficiency is expected to be greater (Leonard et al. 1979). Also, soon after application, concentrations in the upper few mm of soil
may be significantly greater than the average for the soil depth considered, and/or more herbicide may be present on crop residues, giving higher runoff concentrations relative to soil concentration.

Baker (1980), using the data of Baker and Laflen (1979) for atrazine, alachlor and propachlor runoff from small rainfall simulator plots, found a similar strong relationship (R=0.81):

$$C_T = 45 \left( C_{SOIL}^{n} \right)^{1.03} \text{ Eqn. 1-9}$$

Baker (1980) showed graphically that the Leonard et al. (1979) equation (Eqn. 1-8) fitted the Baker and Laflen (1979) data well.

Leonard et al. (1979) also found a strong but different relationship for paraquat, a strongly sorbed pesticide, which included the sediment concentration (SC kg/L) in runoff (R=0.97) (Fig. 1.5):

$$C_T = 1000 \times 2.16 \left[ C_{SOIL}^{n} \right]^{0.83} \text{ Eqn. 1-10}$$

where the coefficient of 2.16 is an “enrichment factor”. The exponent 0.83 was interpreted as indicating a changing sediment composition with sediment concentration. Higher sediment concentrations are associated with more intense events, which transport more coarse sediment and increase rill erosion relative to interrill erosion. Rills eroded deeper soil than interrill. Since paraquat is immobile and remains on the soil surface, rilling would erode soil containing less paraquat. The relationships for the water-transported herbicides and for paraquat are different at high and low sediment concentrations, however there is also considerable overlap, e.g. when SC = 10.7 g/L Eqn. 1-10 becomes:

$$C_T = 50 \left( C_{SOIL}^{n} \right)^{0.83} \text{ Eqn. 1-11}$$

That is, similar to Eqn. 1-8 for water-transported herbicides.

Fig. 1.5. Relationship between concentration of paraquat in 0-10 mm soil times sediment concentration and in surface runoff from catchments. (Source: Leonard et al. 1979, Leonard 1990).

McDowell et al. (1981) found a strong relationship between concentration of toxaphene (K_D= 6,000) in runoff (water plus sediment phases) and concentration of sediment in runoff, for a period starting 7 months after the last application, i.e. when concentrations in soil would vary only slowly. This equation is converted to the form used by Leonard et al. (1979) below:
\[
\begin{align*}
\log (C_T \text{ ppm}) &= -4.34 + 0.71 \log (10^6 \cdot \text{SC kg/L}), \quad (R^2=0.941) \quad \text{or} \\
C_T \text{ (ppm)} &= 0.8433 \cdot \text{SC kg/L}^{0.71} \\
C_T \text{ (ppm)} &= 0.3866 \cdot (C'_{\text{soil}} \text{ SC kg/L})^{0.71} \text{ if } C'_{\text{soil}} = 3.0 \text{ mg/kg} \\
C_T \text{ (ppm)} &= 2.165 \cdot (C'_{\text{soil}} \text{ SC kg/L})^{0.71} \text{ if } C'_{\text{soil}} = 0.265 \text{ mg/kg}
\end{align*}
\]

Concentrations in soil are given as 3.5-2.1 mg/kg in 0-150mm soil, resulting in Eqn. 1-12 with a coefficient 5.6 times smaller than that of Leonard et al. (1979) for paraquat. Surface soil (0-10mm) concentrations need to be about 0.265 mg/kg, due to greater dissipation in the more exposed surface than in the bulk soil, to obtain a coefficient similar to Leonard et al. (1979).

Sharpley et al. (1982) found a strong linear relationship (R=0.988) between dissolved P concentration in runoff and water-extractable P content of surface soil (0-10mm) for four soils, each with a range of rates of P amendment. The resulting equation gave good predictions of soluble P in runoff from catchments with a range of land uses and fertiliser inputs, using water-extractable P measured for catchment soils. Another equation derived from the rainfall simulator data, relating sediment P enrichment ratio (PER) to sediment yield, gave good agreement with measured sediment-bound P in runoff from the catchments, using measured catchment soil total P and sediment yield.

Concentrations in runoff are strongly related to concentrations in the soil within each study and there is some suggestion of similarity across studies for pesticides with somewhat similar sorption properties. These studies are discussed further in Chapter 4.

1.4.2 Pesticide runoff from soil during an event

Taking the simplest case of runoff from bare soil, where washoff from crop foliage and residues is not involved, pesticide transport during a runoff event is determined by the following sequence:
- initial concentration and distribution in the soil resulting from the application rate and dissipation prior to the event (described above),
- decrease in concentration in the soil surface layer due to leaching during rainfall,
- extraction from the soil surface layer into runoff in the water phase and sediment phase, which depends on the degree of erosion.

Thus, once a rainfall event begins, the transfer of chemicals from soil into runoff is the outcome of two processes, leaching and runoff extraction, operating on the concentration in a shallow soil layer (runoff mixing layer) that interacts with runoff and erosion. These three factors, leaching, runoff extraction and the mixing depth are considered in the following sections. Pesticide extraction into runoff from soil is discussed more fully in Chapter 4.

(a) Leaching from the runoff mixing zone

Leaching of a chemical downwards with infiltrating water (advection) reduces the concentration in the soil surface layer that interacts with runoff and erosion. The degree of leaching depends on the flux of water infiltrated and the sorption properties of the chemical and the soil, as discussed in Section 1.3.1(f). The concentration in the soil surface layer declines more slowly with time as it becomes depleted (Eqn. 1-7). The rate of decline ranges from rapid for poorly sorbed chemicals to negligible for highly sorbed chemicals, all else being equal. The strong relationship in Fig. 1.4 is, in part, because the four herbicides have similar sorption properties and therefore have similar potential for leaching out of the soil surface.
Important features of leaching relating to pesticide runoff are:

1. More strongly sorbed chemicals are only slightly affected by leaching and thus leaching processes are irrelevant to their runoff behaviour. This may apply for pesticides with K_d of 100 or greater and possibly lower (Briggs 1981). This reduces the potential for differences in runoff behaviour for this class of pesticides. Heathman et al. (1985) found, in contrast to a non-adsorbed chemical, a surface-applied adsorbed chemical (K+) leached very slowly, remaining near the soil surface and was made available to runoff for a much longer period and proportionally more was transported in runoff.

2. The leaching flux during a runoff producing rainfall event may be limited (e.g. <50mm), relative to the pore volume of the surface layer, if the proportion of runoff is high. Taking condition typical of clays, if the pore volume of a 10mm layer is 6 mm (10mm x 0.62v/v for a soil of bulk density of 1.0), each 10mm of infiltration displaces less than two pore volumes. If a 25mm deep layer is considered (as used in this thesis), pore volume is 15.5mm. If the 0-25mm soil is initially air-dry (e.g. 0.1v/v), 13mm of infiltration is needed to wet the layer and a further 15.5mm of infiltration is needed to displace one pore volume. If the soil is wet, the initial fill volume is small, but up to 80% of rain will runoff from bare soil (Freebairn et al. 1996) also limiting leaching.

3. Weakly sorbed chemicals potentially have lower runoff transport. Leaching, by reducing the concentration in the mixing layer before runoff starts, can significantly reduce runoff of chemicals that are less sorbed to soil. Heathman et al. (1985) found that concentrations of bromide (Br⁻, a non-adsorbed chemical) in runoff were considerably lower for plots with drier antecedent soil moisture, due to displacement of Br⁻ away from the surface with infiltrating water. Hubbard et al. (1989) found that initial runoff concentrations of NO₃-N were higher, and occurred sooner, on soils with low infiltration rates and at higher rainfall intensities.

4. Where leaching is prevented by a restriction to water flow in the soil profile, the large potential effect of leaching in reducing runoff concentrations may be lost, creating a worse case scenario for pesticide runoff. The impact will be greater the closer the restriction is to the soil surface. Two mechanisms are possible: (i) lack of downward displacement of the chemical, which can result in concentrations in runoff 1-2 orders of magnitude higher than where leaching proceeds unrestricted (Ahuja and Lehman 1983); (ii) chemicals previously leached out of the surface can be contributed to runoff by exfiltrating water, in addition to chemicals extracted by the surface exchange processes. Where topsoil overlies less permeable subsoil or a compacted ‘plough pan’ on land of any significant slope, infiltrated water will flow down slope (lateral flow), and may pond to the surface and mix with surface runoff (exfiltration). Snyder and Woolhiser (1985) observed significant exfiltration on sloping flumes, which increased the removal of dye in runoff. The first mechanism is one-dimensional, and therefore can occur at even the smallest catchment scale and on low slopes, whereas the second is two or three-dimensional and may be more prominent as catchment scale and slope increases.

5. At small spatial scales, the characteristic exponential decline in concentration in the mixing layer due to leaching (and runoff mixing itself) will cause poorly sorbed chemicals to exhibit an exponentially declining runoff concentration through time during rain (Baker et al. 1978b, Ahuja and Lehman 1983). Conversely, chemicals that are more tightly sorbed should show little decline in concentration in runoff due to leaching, as their concentration in the mixing zone is not being depleted through time. The pattern of concentration in runoff is considered in section 1.4.2(e).
Entrainment into runoff of pesticides attached to sediment is the product of sediment load or concentration in runoff and the concentration of the pesticide in the sediment (Leonard et al. 1987). The concentration of pesticide in the sediment is related to that of the soil in the mixing zone, after desorption and leaching in infiltration and runoff water, but may not be exactly the same. Concentrations in sediment and soil differ due to: (a) differences in concentrations in the actual depth eroded and in the soil layer sampled, associated with concentration gradients with depth, and (b) selective erosion/deposition of sediment particles with different sorption capacities.

Concentration gradients with depth. The apparent relationship between concentrations in sediment and in any fixed depth of surface soil will vary when there is a gradient in concentration of sorbed chemical in the soil surface, even within the top 0-10mm layer (Baker 1980). Surface applied pesticides may have greater concentrations in the surface few mm of soil for some time after application (probably a matter of only a few days; rate depends on diffusion and sorption) causing greater apparent extraction efficiency (Leonard et al. 1979). In contrast, with greater time after application, the concentration in the surface few mm may be depleted for a pesticide prone to losses by volatilization and/or leaching. Leonard et al. (1979) considered this contributed to lower apparent runoff extraction of trifluralin, a volatile herbicide, compared the herbicides in Fig. 1.4. Similarly, leaching of less sorbed pesticides will create concentration-depth gradients and affect runoff extraction of the sorbed phase during an erosion event. Baker and Laflen (1979) found concentrations of herbicides in sediment were only about 0.2 times the concentrations in 0-10mm soil, after applying 122 mm of rain, presumably because the sediment was eroded from a thin layer where the concentration had been considerably reduced by leaching. While this is largely a sampling problem, i.e. in choosing what soil depth to sample, it is a significant consideration in interpreting measured data (e.g. did sediment enrichment, discussed below, really occur) and will cause some level of ‘noise’ in data comparing pesticide concentrations in soil and runoff/sediment.

Sediment sorting and enrichment. In catchment and plot studies, concentrations of sorbed pesticides, sorption components (OC and clay) and nutrients in eroded sediment are generally equal to or greater than those in the soil surface, that is, they are ‘enriched’, although there are circumstances where depletion, the opposite to enrichment, occurs. The ratio of the concentration in sediment (per kg) to the concentration in the soil is termed the enrichment ratio. Particles in the rainfall-wet soil surface and in eroded sediment are a mixture, including primary particles and aggregates, varying in size and density (and resultant settling velocity) and are subject to detachment (Palis et al. 1990a), transport (Meyer et al. 1983) and deposition rates (Rose and Ghadiri 1991) that may be size selective. Enrichment of any sorbed chemical in sediment depends on two factors, both of which must occur: (a) the sediment load at the point of measurement must be enriched in certain classes of particles and depleted in others (selective sediment delivery), and (b) the sorbed chemical concentrations must differ between these particle classes. Thus if (a) does not occur, such as in the discharge of an actively forming rill, little enrichment is observed (Rose and Dalal 1988), no matter what conditions apply to (b). If (b) does not occur, selective transport of particle classes can result in enrichment of fines (e.g. clay), but no chemical enrichment.

(a) Selective sediment delivery is likely to be more significant the more that rainfall detachment dominates over runoff entrainment as an erosion process (Rose and Ghadiri 1991, Palis et al. 1990a). Sediment from interrill areas is generally enriched in finer particles and in sorbed chemicals (e.g. N, P)
Rainfall detachment or interrill erosion involves substantial particle selectivity because the balance of entrainment and re-entrainment over deposition greatly favours particles of low settling velocity dominating the sediment load (e.g. imagine a mixture of fines and gravel). Rill erosion tends to be non-selective of sediment sizes and result in minimal enrichment, removing soil from the tilled layer *en masse* (Rose and Dalai 1988). With the high flow energies in rills, transport of quite large particles that should settle rapidly is enhanced by rolling, associated with rapid transport (Walker *et al.* 1978, Loch and Donnollan 1983). However, at low slopes, concentrated flow occurs without rill incision and is subject to net deposition if sediment supply (e.g. from up-slope in the flow channel or from lateral interrill areas) exceeds flow transport capacity (Stein *et al.* 1986, Meyer and Harmon 1985). When concentrated flow experiences a decrease in slope (e.g. rill into contour bank) or increase in roughness (e.g. a grass filter), deposition rates exceed entrainment/re-entrainment rates for the more rapidly settling particle classes, resulting in substantial size selectivity and favouring only slower settling particles remaining in the runoff. Sediment settling velocity and transport capacity are both influenced by sediment size and density. Larger, denser sediment particles settle more rapidly and are less easily transported at lower velocities (Meyer *et al.* 1983), and therefore are more easily trapped, than smaller, less dense sediment.

(b) Sediment composition. Finer sediments can have greater sorption capacity, due to greater organic matter, clay content and CEC, for soils where larger particles are primary mineral particles (Karickhoff and Brown 1978, Karickhoff *et al.* 1979). However, for soils that eroded as water stable aggregates, larger sediments contain mixtures of primary particles and can contain considerable silt, clay and OC, i.e. they can be similar in composition to the bulk soil. For aggregated clay soils, pesticide concentrations in coarse particles up to twice those in fine particles have been measured in aggregates (Ghadiri and Rose 1993a) and eroded aggregated sediments (Ghadiri and Rose 1993b, Silburn and Spann, unpublished data). Richardson and Epstein (1971) found higher concentrations of endosulfan on sand sized particles (of high organic matter content and therefore presumably aggregates) than on fines for one of the two silt loam soils they studied, although other pesticides were dominantly sorbed to clay fractions. Under these circumstances, erosion that is selective for fines may result in enrichment ratios less than 1.0.

In most models of chemical transport for field-sized areas an enrichment ratio (ER) is applied (Leonard *et al.* 1987) to reflect the greater clay and OC content often observed in eroded sediment compared with the original soil ($C'_{SOIL}$) (Leonard *et al.* 1979, Willis *et al.* 1983). Sediment-bound pesticide load (L) or concentration ($C_{SED}$) in runoff is:

\[
L \text{ (mass/ha)} = \text{ER. Soil loss (mass/ha). } C'_{SOIL} \text{ (mass per kg soil), or Eqn. 1-13}
\]

\[
C_{SED} \text{ (mass/L)} = \text{ER. SC (kg/L). } C'_{SOIL} \text{ (mass per kg soil)}
\]

Observed enrichment ratios in sediment ($C'_{SED}/C'_{SOIL}$) vary with type of erosion (e.g. interrill, rill), vary somewhat with the chemical considered (due to differences in sorption between particle types), and typically decrease with increasing size of the soil loss event as a ln-ln function (Menzel 1980, Rose and Dalal 1988, Smith *et al.* 1993):

\[
\ln \text{ER} = a + b \ln (\text{sediment yield kg/ha})
\]

\[
\text{ER} = A (\text{sediment kg/ha})^{-B}, \text{ where } A = e^a \text{ Eqn. 1-14}
\]
where the coefficients A and B have values, for example, of 7.4 and 0.2 for both N and P for a wide range of soil-vegetation conditions reviewed by Menzel (1980). ER generally approaches 1.0 for high soil losses and for rill erosion. The relationship in Eqn. 1-14 reflects the fact that runoff during low erosivity events (low rainfall/runoff rates) has less capacity to entrain coarser sediment, and to re-entrain sediment continuously subject to deposition, whereas particulate OM and clay-rich fine sediment, which may be OM-rich, are more easily eroded and transported because of relatively low density and low depositability, respectively. In contrast, more erosive events will erode and transport larger, less OM-rich sediment (e.g. sand), i.e. is less size selective. However, some models calculate ER as the outcome of selective transport and deposition of sediment size classes and using the potential sorption capacity of each class (Leonard et al. 1987), a more robust if more data intensive approach.

The strong relationship between paraquat concentration in runoff and the product $SC.C'_s o i l$ with an exponent close to 1.0 found by Leonard et al. (1979) (Eqn. 1-10, Fig. 1.5) indicates that, for their case of reasonably steep (3-10%), disturbed catchments, a large proportion of the variation in sediment pesticide concentration is accounted for by the soil pesticide concentration and the sediment concentration. The enrichment factor of 2.16 is close to the measured average enrichment ratios for clay, OM and specific surface in sediment for the catchments. The exponent 0.83 was considered to reflect the changing sediment composition (more clay, OM) and greater ER with smaller erosion events, but appears to be somewhat secondary in this case.

Malone et al. (1999) found metribuzin concentrations in sediment followed first order dissipation for a series of runoff events following two successive applications (Fig. 1.6a). However, they observed that metribuzin concentrations in sediment were higher than predicted by the first-order lines when sediment yield was lower than average (for 5 events) and vice versa (5 events) with only two events where this was not applicable. Residuals around the fitted lines were significantly related to sediment yield relative to the average sediment yield (Fig. 1.6b). This is consistent the ln-ln inverse relationship of enrichment ratios with sediment yield in Eqn. 1-14 – larger events had lower metribuzin concentrations in sediment because less enrichment occurred and vice versa for smaller sediment yield. Importantly, these data demonstrate that enrichment was secondary to source concentration in determining concentration in sediment.

![Fig. 1.6.](image)

(a) Metribuzin concentrations in sediment and event sediment yields for a series of runoff events, following two applications, and fitted first order rate equations, and (b) relationship between residuals of sediment yield (relative to average) and ln of residuals of metribuzin concentrations in sediment around the fitted lines in (a). (Source: Malone et al. 1999).
The field-scale runoff studies (on low sloping fields) of McDowell et al. (1981) and Willis et al. (1983) show that for DDT, DDE and toxaphene, which are strongly sorbed compounds, storm runoff loads are highly related to sediment loads ($R^2 = 0.90-0.99$) once time since application is accounted for. Event average concentrations (Willis et al. 1983) were highly related to the sum of concentrations of organic matter and clay (after dispersion) in runoff, more so than to sediment concentration, due to differences in OM and sediment composition between events. Clay and OM in sediment were enriched, on average, 2.0 and 2.4 times compared to the source soil. Clay concentration in runoff increased linearly with event sediment concentration. More importantly for explaining event-to-event variations in sorbed pesticide concentrations in runoff, OM content of sediment was significantly greater (e.g. up to 14%, ER=8.75) for events with low sediment concentrations (e.g. 0.1g/L) and declined exponentially with event sediment concentration, to approach the soil OM content (1.6%) for events with high sediment concentrations (e.g. 10g/L, ER=1.25). The low slopes of the fields in both studies (0.2%) provide opportunities for sediment deposition and for expression of enrichment.

It follows from the preceding sections, that pesticide application rate and persistence, as captured in surface soil concentration, and sediment yield appear to dominate total losses of sediment-sorbed pesticides, while event average concentrations are largely determined by surface soil concentration and sediment concentration in runoff and may be modified by sediment enrichment. In summary, these data illustrate that runoff extraction and transport of sediment-sorbed pesticides is influenced by:

(a) the pesticide concentration in the soil surface,
(b) the amounts of sediment eroded, deposited and delivered to the catchment outlet,
(c) the size distribution of the sediment, which is influenced by
(d) the sediment size selective nature of erosion/deposition, and
(e) the clay and OM composition in each size class, which may lead to
(f) differences in sorption capacity between sediment classes.

The results of Leonard et al. (1979), McDowell et al. (1981), Willis et al. (1983) and Malone et al. (1999) indicate that pesticide concentration in the soil surface and the amount of sediment delivered will account for much of the variation in sorbed-pesticide yield in runoff, and the other factors may be secondary modifiers (e.g. a constant ER may suffice for all events). This is because: (a) soil pesticide concentrations and runoff sediment concentrations can both vary over 4 orders of magnitude whereas ER's varies <1 order of magnitude, and (b) for events where ER is highest, soil loss is relatively low and therefore sorbed pesticide load is low. That is, losses of sorbed-pesticides of most concern are more likely to occur under condition where sediment size selectivity is least and ER approaches 1.0. However, the degree of sediment delivery (and to a lesser extent enrichment) must be considered when estimating pesticide yields at larger scales (e.g. edge-of-field or larger) from soil losses measured or calculated at an interrill/rill or within field scale.

(c) Extraction from soil into runoff in water phase

On soil areas subject to interrill (sheet) erosion, pesticide extraction into the water phase (referred to here as solutes) in runoff may occur through (Leonard 1988, 1990):

(i) diffusion and turbulent transport of pesticides (already) dissolved in pore water into the runoff stream, including movement/mixing of soil pore water into runoff;
(ii) desorption from soil particles directly to runoff water;
(iii) dissolution of stationary pesticide particulates;
(iv) scouring of pesticide particulates and their subsequent dissolution, and
However, a solute present in the soil pore water can only move to the surface by the first mechanism listed and consequently the diffusion and turbulent transport mechanism is significant (Ingram and Woolhiser 1980). Raindrop impacts on exposed soil create surface seals that influence water infiltration (Silburn and Foley 1994), dislodge and suspend soil particles (adding to sediment in runoff), and produce instantaneous pressure gradients affecting mixing between soil pore water and runoff (Ahuja and Lehman 1983). Raindrop impacts on the soil surface cause active jetting or hydraulic penetration of water into pores. Hydraulic penetration is a primary mechanism for water entry into the soil in the early stages of surface sealing (Moss 1991) and continues after complete seal development on soils where significant numbers of larger pores remain open at the soil surface (Foley and Silburn in press); these soils would include many of the Vertosols used for cotton growing in Australia. The turbulence generated by, or pumping action of, raindrop impacts, is suggested to transfer chemicals from below the thin surface soil layer (Ahuja and Lehman 1983). Under these very energetic conditions, extraction of solutes from as deep as 20mm in the soil has been observed (Ahuja et al. 1981) and mixing and desorption are accelerated (Ahuja 1986, 1990) (c.f. normal diffusion). However, mixing is greatest at the soil surface with the degree of mixing decreasing very rapidly, exponentially with depth in the soil, with an ‘effective average depth of interaction’ of 2-3mm (Ahuja et al. 1981).

Extraction of solutes into runoff (and the effective depth of interaction) is affected by the rate of water flux through the soil (Ahuja and Lehman 1983), rainfall intensity and kinetic energy, and soil slope, and indirectly by the depth of surface water (Ingram and Woolhiser 1980, Sharpley 1985), and soil aggregation, cover and residue incorporation (Sharpley 1985), i.e. factors that affect the transfer of raindrop energy and water into soil pores. Thus there tends to be a positive correlation of solute extraction with soil loss (Sharpley 1985).

Complete mixing with pore water in a particular soil depth cannot be assumed. Ingram and Woolhiser (1980) found that concentrations of chemicals in overland flow on interrill areas are much lower than in the pore water and considered that ‘the assumption of an instantaneous equilibrium between the pore water and the overland flow is incorrect’. The pesticide load is likely to be greater than that simply desorbed from the sediment load, due to direct desorption and interaction with pore water described above, but less than the total desorbed load from complete mixing with an arbitrary soil layer e.g. 0-1 cm (Leonard 1988). These uncertainties about both the degree of mixing and the mixing depth are often dealt with in practice by defining an ‘effective depth of interaction’ or an effective mass of soil involved in complete mixing, as discussed in the following section.

Where rill erosion occurs in addition to interrill erosion, water is exposed to deeper soil layers, which may contain different concentrations of pesticides than the surface soil. Shallow interflow (eg. in a tilled layer overlying compacted soil) may also contribute dissolved chemicals to runoff water phase.

**Mixing layer or effective depth of interaction**

The concentration of chemical available for extraction into surface runoff (and movement downwards) in both the water and sediment phases depends on the concentration in the surface soil. Early pesticide runoff models assumed a constant, thin surface soil layer where rainwater, soil and soil water mixed completely and uniformly and where solute concentrations in runoff, pore water and infiltrating water were assumed equal (Steenhuis and Walter 1980, Carsel et al. 1984). The 0-10 mm soil layer gave reasonable empirical relationships for several pesticides (Leonard et al. 1979) and was adopted as a pragmatic compromise in some models (Leonard et al. 1987). In reality the effective depth
of interaction of raindrops and soil pore water during extraction varies with soil conditions (density, tilth, roughness, cover etc.), chemical and rainfall characteristics (Leonard et al. 1987). An ‘extraction coefficient’ is generally used to represent the incomplete mixing of raindrop/runoff water and soil pore water in this layer. Ahuja et al. (1981) studied extraction of $^{32}$P into runoff as a function of depth of placement and found that extraction was at a maximum for tracer placed on the surface and decreased exponentially with depth of placement. Ahuja and Lehman (1983) proposed a modification to previous models where the degree of mixing between rainfall and soil water declines exponentially with soil depth to a maximum depth of 20 mm. This model was tested with data for a number of nutrients and pesticides (Heathman et al. 1985, 1986) and performed well, albeit with calibration. However, models for predicting the detailed distribution of chemicals within the soil surface (0-20 mm) through time for input to these more detailed runoff extraction models appear to be less developed.

While Leonard et al. (1987) used the concentration in the 0-10mm soil layer in runoff calculation (after leaching) in the CREAMS/GLEAMS models, they did not assume complete mixing throughout this depth, but defined an additional parameter (extraction ratio B kg/L), which approximated the mass ratio of soil to water effective in runoff extraction from soil (Leonard 1988). Numerically, a value of $B=0.05-0.2$ gave reasonable model predictions for a wide range of measured plot and catchment data, with $B=0.1$ adequate in most situations (Leonard and Nowlin 1980) and increasing to $B=0.5$ for only slightly sorbed pesticides (Leonard et al. 1987).

The distribution of pesticide concentration with depth within the depth of interaction influences runoff extraction (Baker 1980), as mixing is greatest at the soil surface with the degree of mixing decreasing exponentially with depth in the soil (Ahuja et al. 1981). If concentration decreases with depth in the 0-10mm soil, as would be the case soon after surface application, apparent runoff extraction would be considerably higher than indicated by the concentration in the bulk (e.g. 0-10mm) soil. Conversely, if the concentration in the surface few mm of soil is depleted, say by volatilisation, apparent runoff extraction would be lower. Leonard et al. (1979) measured atrazine concentrations in 10mm soil layers through time after application, showing that concentration in 0-10mm soil were lower than in 10-20mm soil at 13 days after application and beyond, and decreased more with time than in 10-20mm soil.

---

**Fig. 1.7. Schematic diagram of important processes during runoff (Source: Baker 1980).**
This has received little study, given the difficulty in sampling soil layers finer than, say, 10 mm. While greater refinement may be impractical and unnecessary (e.g. for environmental assessment), it may be one of the limiting factors to precision in estimating pesticide runoff from soil and will cause variation in empirical runoff extraction ratios such as in Fig. 1.4 and presented in this thesis.

(e) Concentration through a storm and the 'first flush'

The runoff extraction theory indicated that the temporal pattern of concentration in the soil surface will be directly reflected in the temporal pattern of concentration in runoff (so long as extraction from the soil surface is the major source), but only after runoff commences. As discussed previously, leaching during a rainfall event results in an exponentially declining concentration in the surface soil, with the rate of decline determined by infiltration flux and the pesticide sorption coefficient. If the concentration of pesticide in runoff is solely determined by the concentration in the runoff-mixing layer, and this concentration decreases exponentially during rain, then runoff concentration should have a characteristic exponential decrease (i.e. an approximate first-order function, Leonard 1990). For poorly sorbed chemicals (e.g. Br-, pesticides of KD <~10 and especially for KD <1), such ideal behaviour is observed experimentally (Fig. 1.8), but generally only on small plots, particularly for high soil moisture contents where runoff began soon after start of rainfall (White et al. 1967, Baker and Laflen 1979, Baker et al. 1982, Ahuja and Lehman 1983, Leonard 1988, 1990). This characteristic behaviour applies for both water and sediment phases and continues through series of rainfall events over several days (Baker et al. 1978b, Baker 1980).

![Fig. 1.8. Runoff concentrations of pesticides from (a) small plots as related to time after start of runoff, demonstrating characteristic or 'ideal' behaviour resulting from leaching from the runoff mixing soil layer, and (b) from field-sized catchments as related to time after start of runoff (atrazine KOC=70, ethoprop KOC=100). (Source: Leonard 1988, 1990).](image)

However, several other factors will prevent this characteristic behaviour from operating under many field situations, resulting in only slight or no decline in concentration with time:

Effect of leaching rate. The rate of decline of concentration in soil and potentially in runoff will depend on the leaching flux. Higher leaching flux cause a more rapid decline in soil concentration, but under many circumstances (e.g. high infiltration rates due to dry soil or high permeability) will be associated with more delayed or no runoff, as described in the next section. Conversely, the rate of
Decline in runoff concentration will be slower at lower rates of leaching e.g. the impervious based boxes of Ahuja and Lehman (1983), but may still decline by as much as an order of magnitude. Removal of pesticide from the soil surface via runoff itself will create a first-order decrease in concentration even in the absence of infiltration. Ideal behaviour may also not occur where surface runoff includes leachate returned to the surface via lateral flow and exfiltration (Snyder and Woolhiser 1985).

**Infiltration before start of runoff.** The longer the delay, or the more infiltration, before the start of runoff, the more of the highest concentration solute will be leached into the soil and will not appear in runoff. Concentrations in runoff will reflect the lower, flatter portion of the ideal declining concentration curve. This was clearly demonstrated by Baker *et al.* (1982), who found total losses in water and sediment phases in runoff were reduced significantly with increased cover, because time to runoff was significantly increased with more cover. Concentrations were similar for all treatments at any given time after the start of rain, with concentrations decreasing with time – covered plots ran-off later and thus had lower concentrations, the water with higher concentrations apparently infiltrating. Thus runoff concentration will be reasonably steady in any situation where the start of runoff is delayed e.g. low rainfall intensity or soil that has high infiltration capacity due to high hydraulic conductivity, low water content, high cover and/or roughness.

**Sorption to soil/sediment.** For more sorbed pesticides, fluctuations in runoff concentrations will depend on fluctuations in other factors such as rainfall and runoff rates, and in sediment concentration, and no consistent ‘first flush’ should be expected. Indeed, because these pesticides (with $K_d > 10$) will be sorbed and transported on sediment (more so as $K_d$ increases), the pattern of concentration in runoff should be largely a function of the pattern of sediment concentration through the hydrograph. Such patterns vary due to variations in sediment supply and flow transport capacity (which ever is limiting), due to changes in rainfall and runoff rates. A declining concentration of sorbed chemicals (an apparent ‘first flush’) will occur if sediment supply is depleted during the event (e.g. limited supply of loose soil on a hard soil surface). On unconsolidated cultivated soils, sediment supply is generally not limiting (Loch and Donnollan 1983), but a decline in sediment concentration may occur during the initial stages of interrill erosion as surface sealing becomes established or in the latter stages of rill erosion or furrow irrigation once the channel erodes to a non-erodible layer and establishes a more stable cross section and tortuosity. Concentration of highly sorbed chemicals in runoff also declines if erosion incises into soil of lower chemical concentration, as may occur with rill erosion (Leonard *et al.* 1979).

**Travel time-contributing area.** For spatial scales larger than small plots, ideal transient behaviour is rarely observed (Leonard 1990). Even where ideal behaviour occurred on small-scale elements in a catchment, the difference in travel time for water from these elements to the catchment outlet will significantly alter the concentrations observed at the outlet. This was clearly illustrated by Leonard (1989) (Fig. 1.9) – for a linearly decreasing concentration through time at the unit scale, concentrations at the outlet are near constant through much of the hydrograph, due to travel time alone. Elevated concentrations occur in the first part of the hydrograph, due to runoff from near the outlet, but only represent a small proportion of the runoff. Catchment responses are even more complex in large catchments where runoff generation and pesticide applications vary spatially and temporally, and due to channel processes such as deposition, adsorption, dissipation etc (Finlayson and Silburn 1996).
First flush. The degree of leaching during the rainfall event, especially in rain before runoff commences, and the sorption properties of the pesticide determine the likelihood of decreasing concentrations with time during the event or a 'first flush' (i.e. an initial concentration in runoff 2-10+ time greater than later in the event). Poorly sorbed chemicals should exhibit 'first flush' behaviour, but only strongly so when runoff begins soon after rainfall, leaching is not restricted and only at small scales. Moderately to highly sorbed chemicals should not exhibit “first flush” behaviour due to leaching, as their concentration in the mixing zone is not being depleted through time by leaching, but may do so if sediment concentration decreases strongly through time. “First flush” behaviour, for both poorly and highly sorbed chemicals is basically an exhaustion or depletion phenomena.

1.4.3 Sediment-water partitioning

Pesticides are transported in runoff in solution (water phase) or sorbed to sediments (or as pesticide particulate, beyond the scope of this discussion). Pesticides transported primarily in the sediment phase are more manageable by soil conservation practices (Walter et al. 1979), and may dissipate more slowly and be less bio-available.

Partitioning between sediment and water phases in runoff is analogous to, and began as, desorption and partitioning in soil, but with a higher water-solids (sediment) and possibly under more dynamic conditions. Pionke and Chesters (1973) reviewed interactions of pesticides in sediment-water systems and discuss the distinctions between soils and sediments that can affect sorption. A key distinction is particle size composition – sediment in runoff is composed of a mixture of particles with a range of (a) sizes, densities and settling velocities, resulting in size-dependent deposition, sorting and transport, and (b) physical and chemical properties, of which organic matter and clay content are probably most important for partitioning. The sediment-water ratio is also likely to change through time or distance due to sediment deposition and dilution with water and sediment from non-treatment areas, one of a number of processes operating in field to stream and in-stream transport (see Bowmer 1987, page 307, and Finlayson and Silburn 1996), which are beyond the scope of this study.
Pionke and DeAngelis (1980), in considering distributing pesticide in runoff between solution and adsorbed phase for the CREAMS model, considered that adsorption-desorption hysteresis (as opposed to irreversible adsorption) will not have important impacts on $K_D$ when most of the desorption that will occur has occurred (e.g. in the soil surface under rain, before runoff starts) or where the variability in hydrologic, erosion or other associated data exceeds the error caused by hysteresis. Desorption for some pesticides may be sufficiently rapid that much of the equilibrium concentration is achieved within the time of most storm runoff events (Hance 1976). Novak et al. (1994) found that adsorption of atrazine to aggregates of two Iowa soils was initially rapid followed by a period of slower sorption, with only minor differences in kinetics (and $K_D$) for aggregates of different sizes. Much of the final sorbed concentration (at 72 hrs) was achieved at the first sampling time of one hr.

Karickhoff et al. (1979) found that sorption isotherms for pond and river sediments, for a number of aromatic and chlorinated hydrocarbons, were linear over a wide range of concentrations, independent of sediment concentration and salt content in the suspensions, appeared reversible with no hysteresis, and sorbates in a mixture sorbed independently. Such a set of simple behaviours may not apply under all conditions (e.g. for very high or low pesticide concentrations and sediment-water ratios) (Peterson and Batley 1991) or for all pesticides. They provide a useful starting point for understanding pesticide behaviour and environmental risk (Wauchope et al. in press). However, it is becoming increasingly apparent that the multiple phases (e.g. fast and slow) that occur during adsorption and desorption can have a significant influence on pesticide-soil-water interactions (considered further in Chapter 5).

(a) Partition coefficients observed in runoff studies

One approach to determining partition coefficients ($K_P$) appropriate for pesticide runoff, as opposed to in soil-water partitioning ($K_D$), is to calculate them from concentrations measured in the sediment and water phases in runoff. In summary, $K_P$ values observed in runoff have been observed to:

(a) be greater than $K_D$ values – McDowell et al. (1981), Spencer et al. (1985), Bowmer et al. (1986), Gouy and Belamie (1993), Truman et al. (1998b).

(b) increase with time of contact of the pesticide with the soil – Smith et al. (1978), Leonard and Wauchope (1980), Truman et al. (1998ab); similar to the increase in desorption $K_D$ values in soil with time (Boesten and Van Der Pas 1983).

(c) increase during a rainfall event - Baker et al. (1978b), Truman et al. (1998b).

These phenomena are considered further in Chapter 5.

(b) Observed distribution in runoff related to pesticide properties

Wauchope (1978) summarised measured percentages of pesticide in the water phase in agricultural runoff studies and found they vary reasonably systematically, albeit with wide ranges, depending on pesticide solubility (SOL) (Fig. 1.10). Soluble pesticides are generally transported in the water in runoff (e.g. picloram, 2,4-D salts) while insoluble pesticides are dominantly transported in sediment (e.g. DDT). For intermediate solubilities, there is a large change in percent in water phase over a limited range in solubility (-0.5 to +1.5 log SOL or 0.32-32 mg/L) where pesticides may have a 'foot in each camp'. MSMA and paraquat are strongly sorbed to clay surfaces, which cancels out the effect of their high solubility. Data used in this relationship were mainly from plots or small catchments under cropping, presumably with reasonably high rates of soil erosion. For this relationship to hold in the low solubility range, there must be sufficient sediment in the runoff (see Chapter 5).
Pesticide solubilities are correlated with soil sorption ($K_{OC}$) for many groups of non-ionic pesticides (Wauchope et al. 1992) and the observed data for percent in water phase in Fig. 1.10 also relates well to pesticide $K_{OC}$ (Chapter 5). Leonard et al. (1995) determined from longterm modelling with GLEAMS that at a $K_{OC}$ of 1,000, equal amounts of pesticides were transported in runoff in the water and sediment phases (for a particular set of conditions); as $K_{OC}$ increased, a greater proportion was transported adsorbed to sediment. This is quite compatible with Fig. 1.10; 50% in the water phase in Fig. 1.10 corresponds to a solubility of about 10, which equates to a $K_{OC}$ of about 1000 (using $K_{OC} = 3000/SOL^{0.5}$, Wauchope et al. 1992) or a $K_D$ of about 10 for OC=1%.

(c) Pesticide-sediment size interactions

It is generally assumed that coarse sediments can contain lower concentrations of sorbed chemicals than finer suspended sediments, particularly for soils where larger particles are primary mineral particles (Karickhoff and Brown 1978, Karickhoff et al. 1979, Walter et al. 1979, Rose and Dalal 1988). Karickhoff and Brown (1978) found for paraquat (strongly sorbed via ion exchange) in five natural sediments sampled from river water: (a) concentrations in individual size fractions varied as much as two orders of magnitude within a given sediment, with (b) a strong preference for fine silt and clay fractions, and a definite correlation with CEC, and (c) after centrifuging, greater than 50% of paraquat remaining in the suspended (water) phase was sorbed on particulates not removed by centrifugation. Thus the presence of very small size fractions (non-settling particles, micro-particles such as clay or macromolecules such as humic acids, Peterson and Batley 1991), which are typically not removed from water by filtering (e.g. 0.45μm) or centrifuging, can enhance the apparent solubility and water phase concentration, and decrease the apparent sorption coefficient, of hydrophobic compounds (Peterson and Batley 1991).
Karickhoff et al. (1979) found organic carbon content of the sand size fraction from three natural sediments were considerably lower than for the silt and clay size fraction (e.g. 0.1-0.25 time less). Linear partition coefficients (K_P) for pyrene and methoxychlor were of a similar order for coarse, medium and fine silt, and clay, but were much lower for the sand fraction. K_P increased linearly with OC content of the fine sediment fractions rather than relate to the size class. OC explained 85% of the variance in K_P for both pyrene and methoxychlor – thus KOC values were reasonably consistent between sediments and size fractions of fines for these compounds. However, KOC was considerably lower for the sand fractions. Means and Wijayaratne (1982) found that KOC values for atrazine and linuron were considerably higher on <0.45μm colloids from estuarine waters than commonly found for soil organic matter, e.g. 10-35 times greater, possibly because more organic surfaces were available for sorption.

However, for aggregated clay soils, pesticide concentrations in coarse particles up to twice those in fine particles have been measured in aggregates (Ghadiri and Rose 1993a) and eroded sediments (Ghadiri and Rose 1993b). Richardson and Epstein (1971) found higher concentrations of endosulfan on 'sand sized' particles (of high organic matter content) than on fines for one of the two silt loam soils they studied, although other pesticides were dominantly sorbed to clay sized sediment. Greater concentrations on larger sediments than on fines were also found for total P and algal-available P, for a range of Queensland soils (Phil Moody NR&M, pers. comm.). Novak et al. (1994) found only minor differences in atrazine K_P for various aggregate size classes (from <0.5mm to 4-5mm), whether crushed of whole, for two Iowa soils. There was little difference in dispersed particle sizes and organic carbon content of the aggregate sizes. If finer sediments have lower concentrations than the bulk soil and are selectively transported, firstly, management practices that selectively reduce losses of larger sediments (such as stubble retention and filter strips) will be more effective in reducing off-site transport of sorbed chemicals than otherwise expected, and secondly, enrichment ratios less than one are possible.

Higher pesticide concentrations in larger aggregates and sediments may be related to higher organic matter contents (Ghadiri and Rose 1993b) and preferential preservation of pesticides entrapped within larger aggregates, for example, by greater protection from volatilisation, leaching or microbiological degradation. These processes would presumably be reinforced with aging. The limited data available indicate that the assumption of greater concentrations of chemicals on finer sediments should be applied with caution for aggregated clay soils.

1.5 Management of pesticides in runoff

A range of concerns about pesticides in the cotton industry and possible impacts on the riverine environment was addressed in the LWRRDC/CRDC/MDBC program ‘Minimising the Impact of Pesticides on the Riverine Environment’ (Schofield 1998). These concerns were derived, in part, from continued detections of pesticides used in cotton in inland rivers (section 1.2.1(c)). Program aims included development of practical and economic methods to minimise transport of pesticides from application sites, and development of best management practices (BMP). To achieve these aims, improved cotton farming systems, which reduce sediment and pesticide transport from cotton fields while maintaining or improving production, are needed.

1.1.1  

B LWRRDC Land and Water Resources Research and Development Corporation, CRDC Cotton Research and Development Corporation, MDBC Murray-Darling Basin Commission.
Management options for reducing pesticide transport in runoff (Silburn and Connolly 1998, Silburn et al. 1998) include: (i) pesticide use and choice, (ii) soil and water management within the field, or (iii) managing runoff after it leaves the field. Discussion here will focus on within field management relating to rainfall-runoff (rather than irrigation). Some discussion of nutrients is included as information about pesticides is limited, and behaviour of nutrients provides insights in to the processes operating and to the potential behaviour of pesticides.

1.5.1 Conservation cropping and stubble retention

Historically there has been little development of conservation cropping systems for irrigated cotton in Australia, as evidenced by the bare soil on all but a few small areas of irrigated cotton. In developing such farming systems many general principles of soil and water conservation developed in dryland cropping (Freebairn et al. 1996) should be applicable. Also research specific to cotton, but not under irrigation, in the United States offers some insights.

Several features of furrow-irrigated cotton are different from the dryland grain cropping systems studied in previous conservation cropping research in Australia, apart from use of irrigation. Furrow irrigated cotton is generally on low sloping lands (<1%) whereas erosion research in dryland cropping has been on steeper slopes (>2%). Cotton under furrow irrigation is grown in a hill-furrow system, similar to ridge-till in the United States (Stein et al. 1986); while the coarse scale topography of a field may be virtually flat much of its fine scale surface has steep slopes (e.g. 50%). These differences may alter the dominance of various erosion processes and the effectiveness of control practices.

(a) Runoff and soil erosion

Retention of crop residues to provide surface cover is one of the most effective and robust management principles developed for dryland conservation cropping in Australia (Freebairn et al. 1996) and elsewhere (Laflen et al. 1978, Johnson et al. 1979, Langdale et al. 1979). Retention of cover was also effective in managing soil erosion under cotton in the United States. Mutchler et al. (1985) found that (dryland) cotton production creates very erodible field conditions. Soil losses were considerably higher during conventionally tilled cotton than for soybeans and corn under similar tillage. Soil loss and runoff were reduced significantly when cotton was grown in crop residues retained, without tillage, from wheat and soybeans crops. Mutchler and McDowell (1990) found that soil erosion from fields growing cotton could be controlled with no-till and reduced tillage systems when a winter cover crop provided cover during the cotton crop. No-till gave the greatest control as it retained the greatest cover. Soil loss was not controlled to acceptable levels when conventional tillage (disk, chisel, disk) preparation for cotton planting buried the cover crop residues, or with any of the tillage systems (conventional, reduced or no-till) without cover in addition to the cotton canopy. Both studies used residues from crops prior to the cotton crop to provide cover under the cotton, as it is difficult to provide sufficient cover for erosion control in cotton-cotton rotations.

(b) Pesticides and nutrients

There have been few (if any?) studies that have actually measured effects of surface cover on pesticide and nutrient transport in runoff in Australia, even in dryland cropping where so much erosion research has occurred. Two Australian studies, Rose and Dalali (1988) (using soil losses measured for various stubble retention systems and estimated delivery ratios) and Palis et al. (1990b) (in a laboratory
flume study), found reductions in runoff losses of total N with cover. As total N is mainly organic N, which is strongly sorbed to soil, both results reflect the strong effect of cover on erosion.

In principle, retaining cover should reduce transport of pesticides and nutrients, particularly those transported in association with sediment. The effectiveness of soil and water conservation practices in controlling potential pollutants other than sediment depends on the characteristics of the pollutants (Walter et al. 1979). Effectiveness of cover in reducing pesticide and nutrient runoff depends on:

a) whether the dominant transport agent for the particular chemical is water or sediment. This is largely determined by the properties (e.g. sorption coefficient) of the particular chemical (Wauchope 1978), which vary widely for pesticides (Wauchope et al. 1992).

b) how well cover reduces the dominant transport agent (sediment or water). For chemicals transported entirely in the water phase, cover will limit transport only to the extent that it reduces runoff. For chemicals adsorbed to sediment, erosion control generally reduces runoff of the chemical, but not necessarily in proportion because control practices tend to reduce transport of coarse particles more than fine particles (Leonard 1990).

However, few chemicals are fully non-sorbed (nitrate is one) or fully adsorbed (DDT is close) in soil (Walter et al. 1979). Many are moderately sorbed and will be partially transported on sediment. Also sorption tends to increase with time after application (Wauchope 1978, Leonard 1990).

Cover can also have a direct effect, by intercepting and dissipating pesticide sprays, and can be a source or sink of pesticides in runoff (Wauchope 1987). This aspect is under-researched, but will depend on pesticide chemistry (such as volatility, persistence and sorption) and the nature of the cover (age, microbial activity etc.). Baker et al. (1978b) suggest that residue cover may contribute positively to pesticide losses in runoff (a) by intercepting sprayed pesticides which are later washed off, and (b) soluble organic matter in runoff increased with residue cover and may increase extraction efficiency of the rain water. Conversely, Ritter et al. (1974) attributed observed lower concentrations of atrazine and propachlor in soil and in runoff from ‘ridged planted corn’ compared with ‘contour planted corn’ to interception of sprays on trash on the ridged catchments (they did not report cover levels).

Some pesticides are easily washed off crop residues (Martin et al. 1978, Baker and Shiers 1985). However, much less is known about pesticide persistence on crop residues. If persistence is less than on soil, interception on crop residues may reduce pesticide runoff so long as runoff does not occur soon after application. Available persistence data mainly relate to insecticides on plant foliage, with some data for herbicides, mainly on grasses (Willis and McDowell 1987). Half-lives, particularly for the component dislodgable by rainfall, are generally shorter than for pesticides on soil (Willis and McDowell 1987), indicating potential for cover to provide a direct effect on runoff of pesticides.

(c) Observed effects of tillage treatments (cover) on runoff of agrochemicals

The studies reviewed in this section were all conducted in dryland cropping in the USA. In a review of studies in the United States (Fawcett et al. 1994), conservation tillage, defined as retaining a minimum of 30 % crop residue cover after planting, usually reduced runoff losses of pesticides (mostly herbicides) compared with conventional (bare, tilled) but some data are conflicting. For herbicides the average reductions across all natural rainfall studies were 70, 69 and 42 % for no-till, chisel plow and ridge-till, respectively. This was in spite of the fact that many of the herbicides ran off in the solution phase rather than adsorbed to sediment. In this case reductions in pesticide losses are associated with the degree to which the treatment reduces runoff. However, herbicide runoff from no-till varied from none to twice that from conventional. Application rates were similar on all tillage treatments.
(d) Rainfall simulator studies

Baker et al. (1978b) studied six different tillage practices each on three soils under conditions conducive to pesticide runoff, with large, intense rainstorms (~200mm) simulated shortly after pesticide application. They found two recently applied (48 hrs) herbicides (alachlor and cyanazine) were mostly transported in the water phase and losses were not reduced by additional cover, and on some soils increased, due to higher concentrations from higher cover. Losses in the sediment phase, and of the more sediment-sorbed compound fonofos, were reduced with greater cover. It is somewhat unfortunate that this study, one of the first using a rainfall simulator to ‘screen’ tillage treatments of pesticide runoff, put pesticide runoff from conservation tillage systems in a negative light, and probably somewhat confused the issue, as most later rainfall simulator studies found conservation tillage systems reduced pesticide losses for similar poorly sorbed pesticides (Baker et al. 1982, Kenimer et al. 1987, Felsot et al. 1990, Seta et al. 1993). The response of runoff concentration to increased cover varied, from equal or increased (Kenimer et al. 1987, Sauer and Daniel 1987, Seta et al. 1993) to decreased (Baker et al. 1982, Felsot et al. 1990), but much reduced runoff amounts lead to much lower losses e.g. by an order of magnitude (Baker et al. 1982, Kenimer et al. 1987, Felsot et al. 1990).

However, in a four year catchment study in the same region (Baker and Johnson 1979), where a greater range of times after application were sampled, tillage systems with more cover (20% and 45% of the surface covered with corn residues from the previous year) gave reduced runoff losses of alachlor (76-52% less), atrazine (40-60% less), cyanazine (40-60% less) and fonofos (77% less), due to reduced runoff (40% less) and considerably reduced soil loss (65%-90% less). Herbicide concentrations were lower (e.g. 50%) for conservation tillage catchments in the first major event in a year where 41 mm of rain fell in the interval between application and runoff, but were twice those of conventional catchments for the first runoff event 15 days after application in another year.

Baker et al. (1982) studied runoff of three poorly sorbed herbicides (alachlor, atrazine and propachlor) from simulated rainfall plots 20 hrs after application either above or below four levels of corn residue (0, 375, 500, 1500 kg/ha). Total losses in water and sediment phases in runoff were reduced significantly with increased cover, because runoff amount was significantly reduced with more cover. Flow weighted average concentrations in the water and sediment (mg/kg) phases were reduced, by about one half to two thirds with 1500 kg/ha of corn residue. However, concentrations were similar for all treatments at any given time after the start of rain, with concentrations decreasing with time – covered plots ran-off later and thus had lower concentrations, the water with higher concentrations apparently infiltrating. Application of the herbicides above or below the cover had no significant effects on concentrations in runoff water or sediment, or on total losses.

Kenimer et al. (1987) found atrazine runoff concentrations were greater for no-till plots than tilled plots and increased with greater crop residue level. 2,4-D runoff concentrations were greater for no-till, but had no consistent trend with crop residue level. Total losses of atrazine and 2,4-D were much lower with no-till due to large reductions in runoff and soil loss.

The rainfall simulator studies of Baker et al. (1978b), Baker et al. (1982), Kenimer et al. (1987), Felsot et al. 1990 and Seta et al. (1993) were conducted soon after pesticide application (1-2 days). Sauer and Daniel (1987) studied the effects of tillage systems with cover from 1% to 60-80% on runoff of alachlor, atrazine and chlorpyrifos for a range of times after application (<1-8weeks). Concentrations in runoff were higher from rainfall simulator plots with higher cover at all times, although differences were not significant at 8 weeks. The greater concentrations with greater cover
were offset by lower runoff and sediment amounts, resulting in no differences in total losses between tillage systems, except at <1 week after application, when cover did not as strongly affect runoff amount. All plots were covered to exclude natural rainfall after application, thus greater time after application was not associated with greater rainfall. Also each plot included a wheel track on the down slope side, reducing the infiltration advantage of cover. Thus the instances of greater runoff concentrations with greater cover do not appear to be related to time of rain after application per see, but rather to differences in infiltration.

Seta et al. (1993), who did obtain considerably more infiltration with more cover (e.g. no runoff from NT for the first of three storms), found concentrations of \( \text{NO}_3 \), \( \text{NH}_4 \), \( \text{PO}_4 \) (all water phase only) and atrazine in runoff water increased with greater cover for the second and third storms, though total runoff, sediment and chemical losses were reduced with more cover. Washoff of chemicals from the crop residue cover would not be a significant source of chemicals in runoff after the first event (Martin et al. 1978) and considerable leaching of chemicals out of the soil surface should have occurred by 20min into the second event (88mm total rain) when runoff began from the NT plots. A more likely explanation of the high concentrations in runoff from high cover plots is that runoff occurred due to saturation of the surface soil above a compacted layer and previously leached soluble chemicals returned to the surface as shallow interflow, as noted by Barnett et al. (1972).

All of these studies demonstrate that rainfall and infiltration, both before and during the runoff event, is important in determining pesticide concentrations in runoff – if conservation tillage does not result in differences in infiltration, then concentrations of poorly sorbed pesticide in runoff are not reduced. Andraski et al. (1985) studied runoff from simulated events at different times after planting, for different tillage systems, and observed that differences in runoff amounts between conventional and conservation systems increased with time over the growing season – applying simulated rainfall only early in the growing season would underestimate the runoff-reducing effectiveness of the conservation systems, particularly those with less tillage (no-till and till-plant). Put another way, some runoff reduction benefits are obtained for tilled systems, including conventional (bare) and chisel (low-moderate, variable cover 25-57% at planting), when rain is applied soon after tillage/planting.

(e) Natural rainfall plot and catchment studies

Triplett et al. (1978) found no-till (80-90% cover at corn planting) reduced the amount of runoff, and thus the losses of herbicides from catchments, compared with conventional tillage. Concentrations of atrazine in runoff were not influenced by tillage method, but concentrations of simazine were lower for no-till. Hall et al. (1984) found that, compared with conventional tillage, no-till ‘covered’ systems (retained corn residues and “living mulches”) reduced runoff by 87-99%, soil losses by 97-100% and cyanazine losses by 85-99% from corn plots over 3 years. Cyanazine was transported almost entirely in the water phase (\( K_{OC} 190 \), SOL 170 mg/L). Runoff losses of cyanazine were greater with a higher application rate, but were a similar percent of applied amount. Clausen et al. (1996) found that runoff, sediment, atrazine and cyanazine losses were reduced substantially (i.e. 64%, 99%, 90% and 80% respectively) from a small catchment under reduced till corn (RT, 40% residue cover at planting) compared with a paired conventional till catchment (<10% cover at planting). This occurred even though atrazine and cyanazine concentrations in the water phase were not reduced and sediment-bond concentrations were increase with RT. Other natural rainfall plot or catchment studies to find reduced runoff, sediment and pesticide losses (though not necessarily lower concentrations) with various forms of conservation tillage include: for atrazine and propachlor (Ritter et al. 1974), for atrazine and
However, several catchment studies found that conservation tillage did not reduce pesticide losses. Isensee and Sadeghi (1993) found greater water phase concentrations and annual losses of herbicides (atrazine and cyanazine) from no-till (NT) than conventional till (CT) corn on small catchments, with total runoff about 10% less from no-till. Runoff was greater from NT than from CT when the time between rainfall events was less than seven days, otherwise runoff from CT was greater than or equal to NT. The first runoff events occurred soon after application (3 and 8 days) in both years studied, and had very high herbicide concentrations, particularly for NT, and contributed 90% of total losses. Similarly, Gaynor et al. (1995) found herbicide (atrazine and metolachlor) concentrations in surface runoff were 1.3 times greater from conservation than conventional tillage. Surface runoff amount and herbicide losses were increased, while tile drainage water and herbicide losses were decreased, with conservation tillage. Total herbicide losses (surface and tile drainage) per year were more related to occurrence of surface or tile discharge soon after herbicide application, or wet antecedent conditions before a storm, than to tillage system.

The common features of these studies where conservation tillage did not reduce, or increased, losses of poorly sorbed pesticide (Baker et al. 1978b, Isensee and Sadeghi 1993, Gaynor et al. 1995) appears to relate to (a) occurrence of storms soon after pesticide application with little or no rain in the intervening period to wash surface applied chemicals from the stubble cover and into the soil, and (b) wet soil conditions so that the cover provides no infiltration advantage. These contrasting results illustrate the importance of controlling runoff amount in controlling losses of poorly sorbed pesticides. Large rainfall events (e.g. rainfall simulator studies) occurring soon after pesticide application represent a worst case scenario, because soil concentrations are at their highest. However, they are also less likely to reveal benefits of conservation practices, because pesticides have had less time to dissipate from residue cover and to become more tightly sorbed to soil via the slower phases of sorption kinetics. Similarly, rainfall applied to wet soil is less likely to reveal differences between cover treatments.

Conservation tillage practices can result in several conditions that affect runoff of pesticides, and may contribute to increased runoff losses (following from Seta et al. 1993):

- Surface application for agricultural chemicals, when not followed by tillage, increases the potential for chemicals to be more concentrated near the soil surface and increasing potential for runoff losses, though for pesticides this is also often the case for conventional tillage and may be more of a concern for fertilizers (Baker and Laflen 1983, Seta et al. 1993)
- Periodically higher soil moisture contents under higher cover, leading to lower infiltration and greater runoff (Crutchfield et al. 1985, Glenn and Angle 1987, Isensee and Sadeghi 1993, Clausen et al. 1996). Where infiltration is lower due to wet soil under cover, the large pre-runoff leaching advantage of cover (e.g. Baker et al. 1982) is lost.
- In the more extreme cases of persistent high soil moisture, the infiltration advantage of retaining cover is lost altogether, and runoff and pesticide losses from conservation tillage equals or exceed those from conventional systems, e.g. the case of Gaynor et al. (1995) where rainfall appears to exceed evapotranspiration by some 200-300mm of surface or tile drainage.
- More pesticides may be applied to conservation tillage systems, discussed in a later section.
- Pesticides are intercepted on crop residues, where at least the soluble herbicides appear to be weakly sorbed and susceptible to being washed off (Martin et al. 1978, Baker and Sheirs 1989).
Control of pesticide runoff using conservation tillage/cover retention is by no means as clear-cut as is erosion control and appears to interact with other factors. In particular, concentrations of poorly sorbed chemicals are often not reduced by conservation tillage (Barisas et al. 1978, Baker et al. 1978b, Blevins et al. 1990, Isensee and Sadeghi 1993, Gaynor et al. 1995, Clausen et al. 1996, Malone et al. 1996, 1999), in which case losses of pesticides transported in the water phase are only reduced where runoff amount is reduced. Finally, conservation tillage practices and other best management practices have only been evaluated for a very limited number of pesticides (mostly residual herbicides used in US corn cropping), and for few insecticides. Generally, catchment studies of management of pesticide runoff only 1-4 years, and may not have experienced the full range of climatic extremes. Given the chemical-specific (and soil related) nature of responses to control practices, some local evaluation is warranted for key chemicals in industries such as the Australian cotton industry.

1.5.2 Tillage (incorporation of pesticides)

Tillage incorporates surface applied pesticides and nutrients into a greater depth of soil and reduces concentrations in the runoff-mixing zone (Baker and Johnson 1983, Baker and Laflen 1983) – a proportional reduction in concentrations in runoff is expected. Baker and Laflen (1979) studied runoff of three poorly sorbed herbicides (alachlor, atrazine and propachlor) from simulated rainfall plots 7-11 hrs after application to bare plots, with no treatment (control), incorporation by discing to about 70 mm, or with recent wheel traffic. Concentrations in both water and sediment phases were greatest from wheel tracks and least from incorporated plots. Total losses of herbicides 3-4 times greater where herbicides were not incorporated. Hall et al. (1983) found that when runoff amounts were similar, total season losses of atrazine were 25% lower where atrazine was incorporated to 50 mm than when surface-applied. Where runoff amounts were considerably lower from incorporated plots (for no apparent reason), total losses of atrazine were 75% lower from the incorporated. Willis et al. (1975) found much lower seasonal losses in runoff of trifluralin, which had been double-disk incorporated to 7.5cm, than diuron, linuron and fenac, which were surface applied.

Buttle (1990) found that incorporation of metolachlor (to 150 mm) significantly reduced dissolved, sediment-sorbed and total concentrations in runoff compared with surface broadcast (incorporated 31%, 64% and 40% of broadcast, respectively). As concentrations in 0-150 mm soil were not different between treatments, we can deduce that differences in runoff concentrations were related to differences in distribution of the herbicide within the 0-150 mm soil, with higher concentrations in near-surface soil for the broadcast treatment. Seasonal metolachlor losses were about an order of magnitude lower from the incorporated treatment. However, the incorporated treatment also produced much less runoff and sediment (incorporated 31% and 20% of broadcast, respectively), presumably due to differences in soil tilth and cover produced by the tillage treatments (incorporated was contour-ploughed, while broadcast was ploughed ‘cross-contour’) or in inherent soil properties. For water phase metolachlor losses (incorporated 10% of broadcast), reduced runoff amount and reduced soil concentrations contributed about equally to the observed reduction in losses from the incorporated treatment. For sediment phase losses (incorporated 20% of broadcast), reduction in sediment losses contributed more to reducing metolachlor losses than did reduced soil concentrations. Buttle (1990) did not investigate whether retaining crop residue cover could attain similar reductions in pesticide losses.

Tillage used to incorporate pesticides also affects runoff and soil losses, and therefore pesticide losses, by affecting soil tilth and by incorporating crop residues. For bare soil, tillage may reduce
runoff and soil loss under some circumstances (Baker and Laflen 1979, Buttle 1990), e.g. by creating clods, furrows and roughness. However, the resulting reduction in runoff may be short lived, as the roughness decays under rain. Tillage can increase soil loss under other circumstances, by reducing soil strength and increasing sediment availability on hardsetting soils. Holden (1995) measured twice the soil loss from tilled cotton furrows than from furrows not tilled after planting, during a growing season (6 irrigations). Most importantly, where crop residue cover is available, tillage can lead to greater runoff and soil loss, by reducing cover (Freebairn et al. 1996). Tillage is considered largely incompatible with retention of cover in dryland (Mutchler and McDowell 1990) and irrigated (Silburn et al. 1998) cotton systems, but may be beneficial to reducing pesticide runoff where cover is not available or can be retained above the tilled soil. Thus there are advantages and disadvantages to using tillage to incorporate pesticides.

1.5.3 Controlled traffic

A management practice that is well established in the Australian cotton industry, and is now being adopted in grain cropping, is controlled traffic (Lucy 1993). In an 8-row cotton system, tractor wheel traffic is restricted to two of the inter-rows (furrows) while a further two furrows receive traffic from implement wheels. Furrows used for wheel traffic are expected to be more compacted, and give more runoff and soil loss, than non-wheel tracks (Baker and Laflen 1979). Total losses of herbicides were 3.7 times greater with wheel traffic than without in the study of Baker and Laflen (1979).

1.5.4 Pesticide application rate and method

Hall et al. (1972) studied runoff losses from six application rates of atrazine over two successive seasons after application. Event average concentrations in sediment and water phases, and in total, increased with increasing application rate within each event, and decreased with each successive event during the season. Total runoff losses increased with increased application rate, but losses as a percent of applied were not significant difference between application rates. Hall (1974) found very similar effects of application rate on runoff losses and event average concentrations for atrazine and another s-triazine (GS13529), each at two rates, even though the patterns of rainfall and runoff events were different and total losses were higher. These data indicate a simple and direct relationship between application rate and runoff loss. That is, halving the application rate will halve the average concentration and the total amount lost in runoff. This is compatible with the direct relationship observed between event average runoff concentrations and soil concentrations, presented above.

Banded application should reduce pesticide runoff losses in proportion to the percent banded (for equal application rates on the sprayed band), because the application rate and the soil concentration on a whole area basis are reduced proportionally. In the catchment study of Baker and Johnson (1979), granular fonofos was applied in a 20% band and was incorporated to 50mm; average seasonal runoff losses were 0.36% of applied, compared with 0.96% and 2.1% for alachlor and triazines (atrazine or cyanazine) (average of 3 tillage treatments). Separating the contributing factors is difficult, although at least the fonofos, alachlor and cyanazine had comparable half-lives. Band spraying may be particularly effective where insecticides are band sprayed over the crop row when the plants are small, as a greater proportion of the insecticide is intercepted on the plants (where it will generally dissipate more rapidly than on soil) as well as the reduction in area of soil not sprayed. However, use of banded application and the application rate used on the band are often decided by other factors rather than reducing...
pesticide runoff. Banded application of residual herbicides may not provide the best runoff outcome if interrow tillage is then required to control weed and reduces the amount of residue cover.

Baker and Johnson (1979) observed from their catchment data, and from Baker et al. (1978b), that runoff concentrations in the sediment phase of band applied pesticides are greater from ‘till-plant’, where the banded soil is bare, than from conventional, where sediment is sourced from the whole surface area, including the 80% unsprayed area. Isensee and Sadeghi (1993) found runoff concentrations from small catchments of alachlor applied as a microencapsulated formulation were much lower than the other herbicides (atrazine and cyanoazine). Total runoff losses for the microencapsulated formulation were also reduced using no-till cultivation whereas losses for the other herbicides were not reduced using no-till.

1.5.5 Pesticide use in different farming systems

When a farming system is considered as a whole, chemical applications will vary in type, amounts and timing. For instance, there has been discussion whether conservation tillage may lead to greater pesticide runoff, as herbicides are used for weed control instead of tillage (Walter et al. 1979, Cameron and Green 1991). However, in many intensive cropping industries herbicides are used even in farming systems involving tillage. Day et al. (1999) found in a survey of pesticide used in U.S. corn production, herbicide use was higher in conservation farming systems, particularly no-till, than in conventional tillage systems. However, all systems used herbicides at annual rates of 1-1.5 kg.a.i./ha. Conservation tillage systems used more knockdown herbicides such as glyphosate and paraquat, which possess characteristics that make them more benign towards the environment, in place of more mobile and persistent herbicides used in the conventional systems. Insecticide use was no higher with conservation tillage than for conventional tillage, and was often lower. In cotton production in Australia, repeated tillage and bare soil are the norm; generally, at least two to three herbicides (pre-emergent residual herbicides) are applied. Insecticide use will, in the main, be similar regardless of the tillage system, although some recent work indicates lower insect pressure and more ‘beneficials’ (e.g. three times the number of spiders) when cotton is grown in wheat stubble (Waters et al. 1999, Whyte 2000). Thus tillage systems do not seem to be the main determinant of pesticide use patterns.

1.5.6 Requirements of management practices for controlling pesticide runoff from irrigated cotton

Carroll et al. (1995) determined that the critical period for soil erosion from irrigated cotton in the Emerald Irrigation Area (EIA) was early in the growing season, from pre-plant irrigation to canopy closure. During this period there is a high risk of runoff and soil erosion due to low cover levels, low soil moisture deficits, unconsolidated soil and occurrence of intense storms. Simpson et al. (1998) determined that the early part of the growing season is also the period of major potential risk for pesticide transport in runoff, as concentrations in the soil of herbicides are at their highest and applications of insecticides, particularly endosulfan, occur regularly. The highest risk period for the more water-soluble herbicides (eg. prometryn, fluometuron and diuron) was defined as 4-6 weeks after application. The risk period for endosulfan was extended by repeated applications resulting in a short term build up in the soil. This period may typically extend for some 8-12 weeks after planting, with six applications of endosulfan not atypical. Thus it is highly likely that, when storm rainfall occurs during this period, an endosulfan application was made some time in the previous two weeks. Much of the insecticide, particularly endosulfan, applied early in the cotton season lands on the soil, as plants are
small. During the early part of the season the major potential source of pesticides in runoff is the soil, whereas latter in the season washoff of pesticides applied to the plants will also contribute. Thus it is important to have management practices capable of controlling pesticide transport a) when crop canopy cover is small, early in the cotton season, b) during storm rainfall events, which compared with irrigations, are less easily managed in terms of timing of pesticide applications and the amounts and rates of runoff generated. Also, if a management practice is effective in reducing soil loss and pesticide transport in runoff in a large storm, it will be similarly or more effective for smaller/less intense storms.

1.6 Use of rainfall simulators to study pesticide runoff

1.6.1 Benefits and limitations

Rainfall simulators allow controlled experiments, with thorough, timely collection and storage of high quality samples. For example, the majority of data on sediment sizes has been collected from rainfall simulator plots, as such samples are best collected by hand (aggregated sediments can be broken down, or re-aggregate in auto-samplers) and at a suitable time for laboratory staff to be available for subsequent size determination. Similarly, for studies of pesticides where preservation of samples is important, samples can be collected by hand and refrigerated, filtered, extracted etc. immediately. Detailed time series of runoff concentrations, or flow-weighted average samples, can be obtained. In contrast, measurement of pesticides in runoff from natural rainfall plots and catchments is more problematic and generally use either flow-splitters to obtain event flow-weighted averages (Willis et al. 1975, Glen and Angle 1987, Blevins et al. 1990, Clausen et al. 1996), hand sampling during events (Gaynor et al. 1995), limited sampling and some form of extrapolation/estimation (e.g. hand samples, Buttle 1990; rising stage samples with limited samples during recessions, Baker and Johnson 1979), or automatic pumping samplers generally with refrigeration (Leonard et al. 1979, McDowell et al. 1981, Willis et al. 1983), an expensive option but still with a mixed record of success. Even where a series of samples are collected using pumping samplers, flow-weighted composite samples are often prepared from individual samples to reduce the cost of analysis (McDowell et al. 1981, Willis et al. 1983, 1987).

Most factors involved in pesticide runoff can be controlled in a rainfall simulator study, whereas they may not in a natural rainfall (e.g. catchment) study. For example, time between pesticide application and rainfall occurrence can be controlled and studied as an experimental variable. White et al. (1976) provide a good example. They studied runoff of 2,4-D from a 0.34 ha catchment for 3 years and in the last year used a rainfall simulator on subplots (30.2 m²) within the catchment. The highest runoff concentrations of 2,4-D were measured in the first event after application in each year, at 20, 27 and 34 days after application. However, concentration of 2,4-D in surface soil (0-5mm) was observed to decrease by 95% in only 7 days (from 4.7ppm to 0.23ppm) and was only 0.01 ppm (99.8% decrease) by 34 days, i.e. most of the applied 2,4-D dissipated before the first runoff event. Rainfall simulator plots run at 1, 8 and 35 days after 2,4-D application indicated there was potential for much greater losses of 2,4-D in surface runoff than observed in the 3-year study under natural rainfall, if rainfall occurred sooner after application. While the chance of this occurring was small at their location, the field study would give a false impression of potential runoff losses under other rainfall regimes or where 2,4-D was applied later in the season. This is a good example of combining several types of studies of pesticide behaviour, i.e. field dissipation, field runoff and rainfall simulation, to obtain a more comprehensive understanding.
Simplistic approaches to comparing and using data from rainfall simulators to represent hydrology, erosion and water quality under natural rainfall and for larger scales are problematic. However, there has been considerable success where suitable models, which represent the scaling-up of physical processes, have been used. In order to calculate pesticide runoff, it is firstly important to be able to predict hydrology and erosion. Silburn and Connolly (1995) determined infiltration parameters for a layered transient infiltration model from rainfall simulator plots, with treatments designed to reveal the hydraulic properties of the various soil layers. These infiltration parameters were used in a spatially distributed hydrologic model (which accounted for spatial distribution of soils, cover etc., and flow of runoff) to predict runoff hydrographs. Good predictions (of runoff amounts, peaks and hydrograph shape) were obtained for large rainfall simulator plots and under natural rain for spatially uniform catchments (Connolly and Silburn 1995). Using similar parametization approaches and the same model, Connolly et al. (1997) obtained good predictions of runoff hydrographs for a spatially complex catchment under a range of grazing induced cover conditions.

Similarly, for erosion, Loch et al. (1989) derived parameters for a physically based pseudo 3-D erosion model from small (interrill) and large (rill) rainfall simulator plots, and obtained good predictions of soil losses measured in storm events on each of two hillslope catchments. Silburn and Loch (1992) showed that simpler models, which represented key physical processes more simply or not at all, could not adequately predict these field soil losses using the same rainfall simulator data. Evans et al. (1994) extended the work of Loch et al. (1989) to show that small plots under a laboratory rainfall simulator could be used to derive interrill erosion parameters, which, using the same model, gave good predictions of soil loss under a larger field (interrill) rainfall simulator (thus validating a simpler laboratory procedure for screening interrill erodibility of a range of mine spoils). More recently, Connolly et al. (2001), used GLEAMS, a derivative of the model used by Loch et al. (1989), to model runoff, sediment and pesticide transport from irrigated cotton furrows and fields (taildrains). Important parameters relating to effects of cover, sediment size and pesticide partitioning (which were not studied at the field scale) were derived from rainfall simulator studies (this thesis). The model predicted field behaviour well, although some parameters had to be altered at larger scales, indicating the model did not fully represent some aspects of sediment and pesticide behaviour as scale increased – the pesticide model unfortunately was spatially more simplistic (more lumped) than the sediment model.

Sharpley et al. (1982) used relationships derived laboratory rainfall simulator plots on 4 soils, relating soluble P concentration in runoff to water extractable P in soil (P<sub>x</sub>), and using measured P<sub>x</sub> for catchment soils obtained good predictions of soluble P in runoff from catchments with a range of land uses and fertiliser inputs. They also used an equation derived from the rainfall simulator data, relating sediment P enrichment ratio (PER) to sediment yield, and obtained good agreement with measured sediment-bound P in runoff from the catchments, using measured soil total P and sediment yield.

White et al. (1976) found that 2,4-D concentrations in runoff from rainfall simulator subplots within a 0.34 ha catchment were "about the same" as from the catchment, at 35 days after application. Concentrations decreased from 2.0 to 0.5 µg/L during the 30min simulator storm (48mm runoff), with an event average concentration of 0.7 µg/L, compared with concentration ranges of "2.5-1.1" and "0.6-trace" µg/L in two runoff events from the catchment the day before and the day after the 35 day simulator run. Exact comparison is difficult due to the differences in rainfall and runoff amounts. (More information on White et al. (1976) is presented in Chapter 4).
Wauchope (1978) defined pesticide runoff for ‘critical events’ (within 2 weeks of pesticide application, greater than 10mm rainfall, 50% of which becomes runoff) and ‘catastrophic’ events (first events soon after application) (described above), and considered that rainfall simulator events where severe rainfall is applied soon after application of a pesticide as ‘catastrophic’. Wauchope (1978) also considered that small plots gave reasonable agreement with large fields as far as concentrations are concerned, but they can overestimate long-term losses from larger fields by a factor of two. Rainfall simulators have often been used to apply storms that exceed the ‘critical’ event, e.g. giving greater than 30 mm of runoff and up to 80% of rain as runoff for a single event, which would lead to large loads/losses. This choice by the rainfall simulator scientist is probably related to the history of use of simulators in erosion research, where large infrequent storms cause the majority (>80%) of total soil loss (Wockner and Freebairn 1990) and it is under these conditions that erodibility must be defined and erosion management is of greatest interest. However, it is probably a matter of how the rainfall simulator data are interpreted rather than the method being intrinsically biased.

Rainfall simulator plots were often run very soon after pesticide application, resulting in large losses in runoff (i.e. as % of applied) and leading to events classed as ‘catastrophic’. For example, White et al. (1967) found atrazine losses of 17% and 7.3% of applied at 1 and 96 hr after application, respectively, during 50mm of rain (39mm runoff). Losses of this magnitude are not unheard of in catchment studies (Ritter et al. 1974, Wauchope 1978) and probably represent reasonably well what would happen on a catchment if a large runoff event occurring very soon after spraying. The problem is in the use of such data to define more general behaviour, e.g. seasonal losses, in an overly simplistic manner. Time of the applied storm after spraying is a matter of choice by the rainfall simulator scientist. The main reasons studies are often run soon after spraying are probably logistical (get the study finished before natural rain or farm operations disturb the site) and, given the effort involved and uncertainty in dissipation rates, concerns that concentration will fall below detection limits.

1.7 Aims and scope of study

1.7.1 Current situation

The literature shows that pesticide runoff is strongly related to the concentration in a shallow surface soil layer when the runoff event occurs. This concentration is determined by the amount applied, the time of the event after application and dissipation during that time. The pesticide is extracted into runoff partly as a solute and partly sorbed to sediment, so runoff concentration will also depend on the hydrology, particularly leaching and dilution of the solute, and erosion, particularly the concentration and sorptive capacity of sediment entrained into runoff. The sorption properties of the pesticide, and to a lesser extent the soil/sediment properties, determine the distribution between these extraction pathways. The literature indicates that management of pesticide runoff using erosion control practices is effective for more sorbed pesticides, but that control of weakly sorbed pesticides is less certain. The relative runoff potential of pesticides of different properties is also unclear, because it depends on a multitude of factors and because pesticides are often studied independently.
Despite these extensive studies, questions remain regarding behaviour of particular pesticides. Pesticide runoff under Australian agricultural conditions in general is poorly researched. Specifically, when this study began there had been little study of pesticide runoff, and the underlying hydrology and erosion, in the Australian cotton industry. Cotton growing is dominantly practiced on clay soils on low slopes with a hill-furrow surface geometry, whereas most studies of pesticide dissipation, sorption and runoff have been on more sandy or silty soils, more typical of North America, and on steeper slopes.

1.7.2 Aims

This study set out to answer some of these questions by developing a quantitative understanding of pesticide movement in runoff from cotton hill-furrow systems during storm rainfall, taking into account differences in pesticide and soil properties, by using a rainfall simulator. It sought to:

1. Determine field dissipation rates of pesticides specifically from the soil surface runoff-mixing layer and from crop residues. (Chapter 3)
2. Investigate processes of pesticide runoff extraction from soil by determining the relationship between pesticide in runoff and in soil (the outcome of dissipation), and the key factors that determine differences in runoff extraction for pesticides of contrasting properties. (Chapter 4)
3. Investigate partitioning of pesticides between water and sediment phases in runoff, a key determinant of the efficacy of various management practices. (Chapter 5)
4. Investigate effects of management practices on runoff, sediment and pesticide transport for pesticides of contrasting properties. (Chapters 6 and 7)

1.7.3 Scope of this study

The data presented, and the conclusions drawn, are applicable to pesticides applied to the soil surface as liquid/emulsion sprays and their runoff during rainfall under reasonably erosive conditions. The potentially large contribution to runoff losses from washoff of pesticides applied to plant canopies, and pesticides applied as granules and powders, are not considered. Pesticide runoff concentrations may be larger than found in-stream because dilution and transmission losses are not considered.
CHAPTER 2.
GENERAL METHODS
CHAPTER 2. GENERAL METHODS

Methods that are general to the thesis are presented in this chapter. Details of experimental design and methods that are specific to each chapter are presented in that chapter. This is because each chapter deals with a different aspect of pesticide behaviour using data from the same field studies. While each field study included various pesticide and cultural management practices the thesis aimed to explore general features across the studies.

2.1 Experimental outline and design

Field studies were carried out at four sites (Gatton, Emerald, Warren and Jondaryan) in cotton growing areas (Fig. 2.1). Pesticide dissipation from soil was studied at all sites and pesticide runoff was studied, using a rainfall simulator, at three sites (Gatton, Emerald and Jondaryan). As the focus of the thesis is on pesticide runoff, dissipation from the soil surface was studied, rather than the soil profile. Thus concentrations of various pesticides were measured in surface soil (0-25mm), an approximation of the runoff-mixing zone, and in crop residues where present. These data were used (a) to determine dissipation of potential ‘runoff available’ pesticide residues (Chapter 3), and (b) to investigate relationships between pesticide concentrations in soil and in runoff from the rainfall simulator plots (Chapter 4). The rainfall simulator data is used to investigate partitioning in runoff, between water and sediment phases (Chapter 5), and management of pesticide runoff (Chapter 6 & 7).

The fate of endosulfan (α-, ß- and sulfate) was studied at all sites, together with other pesticides applied as experimental treatments or present from farm spray operations. In all, soil and runoff data were collected for seven insecticides and seven herbicides, to provide a wide range in chemical properties. Most studies concentrated on the period 2-3 weeks after pesticide application when concentrations are highest and potentially changing rapidly. Apart from the initial study at Gatton, they were conducted on commercial cotton farms. This sometimes meant that the studies were interrupted by commercial applications of endosulfan. One study (Jondaryan) included sampling to 62 days after application for a wide range of pesticides.

At each site, pesticide dissipation and runoff were studied for ‘control’ conditions and compared with various spray or cultural treatments. The control conditions, similar to those generally found on cotton farms early in the growing season, were: blanket surface spraying onto bare tilled soil with hill-furrow geometry. Time since spraying, and number of sprays, were an important consideration.

Dissipation studies at the four sites were conducted after one, and sometimes two sequential applications of various pesticides, on bare soil. EC and ULV formulations of endosulfan were compared at Gatton and Warren. Effects of crop residue cover on dissipation of endosulfan were studied at Emerald and Warren. These treatments are described in detail in Chapter 3.
In runoff studies, time since spraying was either studied as part of the experiment or was held constant so that other treatments could be compared. The main experimental treatments/variables in runoff studies, apart from differences between pesticides, were:

(a) Gatton,
   - Time after spraying, through a sequence of two applications to bare soil,
   - ‘One-off’ comparisons at one time after spraying – with and without cover, EC v ULV formulation, plot length (1.6m or 12m) and slope (1-4%), and first v second rainfall event.

(b) Emerald, at one time after spraying,
   - Bare soil versus cover treatments provided by crop residues on the soil surface (0-60% cover),
   - Each cover treatment with and without prior wheel traffic and thus different soil compaction.

(c) Jondaryan,
   - Time after spraying following one application to bare soil,
   - For blanket versus banded spraying.

The details of these studies are presented in the appropriate chapter.

Fig. 2.1. Locations of field sites and main cotton growing areas in Queensland and New South Wales, Australia. (Adapted from Hugo 1999, after Triantafillis et al. 1996)
2.2 Locations and soils

The runoff (rainfall simulator) and dissipation studies were carried out at (Fig. 2.1):

(a) Gatton, April 1994, on the University of Queensland (UQ) research station, east of Gatton, Queensland. The site is adjacent to Lockyer creek on an alluvial levee (27°32.173’ 152° 20.052’). The soil has a dark clay loam to light clay (crusting or cloddy) surface, is mapped as a ‘Lockyer’ soil (UQ station map, Dr. Brian Schafer, pers. comm.) based on Powell (1982) (survey on the adjoining QDPI research station), a Udic Argiustoll (Soil Taxonomy, Soil Survey Staff 1975).

(b) Emerald, October 1994, on an irrigated cotton farm in the Emerald Irrigation Area (left bank, portion 137, SW ends of ‘Block 2’ and ‘Block 5’), 4 km west of Emerald, Queensland (23°31.6'S, 148°9.3'E). The site was the Queensland field site for the LWRRDC/CRDC/MDBC program “Minimising the Impact of Pesticides on the Riverine Environment” (Simpson et al. 1998) and has been used to study erosion by Carroll et al. (1991, 1995). The soil is a Black Vertosol (Australian Soil Classification, Isbell 1996), Typic Haplustert (Soil Taxonomy), locally ‘TbUg-2’ (McDonald and Baker 1986), derived from Tertiary olivine basalt, and is strongly self mulching and strongly cracking. The site was used for irrigated cotton growing for more than 20 years.

(c) Warren, November 1994, Field 23 (NW corner) on Auscott’s farm between Warren and Nevertire, NSW. This was one of the NSW field sites for the LWRRDC/CRDC/MDBC pesticides program (Kennedy et al. 1998, 2001). The soil is a sodic grey cracking clay, a Grey Vertosol (Isbell 1996), on Old Alluvium Backplain (McKenzie 1992), most likely a ‘Snake’ soil (David McKenzie, pers. comm.), a fine Entic Chromustert (Soil Taxonomy), used for irrigated cotton for more than 20 yrs.

(d) Jondaryan, October-November 1996. The site is located between Oakey and Jondaryan on the Darling Downs, Queensland (27°25’50” 151°37’40”) on the gently undulating alluvial plain of Oakey Creek. The soil is locally known as ‘Waco’ of basaltic origin, a Haplic self-mulching Black Vertosol (Isbell 1996), Udic Haplustert (Soil Taxonomy) (Andrew Biggs, NR&M, pers. comm., 1996). The site was used for cultivated cropping for at least 30 years and in recent years for furrow irrigated cotton in rotation with winter cereal crops. Properties of these soils are given in Table 2.1.

Table 2.1. Properties for surface soil from sites used for rainfall simulator and soil pesticide studies.

<table>
<thead>
<tr>
<th>Site</th>
<th>Coarse Sand (%)</th>
<th>Fine Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Organic Carbon (%)</th>
<th>CEC (cmol+ kg(^{-1}))</th>
<th>pH (H(_2)O 1:5)</th>
<th>Texture (Local Name) [Reference]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gatton Apr 94 (0-50mm)</td>
<td>4</td>
<td>32</td>
<td>26</td>
<td>40</td>
<td>1.3</td>
<td>35</td>
<td>7.2</td>
<td>Clay/clay loam (Lockyer) [1]</td>
</tr>
<tr>
<td>Warren Nov 94 (0-25mm)</td>
<td>8</td>
<td>24</td>
<td>13</td>
<td>55</td>
<td>0.78</td>
<td>31</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Jondaryan Oct 96, (0-25mm)</td>
<td>5</td>
<td>13.5</td>
<td>15</td>
<td>66.5</td>
<td>1.1</td>
<td>53</td>
<td>8.1</td>
<td></td>
</tr>
</tbody>
</table>

2.3 Hill-furrow geometry and plot conditions

All studies were conducted on hill-furrow layouts on cotton farms with 1-metre row spacing, except Gatton (described separately below). In this system, cotton is planted into the top of hills or permanent beds, separated by furrows that are used for irrigation and wheel traffic. Typically, hills were 0.25 m high, with a flat top about 0.1 m wide formed by the planter, with linear side-slopes to the furrow bottom, which may be V-shaped or have a narrow flat section (Fig. 2.3). The sides of the hill were about 50% slope and 0.4 m long. Mean downfield furrow slopes were low, typical of most irrigated cotton fields (0.2-1.5%, Table 2.2). Rainfall simulator and soil dissipation plots were laid out so that they included a wheel track and a non-wheel track furrow, which were bulked at soil sampling.

Studies were conducted early in the cotton season, in the window between planting and first irrigation, when the first commercial insecticide sprays occur (depends on insect pressure). All sites had low plant cover (<5%) and were bare of crop residues, except where cover was used for experimental purposes. Surface soils (e.g. 0-50mm) were loose and at about air-dry moisture content, though the surface had a strong crust at Jondaryan. Subsoils were moist and firm, with no cracks, having been pre-irrigated (Emerald and Warren) or fallow for about 12 months (Jondaryan). At Gatton, row spacing was 0.75-m with 50% side slopes, the study was run in April, no crop was present, wheel traffic was random and the site had a history of general cropping rather than furrow irrigated cotton. Surface soil was loose, with a fine crumb structure (not crusted) while subsoil was firm and moist. A feature common to all sites was a shallow layer of loose soil in the furrow bottoms (a few cm) underlying firm moist soil, compacted to varying degrees depending on prior wheel traffic.

Table 2.2. Dimensions, rainfall applied and numbers of rainfall simulator plots, at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>Block</th>
<th>Mean Furrow slope (%)</th>
<th>Rainfall simulator plots</th>
<th>Rainfall simulator plots</th>
<th>Rainfall simulator plots</th>
<th>Rainfall simulator plots</th>
<th>Rainfall simulator plots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Length (m) WidthA (m)</td>
<td>Rainfall intensity (mm/hr)</td>
<td>Rainfall duration (min)</td>
<td>Rainfall amount (mm)</td>
<td>Number of plots</td>
</tr>
<tr>
<td>Gatton</td>
<td>1.5</td>
<td>1.6</td>
<td>0.75</td>
<td>95</td>
<td>40</td>
<td>63</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emerald</td>
<td>B2</td>
<td>1.0</td>
<td>12</td>
<td>1.0</td>
<td>95</td>
<td>40-50</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>1.3</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jondaryan</td>
<td>0.2</td>
<td>12</td>
<td>1.0</td>
<td>67</td>
<td>40</td>
<td>47</td>
<td>10</td>
</tr>
<tr>
<td>Warren</td>
<td>0.5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

A – plot width equal to crop-row width, from top-of-hill to top-of-hill.
B – rainfall was applied for 40 min or more, but data were always analysed for the specified amount of rainfall.
2.4 Rainfall simulator

The rainfall simulator (Fig. 2.3, Fig. 2.2) is based on the design of Meyer and Harmon (1979) and Loch (1989), using 13 in-line oscillating flat-fan Veejet 80100 nozzles spraying downwards, wetting a area 13 m long and 2.5 m wide. A 3-nozzle module was used for short (1.6m) plots. The kinetic energy of the simulated rain was approximately 29.5 J/(m².mm) (Duncan 1972), consistent with the average energy of natural rain in eastern Australia at intensities greater than 40 mm/hr (Rosewell 1986). Drop size distribution and drop impact frequency are similar to average values for natural rain (Jenny Foley, NRM, pers. com.). Rainfall intensity is controlled by the frequency of passes of rainfall over the plot using an electronic control box. Rainfall intensity was calibrated by covering plots with plastic sheet and recording the runoff. Rainfall was also measured in a series of rain gauges along each plot. Rain was applied for 40 min or more, at 95 mm/hr (Gatton and Emerald, 65 mm rain) and at about 70 mm/hr at Jondaryan (47mm) (Table 2.2). Reasonably intense storms were applied, as they cause the majority of total soil loss in this type of environment (Wockner and Freebairn 1991). It is important that management practices are effective for such storms.

Fig. 2.2. Rainfall simulator on two cotton furrow plots, with sample bottles laid out for runoff and sediment, sediment size and pesticide runoff.

The simulator applied rain to two adjoining plots simultaneously (Fig. 2.3). At Emerald and Jondaryan these always included a wheel track and a non-wheel track. Each plot was one row-width wide (0.75 or 1 m wide) and 1.6 or 12 m long (Table 2.2), and consisted of a central furrow and two
hillsides. Plots were defined with metal walls that were installed after spraying so they did not contribute to pesticides washoff.

2.4.1 Runoff and sediment measurements

Runoff rate and sediment concentration were measured at the outlet of each plot every 1-2 min (Fig. 2.3). Towards the end of each run, width and depth of flow were measured at six locations and velocity measured in three 1-m sections along each furrow. Flow velocity was measured by timing the passage of dye over 1-m lengths, giving the maximum velocity in the cross section, and was not adjusted to obtain an average velocity. During steady state runoff, metal pegs were pushed into the soil to the depth of the water surface at known distances along the furrow. After rain the elevation of the top of the pegs and the adjacent soil surface were recorded with an electronic or manual theodolite. The resulting water surface profile was used to calculate the furrow slope. This gave a more reliable and useful slope than surveys of the furrow soil surface either before or after rain, as slopes were low.

Fig. 2.3. Rainfall simulator on two cotton furrow plots (a) overview including nozzle units, supply and return pipes at the top of the A-frame, shade-cloth wind shelter, and (b) detail of plot outlets used for sampling runoff, rain gauges and velocity measuring sections along the furrows.

Additional samples of runoff were collected for determination of the undispersed sediment size distribution. These data are only presented for Emerald and methods are presented in Chapter 6. Soil moisture content was measured in 50 mm depth intervals, before and after rain, using a sharp edged 100mm diameter core. Bulk density was calculated from the cores taken after rain and used to convert concentrations in soil (mg/kg) to areal loads (g/ha). At Emerald, nitrogen (N) and phosphorous (P) were measured in runoff and soil, as described in Appendix B.
2.5 Pesticide treatments and analysis

2.5.1 Pesticides studied and their properties

Endosulfan (applied as ~7:3 α and β isomers), endosulfan sulfate (a toxic breakdown product) and prometryn were measured at all sites. A range of other pesticides used in cotton was studied, being either applied as experimental treatments or present in soil from farm operations (Table 2.3). Only those pesticides applied as experimental treatments were used in dissipation studies, however, pesticides applied during farm operations or present in the soil from historic applications (Table 2.3) were determined in runoff and soil samples and were used in runoff studies.

Table 2.3. Pesticides studied and amount applied.

<table>
<thead>
<tr>
<th>Site</th>
<th>Product and Formulation</th>
<th>Type</th>
<th>Application type</th>
<th>First Spray</th>
<th>Second Spray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gatton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td>EC 350</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>720</td>
<td>780</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Roger 400 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>145</td>
<td>145</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Bandit EC</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>570</td>
<td>560</td>
</tr>
<tr>
<td>Emerald</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Thiodan ULV</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>890</td>
<td>1000</td>
</tr>
<tr>
<td>p,p’ DDE</td>
<td>DDT</td>
<td>Residue</td>
<td>Historic</td>
<td>Unknown</td>
<td>Unknown</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Cotogard</td>
<td>Herbicide</td>
<td>Farmer</td>
<td>625</td>
<td>None</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Trelfan</td>
<td>Herbicide</td>
<td>Farmer</td>
<td>1120</td>
<td>None</td>
</tr>
<tr>
<td>Warren</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blanket ULV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Thiodan ULV</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>680</td>
<td>None</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Perfection EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>160</td>
<td>None</td>
</tr>
<tr>
<td>Banded EC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied as a ~40cm band on the hill</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Thiodan EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>166</td>
<td>None</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Perfection EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>32</td>
<td>None</td>
</tr>
<tr>
<td>Jondarvan A Insecticides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Thiodan 350 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>1456</td>
<td>None</td>
</tr>
<tr>
<td>Chlordpyrifos</td>
<td>Lorsban 500 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>747</td>
<td>None</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Roger 400 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>192</td>
<td>None</td>
</tr>
<tr>
<td>Profenofos</td>
<td>Curacron 250 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>1000</td>
<td>None</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>Nuvacron 400 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>800</td>
<td>None</td>
</tr>
<tr>
<td>Parathion-methyl</td>
<td>Folidol 500 EC</td>
<td>Insecticide</td>
<td>Experimental</td>
<td>350</td>
<td>None</td>
</tr>
<tr>
<td>p,p’ DDE</td>
<td>DDT</td>
<td>Residue</td>
<td>Historic</td>
<td>Unknown</td>
<td></td>
</tr>
<tr>
<td>Herbicides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dihuron</td>
<td>Dihuron</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>2000</td>
<td>None</td>
</tr>
<tr>
<td>Fluometuron</td>
<td>Fluometuron</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>1510</td>
<td>None</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Dual 720</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>1440</td>
<td>None</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>Stomp 33E</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>660</td>
<td>None</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Cotogard 500 FW</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>750</td>
<td>None</td>
</tr>
<tr>
<td>Pyrithiobac sodium</td>
<td>Staple 85% active</td>
<td>Herbicide</td>
<td>Experimental</td>
<td>102</td>
<td>None</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Trelfan</td>
<td>Herbicide</td>
<td>Farmer</td>
<td>Unknown</td>
<td></td>
</tr>
</tbody>
</table>

A – All pesticides were applied to different dissipation/runoff plots on four dates over 34 days, as either blanket or banded sprays (Chapter 3). Application rates for some treatments varied from those given here.
The pesticides studied covered a wide range of chemical properties (Table 2.4). Common names of pesticides are used throughout and are consistent with those used in Wauchope et al. (1992), Hornsby et al. (1996) and Tomlin (1994). These sources give the chemical name and molecular formula associated with each common name and this information is not repeated here. One exception is pyrithiobac sodium, for which further information is given in Table 2.4. Properties and behaviour in the environment of endosulfan are reviewed in Appendix A.

Table 2.4. Published properties of pesticides used in runoff and dissipation studies. Properties are from Wauchope et al. (1992), unless otherwise indicated. Class is according to Weber (1972). Vapour pressure from Weber (1994) and Tomlin (1994) are given where published values differ. Volatility based on Henry's coefficient \( K_H \) from USDA-ARS (1995), with ratings of Gerritse et al. (1991) – negligible \( K_H < 10^{-6} \), low \( 10^{-6} - 10^{-3} \), significant \( 10^{-3} - 10^{-1} \), high \( > 10^{-1} \).

<table>
<thead>
<tr>
<th>Pesticide (common name)</th>
<th>Type and class</th>
<th>Solubility In water (mg/L)</th>
<th>Soil sorption ( K_{oc} ) (L/kg)</th>
<th>Field dissipation ½-life (days)</th>
<th>Vapour Pressure (mPa)</th>
<th>Volatility Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Insecticides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>Organophosphate (OP)</td>
<td>0.4</td>
<td>6,070</td>
<td>30</td>
<td>2.26</td>
<td>Low</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>OP</td>
<td>39,800</td>
<td>20</td>
<td>7</td>
<td>3.32, 1.1</td>
<td>Neg.</td>
</tr>
<tr>
<td>Profenofos</td>
<td>OP</td>
<td>28</td>
<td>2,000</td>
<td>8</td>
<td>2.5, 0.12</td>
<td>Low</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>Cyclodiene,</td>
<td>0.32</td>
<td>12,400</td>
<td>50</td>
<td>0.023, 0.83</td>
<td>High</td>
</tr>
<tr>
<td>a-isomer</td>
<td>Organochlorine</td>
<td>0.53&lt;sup&gt;CB&lt;/sup&gt;</td>
<td>4,000&lt;sup&gt;A&lt;/sup&gt;</td>
<td></td>
<td>6.08&lt;sup&gt;CB&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>b-isomer</td>
<td></td>
<td>0.28&lt;sup&gt;CB&lt;/sup&gt;</td>
<td>20,000&lt;sup&gt;A&lt;/sup&gt;</td>
<td></td>
<td>3.04&lt;sup&gt;CB&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td></td>
<td>0.17&lt;sup&gt;CH&lt;/sup&gt;</td>
<td>7,240&lt;sup&gt;B&lt;/sup&gt;</td>
<td></td>
<td>0.023, 0.83, 0.023</td>
<td></td>
</tr>
<tr>
<td><strong>Herbicides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diuron</td>
<td>Phenylurea, non-ionic</td>
<td>42</td>
<td>480</td>
<td>90</td>
<td>0.009</td>
<td>Neg.</td>
</tr>
<tr>
<td>Fluometuron</td>
<td>Phenylurea, weakly acidic, non-ionic</td>
<td>110</td>
<td>100</td>
<td>85</td>
<td>0.125</td>
<td>Neg.</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Substituted Acetamide</td>
<td>530</td>
<td>200</td>
<td>90</td>
<td>4.17, 2.7</td>
<td>Neg.</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>Dinitroaniline</td>
<td>0.275</td>
<td>5,000</td>
<td>90</td>
<td>4.0, 1.25</td>
<td>Low</td>
</tr>
<tr>
<td>Prometryn</td>
<td>s-triazine, basic</td>
<td>33.0</td>
<td>400</td>
<td>60</td>
<td>0.27, 0.165</td>
<td>Neg.</td>
</tr>
<tr>
<td>Pyrithiobac sodium&lt;sup&gt;C&lt;/sup&gt;</td>
<td>Pyrimidinyl carboxy, very polar, anionic</td>
<td>64,000 pH5</td>
<td>5-35</td>
<td>---</td>
<td>&lt;4.8 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Neg.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>05,000 pH7</td>
<td>9-21&lt;sup&gt;U&lt;/sup&gt;</td>
<td>11,14,46&lt;sup&gt;U&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additional in runoff studies</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parathion-methyl</td>
<td>OP</td>
<td>60</td>
<td>5,100</td>
<td>5</td>
<td>1.99, 0.4</td>
<td>Neg.</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>OP</td>
<td>10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1(est.,)</td>
<td>30</td>
<td>21.3, 9.3</td>
<td>Neg.</td>
</tr>
<tr>
<td>DDE&lt;sup&gt;U,H&lt;/sup&gt;</td>
<td>DDT residue</td>
<td>0.1 (est.)</td>
<td>50,000&lt;sup&gt;H&lt;/sup&gt;</td>
<td>1000</td>
<td>---, 0.86</td>
<td>Sign.</td>
</tr>
<tr>
<td>DDT&lt;sup&gt;H&lt;/sup&gt;</td>
<td>Organochlorine</td>
<td>0.006&lt;sup&gt;0.38-0.88&lt;/sup&gt;</td>
<td>(2-16yrs)</td>
<td>30</td>
<td>13.7, 14.6</td>
<td>Sign.</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Dinitroaniline, non-ionic</td>
<td>0.32</td>
<td>8,000</td>
<td>60</td>
<td>13.7, 14.6</td>
<td>Sign.</td>
</tr>
</tbody>
</table>


2.5.2 Pesticide application

Experimental applications of pesticides (Table 2.3) were made using hand applicators or booms with appropriate EC (high volume e.g. 50L/ha) or ULV (ultra low volume e.g. 3-4L/ha) emitters. At Gatton, Emerald and Warren spraying was conducted by staff from C-PAS (Centre for Pesticide
Application and Safety, University of Queensland, Gatton) and at Jondaryan by Mr Geoff Cornwell (Du Pont Development Advisor, Toowoomba). At each site, a series of strips (along the furrows) were sprayed on the various cultural treatments (e.g. cover, wheel traffic), with areas allocated for rainfall simulator and dissipation studies. Prior to application, the surface soil (0-25 mm) contained no detectable α- or β-endosulfan at all sites, but did contain some endosulfan sulfate carried over from the previous season at Emerald and Warren. Some other pesticides were also applied prior to experimental spraying during normal farm operations (Table 2.3). Confirmation of application rates using paper strips was no better than using soil samples, with more reliable results obtained by sampling the soil as soon as possible after application (20 min to 12 hrs). Application rates could often be confirmed with initial soil concentrations of a number of pesticides where tank-mixes were used. Temperature, relative humidity and wind speed were recorded at the time of spraying.

2.5.3 Sampling for pesticide analysis

Runoff samples. Two types of runoff sample were taken from the outlet of each rainfall simulator plot for pesticide analysis:

(a) Samples of runoff water (~500mL) at five times evenly spaced during the runoff hydrograph, analysed for total concentrations of each pesticide (i.e. in water and sediment),

(b) A composite (bulked) sample of runoff during the hydrograph. These samples were filtered and analysed for concentrations of pesticides in the water and sediment phases (separately), to determine average partitioning for the runoff event (Chapter 5). Immediately after each runoff sample was taken, a portion of runoff was added to a single bottle (per plot). The duration of sampling for each portion added was kept constant, providing a flow weighted sample of runoff. This approach was used to provide the most information at the least cost (filtered samples being more than twice the cost of total samples). The two separate estimates of total concentration obtained also provided a crosscheck. Total concentrations in runoff and bulked samples are compared in Appendix C. Each load of ‘rainwater’ used in the simulator was also sampled.

Soil samples. Within a sprayed area (dissipation studies) or simulator plot, separate samples were taken for soil (0-25mm) from the top of the hill and the bottom of the furrow. In each case samples were taken from eight locations, composited and thoroughly mixed. Samples were composited for the two plots under each rainfall simulator run. A flat trowel, about 80mm by 100mm, with 25mm high vertical sides was used, being inserted horizontally from a cut vertical face. For deeper samples (at Jondaryan), 0-25mm and 25-50mm samples were taken with this trowel. A 45mm-diameter core was then used for 50-100mm samples. Layers were removed in sequence to avoid contamination. Gravimetric moisture content was measured on a sub-sample of each soil sample.

Crop residue samples. At Emerald and Warren where crop residues were studied, sub-samples of crop residues (either wheat stubble or cotton trash) were taken from a known area (a 200mm square), and the 0-25 mm soil samples taken from these areas. Thus these soil samples did not contain pesticides intercepted by the crop residues. Crop residue sub-samples were prepared as composites.
The mass of crop residue per unit area was measured, so that concentrations (mg/kg) could be converted to areal loads (g/ha) and to determine the total pesticide load in crop residue and soil.

Samples for pesticide analysis were placed in glass jars with Teflon or aluminium foil sealed lids to prevent contamination. All samples were placed in insulated boxes with ice immediately after collection, and either transferred to the laboratory by air courier (at 4°C) or placed in a freezer later that day. Filtering and extraction of runoff and rainwater samples commenced in the laboratory within one day of sampling. Soil and trash samples were stored at -15°C until analysis was commenced.

2.5.4 Pesticide analysis

Runoff, rainwater and soil samples were analysed for the pesticides listed in Table 2.4 for each study, with endosulfan (α-, β-isomers and endosulfan sulfate) measured at all sites. Crop residue were only analysed for endosulfan. Rainwater samples were treated in the same way as runoff samples.

Runoff samples. The initial phase of analysis was different for hydrograph and bulked samples:

(a) Samples of runoff taken through the hydrograph and rainwater were analysed for total pesticide concentration (i.e. water and sediment). However, to enhance extraction, sediment and water were separated by flocculation with calcium sulfate, decanted and filtered through glass fibre papers. The sediment portion was extracted by refluxing with dichloromethane/acetone (1:1) and the resulting extract reduced to a small volume and added to the water portion of the same sample. This recombined sample was then extracted with dichloromethane and hexane.

(b) Bulked runoff samples were used for separate analysis of sediment-sorbed and soluble forms of pesticides. Samples were separated into water and sediment portions by filtering through glass fibre filter paper (0.7μm pore size). The water portion was extracted by shaking with dichloromethane and hexane separately. Sediment was extracted by refluxing with a mixture of dichloromethane and acetone (1:1). The resulting sediment extract was reduced to a small volume and added to 500 mL distilled water and extracted with dichloromethane and hexane.

Runoff samples from Gatton and Emerald were analysed by the Pesticides Laboratory, Indooroopilly, NR&M (Bruce Simpson pers. comm.). Following extraction (described above), pesticides were partitioned into hexane and cleaned up on a Florisil column. Pesticide residues were determined using gas chromatography with ECD (electron capture detector), NPD (nitrogen phosphorous detector) and mass spectrometry, as appropriate, using a 30 m DB-1 capillary column.

Runoff samples from Jondaryan, other than pyrithiobac sodium, were analysed by the Queensland Health Scientific Services, using standard multi-residue GC and HPLC methods described in Appendix D. Extra runoff samples were taken from the Jondaryan plots and analysed for pyrithiobac sodium in water and in filtered sediment by Analchem Bioassay (Sydney) using a GC-MS method, using analytical methods from Bruns and Tauber (1992) and Sumpter et al. (1996).
Soil and crop residue samples were analysed for endosulfan (α-, β-isomers and endosulfan sulfate) and other pesticides (Table 2.3), as follows:

(a) For Emerald, Warren and Gatton by the Pesticides Laboratory, Indooroopilly, NR&M. Bruce Simpson (pers. comm.) provided the following summary. Pesticides were extracted from soil and crop residues with methanol/water (4:1) and partitioned into hexane and cleaned up on a Florisil column. The pesticide residues were determined using gas chromatography with ECD, NPD and mass spectrometry, as appropriate, and a 30m DB-1 capillary column.

(b) For the Jondaryan study, pesticides in soil other than pyrithiobac sodium were analysed by the Queensland Health Scientific Services, using standard multi-residue GC and HPLC methods.

Pyrithiobac sodium in soil (Jondaryan) was analysed by two methods (described in more detail as the methods were somewhat unusual compared with standard solvent extraction/GC):

(a) GC-MS method based on Bruns and Tauber (1992) (GC/MS analysis) and Sumpter et al. (1996) (extraction and cleanup). Analchem Bioassay (Sydney) provided the following summary (Analchem Bioassay Report No. 97/1526A): “Pyrithiobac sodium (pyrithiobac, DPX-PE350, KIH-2031, sodium 2-chloro-6 [4,6-dimethoxypyrimidin-2-yl thio] benzoate) was extracted from 10gm of soil by Milli-QR water at subcritical conditions (100°C and 2000psi) using a DIONEX ASETM200 Extractor (Accelerated Solvent Extraction or ASE). Pyrithiobac was separated from the resulting extract using a graphitised carbon column. Pyrithiobac was selectively eluted from the column from the co-extracts and then analysed by gas chromatography with mass spectrophotometric detection. The efficiency of the method was checked by analysis of control soil samples fortified before analysis with pyrithiobac sodium over the range 2-317 µg/kg. These were analysed concurrently with treated samples. The average recovery was 90%. Residues of pyrithiobac sodium greater than the limit of quantification (LOQ) were detected in all of the soil/sediment samples. The method detection limit (MDL) and limit of quantitation (LOQ) for the method were 0.3 and 1.0 µg/kg (ppb), respectively.”

(b) ELISA method by CRC for Sustainable Cotton Production (Dept. of Agricultural Chemistry and Soil Science, University of Sydney), similar to the immunoassay for endosulfan (Lee et al. 1997). When validating this method, Wang et al. (1998) used soil samples and GC data from the Jondaryan study. Two extraction methods were used with the ELISA for each soil sample - ASE (Sumpter et al. 1996) and PBS, a simpler method (10gm soil shaken overnight with 20mL of phosphate-buffered saline and filtered prior to dilution and analysis). Mean (PBS and ASE) ELISA concentrations were not significantly different from GC data (two-way ANOVA with blocking on log transformed data), whereas ASE/ELISA gave significantly greater concentrations. PBS/ELISA concentrations were not significantly different from GC according to ANOVA but had a poorer regression fit. On balance, means of the two extraction methods were most consistent with GC data, and were used for soil samples not analysed by GC.
2.6 Data presentation

In the thesis, results are presented as the total loss and average concentration in runoff for the applied rainfall event, as described below. **Detailed results from rainfall simulator plots**, for instance patterns of runoff, sediment and pesticide concentrations through time, are not presented. To illustrate the data behind the summarised values, typical rainfall simulator results are shown here.

2.6.1 Runoff, sediment and soil loss

Runoff and sediment data from a typical rainfall simulator run are shown in Fig. 2.4. In this example, the two plots (left and right) had similar soil conditions and resulted in similar patterns of runoff and sediment movement.

![Fig. 2.4 Pattern of rainfall, runoff, sediment concentration and cumulative soil loss from a typical rainfall simulator run, with two hill-furrow plots (denote left and right) under the simulator. Plots were bare, 12m long by 0.75m wide, at Gatton, April 1994.](image)

The data show the rapid rise in runoff followed by a steady state typical of rainfall simulator plots on bare soil. Sediment concentrations were reasonably consistent, with minor variations probably associated with small transient erosion features near the plot outlets. Elevated sediment concentrations did not occur early during runoff (a ‘first flush’) and sediment concentrations did not drop off towards the end of the event, because of continuous supply of sediment from the steeply sloping hills in the hill-furrow surface geometry.

Results are presented as totals, for runoff (mm) and soil loss (t/ha), and as event average (flow weighted mean) sediment concentration (g/L) for a consistent amount of applied rain at each site (Table 2.2). A consistent amount of rain was used to account for minor differences in rainfall intensity. Results were also calculated for smaller storms. For example, at Emerald total runoff and soil loss from the first 35, 45, 55 and 65 mm of rain were derived. These storms approximate average
annual recurrence intervals (ARI) of 5, 10, 20 and 30 years, respectively, for 95 mm/hr rainfall at Emerald (Pilgrim 1987). Flow weighted mean sediment concentration was calculated as the total sediment divided by total runoff for the event duration, rather than using the arithmetic mean of sediment concentrations during the event.

2.6.2 Pesticide data presentation

Typical time patterns of pesticide concentrations in runoff are shown in Fig. 2.5 (runoff and sediment data for these plots are shown in Fig. 2.4).

![Fig. 2.5. Rainfall, runoff and pesticides concentrations for a typical rainfall simulator run, with two hill-furrow plots (denote left and right) under the simulator. (Gatton, April 1994, 12m plots.)](image)

Pesticide runoff concentrations rank in order of their application rates (Table 2.3). Concentrations are reasonably consistent between plots for each pesticide, except for the earliest sampling. Concentrations were also reasonably consistent, with a gradual decline, through time. The two least sorbed pesticides, prometryn and dimethoate, did not exhibit the strongly exponential decaying concentrations sometimes observed for poorly sorbed pesticides in the literature (Chapter 1). The decreasing concentrations for endosulfan probably relate to progressive erosion of the shallow surface soil layer containing the recently sprayed endosulfan. The implications are that the sampling regime used should be adequate to obtain a reasonable estimate of event average concentration and that these concentrations do not change dramatically (e.g. 5-10 times) with event duration.

The runoff hydrograph and pesticide concentration data for each rainfall simulator plot were used to calculate the flow weighted average concentration (µg/L) and total loss (grams active ingredient per ha, g/ha) for a consistent amount of applied rain at each site (Table 2.2). Concentration in runoff refers to concentration in water and sediment combined (µg/L of runoff). Concentrations of pesticides transported on sediment are presented as µg/L (i.e. per L runoff) so they are directly
comparable with concentrations in runoff and in the water phase. Concentrations in sediment as mg/kg (i.e. per kg of sediment) are also presented (as is often the case in the literature) where appropriate.

2.6.3 Statistical analysis

Runoff extraction (Chapter 4). Two forms of analysis were used. Firstly, analysis of variance (ANOVA), using general linear models, was used to determine differences between means for treatments. Secondly, regression analysis was used to examine how well soil concentration explained the variance and trend in pesticide concentrations in runoff, and whether these relationships were different for the pesticides. The slope of this relationship, fitted through the origin, is the runoff extraction ratio ($E_{RO}$). Mean extraction ratios calculated by ANOVA and calculated as the regression slope were different, due to the different weighting given to the data. Extraction ratios calculated by regression, with a least squares weighting, were preferred. Regression analysis, with grouping for pesticides, was also used to describe effects of variables such as slope, infiltration amount, sediment concentration, days since spraying and cover on runoff extraction ratios calculated for each pesticide for each runoff plot.

Emerald study (Chapter 6 and 7). Two forms of analysis were performed. Firstly, analysis of variance (ANOVA), using general linear models, was used to determine differences between means for main treatments (cover and wheel traffic). Initially, Block (2 versus 5), furrow slopes, rainfall intensities and time since pesticide application for individual plots, and interactions were included. These variables were not significant in the analysis in all but one case (Chapter 6). Thus, only main factors (wheel traffic, cover treatment and their interactions) were considered in the maximal model. Secondly, regression analysis with blocking (for wheel traffic) was used to examine how well cover for individual plots (as opposed to cover treatments) explained the variance and trend in pesticide concentrations and losses in runoff, whether these relationships were different for non-wheel tracks and wheel tracks, and if this difference was constant across the range of cover. The resulting equations were not intended for predictive purposes and in some cases give negative predictions at high cover, because runoff approached zero with 50-60% cover; predicted $y$-values should be taken as the maximum of predicted $y$ and zero.

Genstat 5 release 3.2, second edition (copyright 1996, Lawes Agricultural Trust, IACR-Rothamsted) was used.
CHAPTER 3
Dissipation of Pesticides in Surface Soil and Crop Residues
CHAPTER 3.  DISSIPATION OF PESTICIDES IN SURFACE SOIL AND CROP RESIDUES

3.1 Introduction

Pesticide movement in runoff has been shown to be related to the amount of pesticide present in the soil surface when runoff occurs (Leonard et al. 1979, Spencer et al. 1985, Leonard 1990, Chapter 4). The amount of pesticide in the soil surface depends on the application rate and the dissipation rate. Because pesticides dissipate, the timing of rainfall and runoff relative to application is a critical factor affecting runoff potential. Rapidly dissipated pesticides present a shorter period of risk, while slowly dissipated pesticide’s maintain their potential level in runoff for an extended period. Dissipation may involve losses by volatilisation, degradation or transformation (chemical, biological or photochemical) and, for more mobile pesticides, leaching or diffusion deeper into the soil. A range of factors affects a pesticides resistance or susceptibility to the various dissipation processes. These include climatic, soil, pesticide and management factors that interact in a complex manner (Leonard 1990).

Pesticide runoff from soil is thus the outcome of two sets of processes, those that define the concentration in the surface soil through time (application and dissipation), considered in this chapter, and those that determine how much is transported in runoff when a storm occurs (referred to as runoff extraction), considered in Chapter 4.

3.1.1 Depth and conditions of the runoff mixing layer

The soil depth contributing pesticides into runoff on interrill erosion areas involves a mixing layer of only a few mm; mixing is greatest at the surface and decreases exponentially with depth, with some contribution from as deep as 20mm due to raindrop-accelerated diffusion (Ahuja et al. 1981, Sharpley 1985, Ahuja 1986). Dissipation rates in this runoff mixing layer are most relevant to assessment of pesticide runoff potential and may differ from that of deep or bulk soil. Leonard (1990) considered that pesticides dissipate more rapidly in the surface layer than expected based on conventional estimates of persistence (e.g. well mixed or deeper layers of soil), as pesticides on or near the soil surface are subjected to environmental extremes. The surface layer is subject to large and rapid changes in water content compared with deeper soil, but can also remain dry (e.g. near air-dry) for extended periods, which may inhibit chemical degradation and microbial activity. Dissipation from a discrete surface layer potentially includes losses due to leaching into the underlying soil.

Dissipation rates are often determined in field studies by summing the mass of pesticide found in the depth of sampling to considerable depth e.g. 0.5m (Kookana et al. 1995), 0.15m (Agnihotri et al. 1996). This may underestimate dissipation in any one layer, as leached pesticide is recaptured in lower layers. The soil surface also experiences extremes in concentrations because many pesticides are surface applied. Initially concentrations are high in the surface layer few mm, until diffusion, dispersion, or leaching moves the pesticide deeper into the soil.
While the actual depth of soil studied (measured and modelled) is obviously important, it is difficult to define a distinct or universally applicable layer and in practice it is difficult to sample such thin soil layers with precision. Ahuja et al. (1981) studied extraction of $^{32}$P into the water phase in runoff as a function of depth of placement and found that extraction was at a maximum for tracer placed on the surface and decreased exponentially with depth of placement. They mathematically defined an effective depth of interaction, which was of the order of 2-3mm for several soils at 4% slope. In reality the effective depth of interaction of raindrops and soil pore water varies with soil conditions (density, tilth, roughness, cover etc.), chemical and rainfall characteristics (Leonard et al. 1987, Ahuja 1986). Sharpley (1985) found the effective depth of interaction related best to soil loss, which integrates many of these factors. The 0-10mm layer gave reasonable empirical relationships with runoff concentrations for several pesticides (Leonard et al. 1979) and was adopted as a pragmatic compromise in some models, although complete mixing is not necessarily assumed (Leonard et al. 1987). Sampling a deeper layer e.g. 0-25mm gives an approximate concentration for the mixing layer – the depth chosen will only matter if there is a steep gradient in concentration with depth.

3.2 Pesticide dissipation

A general review of pesticide dissipation was presented in Chapter 1. In general, pesticide concentrations in soils will decrease exponentially with time after application, and can be approximated by a first-order rate equation. However, several phases are sometimes found and are expected where dissipation shifts from rapid to slower mechanisms, i.e. volatilisation to hydrolysis to microbial decomposition (Nash 1980) and where data are combined for isomers and/or metabolites with different properties, e.g. for endosulfan, $\alpha$- (more volatile), $\beta$- and sulfate (more stable, less volatile). Studies specifically relating to dissipation of endosulfan, the main pesticide of interest, are presented below.

3.2.1 Endosulfan

Endosulfan is of particular interest, as it was the main focus to the ‘Pesticides in the Riverine Environment’ program (Schofield 1998) and had the greatest potential risk of aquatic impact from the Australian cotton industry (Barrett et al. 1991, Batley and Peterson 1992). Wauchope et al. (1992) give an initial half-life of endosulfan in soil of 50 days; based on the available literature, mainly from temperate climate zones. Stewart and Cairns (1974) found half-lives of $\alpha$- and $\beta$-endosulfan of 60 and 800 days, respectively, in soil in Canada. Spencer et al. (1985) reported a half-life of 151 days, based on limited data from California. However, more rapid dissipation was observed in a number of studies in India and Australia, discussed below, possibly because of hotter climates.
Rao and Murty (1980) studied endosulfan in one wet (paddy, flooded soil) field (clay soil pH 8.4) and three dry (non-irrigated) fields (with low, normal and high application rates) (loamy clay pH 7.8). Fields were under local farmer practices and crops were not dense at the time, so large quantities of pesticide reached the soil. Rapid losses were found by the second soil sampling at 20 days after application; 87-95% of endosulfan applied on dry soils (depending on application rate) and 95% on flooded soil. Dissipation rate was progressively slower through time. Dissipation was initially more rapid in wet soil than dry, but after 20 days slowed in wet soil while continuing more rapidly on dry soil. Persistence was dependent on initial concentration - rate of breakdown was slower in soil receiving higher doses. My estimates of initial (0-10 days) half-lives for total endosulfan based on the data of Rao and Murty (1980) are, for dry soil, 4 days for normal and low application rates and 5 days for high application (similar to rates used in Australia), and 3 days for wet soil. Endosulfan sulfate was the principal metabolite, except on dry soil with highest dose (greater/extended inhibition of soil fungi). More sulfate formed in wet soil than dry soil with the same dose. Alpha dissipated more rapidly than beta. After 100 days (620 mm rain) 95% of endosulfan and of sulfate was in 0-75 mm soil, with traces of $\alpha$- and $\beta$-isomers in 75-100 mm, and no endosulfan or metabolites below 100 mm.

Agnihotri et al. (1996) studied endosulfan dissipation in a sandy loam soil (pH 7.4, 0.3% OM) under wheat cultivation in India. Residues of endosulfan persisted in soil (0-150mm) for 60 days, with a half-life of 10.3-10.6 days. $\beta$-endosulfan was more persistent than the $\alpha$ isomer. Endosulfan sulfate concentrations gradually increased up to day seven and then declined. Residues of $\alpha$ and $\beta$ endosulfan (but not sulfate) were detected in soil to 1.05m before, and 100 days after, the experimental application, possibly accumulated over time from previous sprays.

Kathpal et al. (1997) measured dissipation of endosulfan in a sandy loam (pH 8.1 OM 0.5%), kept bare but irrigated (375 mm) for 0-238 days after spraying in sub-tropical northern India. Half-lives were reported for total endosulfan rather than for individual compounds. However, $\alpha$-endosulfan was no longer detected after 14-28 days. At longer times residues consisted of $\beta$- and sulfate endosulfan or sulfate only. Kathpal et al. (1997) report two distinct first-order phases of dissipation with a change in rate at 28 days. This is probably related to the more rapid loss $\alpha$-endosulfan in the first few weeks after application. Initial half-lives for total endosulfan were 5.4 and 7.3 days for 0-28 days, for two treatment areas (sprayed 21 days apart). Half-lives during the second phase were 115 and 79 days. Endosulfan sulfate was first detected 7 days after spraying and was still detected at day 238. Endosulfan diol was first detected (in one treatment) at 7 days and dissipated within 28 days. Endosulfan parent isomers, sulfate and diol remained mostly in the 0-50mm soil, with lower level of parent isomers and sulfate found in 50-100mm soil and none in lower soil layers.

Dissipation of endosulfan was reported as following first-order kinetics by Agnihotri et al. (1996) (0-150mm soil over 0-60 days), whereas Kathpal et al. (1997) report two-phases in first-order kinetics with a change in rate at about 28 days, and Rao and Murty (1980) report dissipation rate was progressively slower through time.
Ghadiri et al. (1995, 1996) conducted a controlled environment laboratory study of endosulfan degradation in a Vertosol from Emerald (similar to the Emerald soil in this study). They found large initial losses (in the first 2 weeks after application) of \( \alpha \)-endosulfan (~63\%) from dry soil at higher temperatures (30°C and 40°C), but lower initial losses (35\%) at 20°C. Initial losses were about 90\%, or an order of magnitude, for moist soil (0.25-0.45v/v). Half-lives for dissipation, after the initial loss, were also shorter (4-8d) for moist soil at all temperatures, than at low moisture content where they increased with increasing temperature (10-27d). In contrast, \( \beta \)-endosulfan dissipated more slowly than for \( \alpha \)-endosulfan under all conditions, exhibited little or no initial loss, was not affected by moisture content but was considerably enhanced at higher temperatures.

The dissipation rate of endosulfan from field soils on Australian cotton farms is considered to be rapid compared to that of, for instance DDT/DDE, and it is not expected to accumulate from one year to the next in alkaline soils (Kimber et al. 1994, Kennedy et al. 1995, Simpson et al. 1995). Endosulfan concentrations in soil (0-50mm) in a cotton field at Narrabri NSW almost 2 years after the previous spraying were low, with little or no \( \alpha \)- and \( \beta \)-endosulfan, and 0.05-mg/kg of sulfate (Kennedy et al. 1994). Even so, this is equivalent to 85 gai/ha or 11\% of a normal application rate (~750 g/ha), indicating a reasonably large number of applications and/or persistence of at least the sulfate if not one of the parent isomers. A comparatively large proportion of sulfate tends to build up in the soil in irrigated cotton fields subjected to repeated applications of endosulfan (Kimber et al. 1994, Kennedy et al. 1995, Simpson et al. 1995). Kimber et al. (1994) found very little \( \alpha \)- and \( \beta \)-endosulfan and a small concentration of sulfate in soil below 50mm depth, indicating low rates of leaching.

Kimber et al. (1994) reported incomplete recovery several days after endosulfan was sprayed on soil, an initial loss attributed to volatilisation. Half-lives were 43, 76 and 101 days for \( \alpha \)-, \( \beta \)- and sulfate endosulfan, for 0-100mm soil over 8 months in commercial cotton crops (i.e. representing longer times after spraying). These half-lives contrast with those determined by Kennedy et al. (1995) at Warren (NSW) for 0-50mm soil for the period 1-20 days after successive sprays of 10, 3.7 and 1.6 days for \( \alpha \)-endosulfan, and 3.7 and 6.5 days for \( \beta \)-endosulfan. Simpson (1996) reports a half-life of "approximately one week" for total endosulfan in 0-25mm soil in commercial cotton fields near Emerald. Kennedy et al. (1995) considered that volatilisation from soil was a major dissipation mechanism for \( \alpha \)-endosulfan in the first 7 days after spraying (>75\%) and a smaller contributor to dissipation of \( \beta \)-endosulfan (~25\% or less). Volatilisation probably continues throughout, but at a decreasing rate as the endosulfan diffuses into, and is sorbed onto, soil and organic particles.

In summary, \( \alpha \)- endosulfan generally dissipates more rapidly than \( \beta \)- endosulfan, while the sulfate breakdown product appears more persistent. However, reported half-lives of endosulfan vary considerably depending on the temperature, and the period after spraying and soil depth considered. Large initial losses sometimes occur in the first 1-2 days after spraying, particularly for the \( \alpha \)-isomer, and half-lives are generally longer at longer times. This is consistent with two processes, with volatilisation dominating early on, and biological/chemical degradation at longer times. While these
insights are helpful in principle, quantitative dissipation data for predicting the runoff potential for the entire life cycle of endosulfan sprayed on the surface of cotton field soils are lacking. Studies of endosulfan in Australian cotton soils (up until 1996) defined the general pattern over the growing season but did not sample the soil in detail after each application (Kimber et al. 1994, Kennedy et al. 1995, Simpson et al. 1995). The depths of soil previously considered (50 or 100 mm) are generally deeper than the depth of runoff mixing (0-25mm or less). This shallower layer may act more like a surface than a matrix and is subject to greater climatic extremes than the deep soil. While downward movement in soil (e.g. below 50 or 100 mm) appears small, its contribution to dissipation from the shallower runoff-mixing zone is unclear.

3.2.2 Scope and aims of this chapter

During the rainfall simulator studies, considerable data were collected on pesticides in soils and on crop residues. In this chapter, data relating to dissipation rates of pesticides from the surface soil, that is, concentrations in 0-25mm, and from crop residues are summarised. Losses of pesticides from these layers are referred to as dissipation, a term which does not imply any particular loss mechanism. Losses may be due to volatilisation, biological or chemical degradation, diffusion or leaching deeper into the soil. Data for endosulfan are considered first, then data for various other pesticides.

These studies differ somewhat from other studies of pesticides in soils, as (a) they mainly consider the period of elevated concentrations soon after application rather than persistence in the long term (partly due to repeated applications of endosulfan in the commercial sites used and for logistical reasons), (b) they related almost entirely to the soil surface (0-25mm) where runoff extraction occurs rather than the soil profile, and (c) pesticides were applied by spraying over the soil or crop residues rather than being mixed into the soil as in some laboratory studies. Thus it was intended that results would be applicable to dissipation in the field after spraying and relate to the surface where pesticides are extracted into runoff.

Retention of crop residues on the soil surface (where it will intercept pesticides) is suggested as a best practice to reduce pesticide runoff (Fawcett et al. 1994, Chapter 7). However, washoff of pesticides from crop residues is sometime suggested to increase runoff of pesticides (Baker et al. 1978, Blevins et al. 1990, Gaynor et al. 1995). It is therefore important that we know whether these pesticides will become available for transport in runoff during rain. Little is known about dissipation of endosulfan, and most other pesticides, from crop residues and subsequent potential to be washed off.

The aims of this chapter are to:
1. Determine field dissipation rates of pesticides from the soil surface (runoff mixing zone), with particular emphasis on endosulfan, and
2. Determine field dissipation rates of endosulfan from crop residues.
3.3 Methods

3.3.1 Experimental outline and design

Concentrations of various pesticides in the surface 0-25mm soil layer were measured at four sites in conjunction with rainfall simulator studies (Chapter 2). This depth was chosen to represent the soil layer potentially contributing chemicals into runoff, being the shallowest depth that could be sampled reliably on a range of soils and tilth. Concentrations were measured through time after experimental applications of various pesticides to bare soil, following one or in some cases two sequential applications. Pesticide concentrations on crop residues, and in soil under crop residues, were also measured in several studies. Endosulfan (α, β and sulfate) was studied at all sites, with various other pesticides (Table 2.3), mostly for short periods after application (e.g. 2-3 weeks). No natural rainfall occurred during these short-term studies and surface soils were at about air-dry moisture content. Effects of (simulated) rain after pesticide application were studied in several cases. The final study (Jondaryan) was different in several aspects; sampling continued for 62 days after spraying during which 150 mm of rainfall occurred and data were collected for six herbicides and four insecticides, including endosulfan.

Samples of surface soil and crop residues were collected through time at the four sites (Chapter 2), after the following pesticide application treatments: -

(a) Emerald (Oct 94), following
   - One application of endosulfan to bare soil and to wheat crop residue (100% cover).
   - Two applications of ULV endosulfan to bare soil, with and without 65 mm of (simulated) rainfall four days after the second application.

(b) Warren (Nov 1994), following
   - One application of endosulfan ULV formulation to bare soil, wheat stubble and cotton trash.
   - One application of endosulfan EC formulation, applied as a band on the hills only, with and without rain applied one day after application.

(c) Gatton (Apr 94), through a sequence of two applications of endosulfan, dimethoate and prometryn to bare soil.

(d) Jondaryan (Oct-Nov 96), following one application of endosulfan, three other insecticides and six herbicides to bare soil. Some samples were also collected from 25-50mm and 50-100mm soil depths and from rainfall simulator plots at 2, 5, 25 and 34 days after spraying.

The locations, soil properties, pesticides applied, methods and rates of application, and analysis procedures for pesticides in soil and crop residue samples are described in Chapter 2. Temperature, relative humidity and wind speed were recorded on-site at the time of spraying. These data, plus solar radiation and rainfall, were available for the duration of the experiments from automatic weather stations on the farms at Gatton (UQ), Emerald (NR&M) and Warren (C-PAS). At Jondaryan, rainfall
was recorded on-site with a tipping bucket gauge and climate data were available from the Bureau of Meteorology at Oakey.

3.3.2 Calculation of half-lives and initial loss

Dissipation was represented using a first-order equation (Haigh and Ferris 1991, Wauchope et al. 1992) or exponential decay:

\[ C_{t2} = C_{t1} e^{-kt(t2-t1)} \quad \text{Eqn. 3-1} \]

where \( C_{t2} \) and \( C_{t1} \) = concentration at times \( t2 \) and \( t1 \) (days), \( k \) = rate constant (d\(^{-1}\)). Half-life \( (t_\frac{1}{2}) \) is defined as the time for dissipation to half of the initial concentration, and is related to \( k \) as:

\[ t_\frac{1}{2} = \ln_e (2)/k = 0.693/k \quad \text{Eqn. 3-2} \]

If the first-order equation is obeyed, \( t_\frac{1}{2} \) is independent of the initial time and concentration. \( T_{\frac{1}{2}} \) was calculated from the soil concentration data by taking the ln of the concentrations and fitting a linear regression against time, where the slope of the regression is \( k \), or by fitting an exponential equation. In some cases, ln(concentration) indicated two phases, with distinctly different (steeper) slope initially after spraying, and \( t_\frac{1}{2} \) was calculated separately for the two phases. For the breakdown product endosulfan sulfate, approximate half-lives were calculated for dissipation after the peak in concentration, if possible. The true half-life would be shorter than these values as the concentrations would be simultaneously decreasing due to dissipation and increasing due to continued formation of sulfate.

In some instances considerably less pesticide was found in the soil soon after spraying (e.g. <1 day) than was nominally sprayed. While errors and losses in actual spray rates can contribute to this initial loss, sampling within day 1 and cross checking with other pesticides in the same tank-mix often show that these losses are real, and are probably due to rapid loss processes such as volatilisation. These rapid initial losses must be quantified to allow correct calculation of soil concentrations during dissipation. Initial losses were calculated as the difference between spray rate and the intercept (at time =0 days) of the fitted first-order equation. This approach is consistent with the ‘application efficiency’ used in daily time-step models such as GLEAMS (Leonard et al. 1987). Where sufficient samples were collected in the first 1-2 days after spraying, a first-order equation was fitted for the early phase of dissipation, as described above.
3.4 Results and discussion

3.5 Part A. Endosulfan dissipation from surface soil

(a) Emerald

Endosulfan dissipated rapidly during the first two days after application to dry soil (Fig. 3.1a). Half of the applied α- and β-endosulfan dissipated from the soil in 2-3 days. The air temperature was 28°C when the endosulfan was applied at 7am, increasing to a maximum of 38°C during the day. Volatilisation, which is enhanced at higher temperatures, appears a likely pathway for dissipation, as discussed elsewhere. The β-isomer was lost as readily as the α-isomer. After two days, dissipation slowed considerably. Fitting of first-order equations indicate two phases of dissipation. Second phase half-lives were 11 and 17.5 days for α and β, respectively (Table 3.3). Half-lives after initial losses were reasonably similar for the bare hills in the wheat stubble plot - 7.7 and 16.1 days for α and β, respectively, and in soil under wheat stubble - 8.7 and 17.6 days for α and β, respectively (Table 3.3).

![ graphs showing dissipation of endosulfan](image)

Fig. 3.1. Endosulfan dissipation from bare, dry soil (0-25 mm), sprayed in the morning on a hot day, Emerald Oct. 1994. (a) After one application, showing two phases, (b) After two sequential applications compared with a single application. Examples of fitted equations are given for total endosulfan and sulfate. (All data are means of samples from hill and furrow.)

Similar results were obtained after a second (sequential) application was made under similar conditions four days later (Fig. 3.1b) - 56% of the ‘new’ α-endosulfan dissipated in the first 10 hrs after application, while 27% of the ‘new’ β- dissipated. After these initial rapid losses, dissipation rates were similar to those on the single application plot. However, both α- and β-endosulfan took about 6 days to decline to half of the total amounts present after the second application, due to a more rapid transition to the slower rate and the relative stability of the ‘old’ α- and β-endosulfan. Second

---

1 Half-lives for endosulfan are collected in Table 3.3 at the end of the results, to allow discussion across sites.
phase half-lives were 14 and 22 days for $\alpha$ and $\beta$, respectively (Table 3.3), somewhat longer than for the first application.

Sixteen days after the first application, the ratio of $\alpha$- and $\beta$-endosulfan was reduced from the 7:3 ratio applied to about an equal ratio, due to the more rapid dissipation of the $\alpha$-endosulfan. The one-application plot had 243 g/ha of endosulfan in the surface 0-25 mm of soil while the two-application plot had 600 g/ha, 24% and 30% of the total amount applied, respectively.

Only small amounts of endosulfan sulfate formed in this period, increasing slightly above what was present from the previous season (26 g/ha). Similar amounts were found in soil receiving one and two applications, peaking at 40-43 g/ha about 7 days after each application and declining to pre-application levels by 15 days. The half-lives measured for dissipation after the peak were about 10 days for both applications, much more rapid than the half-lives (92±47d) determined over longer times and for deeper soil (0-50mm) by Kennedy et al. (2001). The soil surface was very dry throughout the study (slightly less than the laboratory 40°C air-dry moisture content), not atypical of a dry spell in the region. This appears to have enhanced the volatilisation of endosulfan before it had sorbed strongly to and diffused into the soil, and presumably retarded hydrolysis and biological degradation in the soil.

(b) Warren

At Warren, ULV (blanket) and EC (banded) applications of endosulfan were compared. Endosulfan was applied at night (8 pm) and temperatures were cooler than at Emerald. This had a marked effect on the (apparent) degree of volatilisation – soil sampled a day after application still contained the majority of the amount applied (Fig. 3.2a,b). Two phases (rapid/slow as seen at Emerald) were not apparent. However, the average rate of dissipation over seven days was similar at the two sites. For the ULV formulation (Fig. 3.2a), half-lives were 5.0, 8.5 and 6.3 days for $\alpha$-, $\beta$- and total endosulfan, respectively (Table 3.3). Sulfate increased from pre-application level of 20g/ha to a peak of 26g/ha on day 4.5, decreasing to 20g/ha by day 7.6 – a half-life of 9.5 days after the peak.

The EC formulation (Fig. 3.2b) banded on top of the hill (30 cm band) dissipated slightly more rapidly than the ULV-endosulfan. Half-lives were 4, 9 and 6 days for $\alpha$-, $\beta$- and total endosulfan, respectively (Table 3.3). This does not appear to be related to greater exposure to environmental conditions (radiation, wind etc.) on the top of the hill, as the data for ULV indicate no difference in dissipation between hill and furrow soil for both $\alpha$- and $\beta$- endosulfan. Sulfate concentrations increased from 21g/ha before application to 48 g/ha on day 5.6, and no half-life could be calculated.

Furrow soil on the EC–banded plot contained endosulfan even though it was not sprayed intentionally (about 13% of application rate). Concentrations were about one tenth of those on the hill (Fig. 3.2b). Dissipation of $\alpha$-, $\beta$- and total endosulfan in the furrow was similar to EC on the hill, with half-lives of 5.7, 9.3 and 6.2 days, respectively. Sulfate increased from 18 g/ha before application to 42 g/ha on day 3.5 and decreased to 12 g/ha on day 5.6, a half-life of 11.6d after the peak.

Dissipation in soil under cotton trash was similar to that in bare soil, with half-lives of 6.7, 10.5 and 8.8 days for $\alpha$-, $\beta$- and total endosulfan, respectively (Table 3.3).
Fig. 3.2. Dissipation of endosulfan from bare, dry soil (0-25 mm), after application (8-9pm) at Warren Nov 1994: (a) ULV blanket (Means of hill and furrow, error bars are ±1 Std. Err.), (b) EC 30cm band on the hill, for hill and furrow (13% drift of spray into furrow). Fitted equations are for total endosulfan and sulfate after the peak for ULV, and for total endosulfan in hill and furrow for EC.

(c) Gatton

Endosulfan dissipated rapidly after the first spray at Gatton (Fig. 3.3), with half-lives of 3.0 and 3.8 days for α- and β-endosulfan, respectively. Soil concentrations 0.2-2 hr after spraying, and even at one day, were similar to the applied amounts, with no rapid initial loss or two-phase behaviour during the 6 days monitored. Rather, dissipation proceeded at a rate approaching the rapid initial rate in the first 2 days at Emerald (t1/2=2-3d) for the entire period. After the second spray, soil concentrations within 2 hrs of spraying were similar to the applied amount plus residual from the first spray, confirming the spray rate. However, dissipation of both α- and β-endosulfan was much slower, with
half-lives of 29 and 40 days, respectively. Samples from one day after the second spray (day 7) indicate no initial loss.

The large differences in dissipation rates for the two applications are not related to climatic differences; no rain or cloudy conditions occurred and temperatures were consistent throughout. The result may be related to a category of pesticide-soil microbial interaction where compounds are broken down by microorganisms and in doing so the microbes themselves are inhibited, observed for endosulfan by El Beit et al. (1981). This interaction is more prevalent at high concentrations of the pesticide and so might have been initiated by the second spray. The Gatton site had limited previous exposure to pesticides, unlike the other sites, and the soil microbes may be less adapted to pesticides.

Endosulfan sulfate was not detected until day 7 (i.e. 1 day after the second spray), peaked on day 15 (at 7.5 g/ha) and then declined with a half-life of 7 days (based on limited data). Soil samples taken 2 hrs after the second spray on a plot sprayed with endosulfan ULV formulation in the same pattern indicate similar dissipation to EC formulation (Fig. 3.3), within the limits of spray and soil sampling accuracy.

![Fig. 3.3. Concentration of endosulfan in soil (0-25mm) during sequential EC applications, Gatton April 1994. Examples of fitted equations are given for total endosulfan and sulfate. (The second Y-axis gives alternative units. Data are means of hill and furrow. Error bars are ±1 Std. Err.).](image)

(d) Jondaryan

This dissipation study had only minor rainfall up to day 20 followed by a period with 75mm of rain to day 39 (Fig. 3.4). On day 41, endosulfan sprayed on a neighbouring field drifted onto the plots, ending the dissipation study. Concentrations of α- and β-endosulfan in soil 0.5d after application were 11% and 6% less than nominal applied amounts and are probably within errors expected in the spray
Concentration in soil (mg/kg) and soil sampling. Thus no initial rapid dissipation could be distinguished (Fig. 3.4), in contrast with chlorpyrifos and profenofos, which show a distinct change in slope at day 5 (Fig. 3.5).

Fig. 3.4. Concentrations of endosulfan in soil (0-25mm) at Jondaryan, first application. The first data points are the spray rate, the second data points are samples 0.5 days after spraying. Data are means for hill and furrow. Error bars are ±1 std error. Drift onto plots occurred on day 41.

Fig. 3.5. Dissipation of endosulfan from surface soil (0-25mm), for two separate applications (day 0 and 14), compared with chlorpyrifos and profenofos, at Jondaryan.
From 0.5 to 39 days, dissipation for α-, β- and total endosulfan followed first-order decay (Fig. 3.5) with half-lives of 8.3d, 26.9d and 19.8d, respectively. Dissipation of β-endosulfan was slower during the initial drier period and more rapid from 25-34 days (Fig. 3.4), when soil was moister, coinciding with increased formation of sulfate. Endosulfan sulfate was not detected at significant concentrations until day 34, after the start of the wetter period (Fig. 3.4), similar to other results indicating sulfate is formed more rapidly in moist soil (see next section). Sulfate concentration on days 34-40 approached that of the sum of α- and β-, making a significant contribution to total endosulfan and its persistence.

Half-lives were reasonably similar for soil from the sprayed hills on a band sprayed plot (Table 3.3). After an application to a second plot (non-sequential) on day 14 (Fig. 3.5), just prior to the wetter period, dissipation was somewhat more rapid than for the first application, with half-lives 6.0, 19.6 and 18.6 d, for α-, β- and total endosulfan, respectively. This is probably related to the rainfall and resulting moister soil. Sulfate again made a large contribution (~1 mg/kg) to total endosulfan by day 39, exceeding the sum of α- and β-. (Data were not available to calculate half-lives for sulfate).

3.5.2 Effects of rainfall on dissipation

At Emerald, soil that received two sequential applications of endosulfan (discussed above, Fig. 3.1b) and 60 mm of (simulated) rain four days after the second application was sampled for endosulfan soon after rain and nine days later (Fig. 3.6). Mean endosulfan concentration (for hill and furrow) was similar to that in soil that received two applications and no rain. However, while the rain apparently did not increase dissipation via volatilisation and/or degradation, it did alter the distribution between parent isomers and sulfate, and the spatial distribution between hills and furrow.

![Fig. 3.6. Endosulfan concentration in soil (0-25 mm) after 65 mm of rain 4 days after the second application (solid symbols), compared with plots not receiving rain (open symbols) (from Fig. 3.1b), at Emerald. Data are means of hill and furrow (H&F), except where indicated.](image-url)
Endosulfan sulfate concentrations were greater in the rained-on soil, about double on top of the hills (which dried more quickly) and 6-7 times greater in the furrows (where the soil dried more slowly). There was a corresponding decrease in the parent isomers, particularly α-endosulfan. Also erosion of soil and associated endosulfan from the hills into the furrows during rain (about 20 t/ha, Chapter 6) increased concentrations in the furrow soil and decreased concentrations on the hill. This process increases the endosulfan, and the proportion of sulfate, available for movement during subsequent furrow irrigation.

When an EC-banded plot at Warren (discussed above, Fig. 3.2b) received 50 mm of (simulated) rain 0.7 days after spraying, soil and associated endosulfan was washed from the (sprayed) hills into the furrows. Concentration in the surface soil on the hills decreased markedly due to soil erosion (Fig. 3.7a) with a similar increase in concentration in furrow soil (Fig. 3.7b). Concentrations were similar in hill and furrow soil after rain, i.e. negating effects of band spraying. Also the rainfall increased the soil moisture content, particularly in the furrow, which then decreased over the next 4 days (Fig. 3.7).

![Fig. 3.7. Concentrations of total endosulfan and endosulfan sulfate (ESS) in bare soil (0-25mm) at Warren, after EC-banded spray on the hill, without (from Fig. 3.2b) and with 50 mm of rain 0.7 days after spraying, and soil moisture content (0-25mm) after rain, (a) on the top of the hills, (b) in the furrows. Arrows indicate the change in concentration from before to after rainfall.](image)

After the initial change due to rainfall erosion, concentrations of total endosulfan (and α- and β-endosulfan, data not shown) did not decrease for several days, particularly in the furrow where soil dried more slowly (Fig. 3.7), and consistent with results from Emerald. Wetting the soil increased the rate of formation of sulfate and reduced the overall dissipation rate of total endosulfan, rather than increasing it as might be expected, e.g. due to enhanced soil biological activity. The concentration of sulfate was markedly greater after rain, but only persisted at elevated levels in the moister furrow soil.

Results from Emerald, Warren and Jondaryan (where natural rainfall occurred; discussed previously), all indicated increased formation of endosulfan sulfate in moister soil, which changed the
distribution between parent isomers and sulfate, but did not change the dissipation rate of total endosulfan greatly. Ghadiri et al. (1995) observed greater formation of sulfate in moist soil (e.g. 25-45% moisture) than in either dry or submerged soil in laboratory studies. This is also consistent with the progressive build-up of sulfate in soils within each growing season in irrigated fields subjected to multiple sprays (Simpson et al. 1998, Kennedy et al. 1998, Connolly et al. 1998). Greater formation of sulfate in moist soil (e.g. frequent irrigations), and recent data showing greater persistence of aged endosulfan sulfate (Kennedy et al. 2001), would increase the risk of endosulfan runoff from irrigated fields, but also indicate that sulfate formation and runoff may be lower in dryland cropping systems.

3.5.3 Effects of soil depth

(a) Movement to deeper soil

In the Jondaryan study, concentrations of endosulfan were measured in deeper soil layers, from 2.4 to 62 days after application (Table 3.1). A small amount of endosulfan had already moved into the 25-50mm soil by 2.4 days after spraying and concentrations increased only slightly through to day 40. Concentrations of α- and β-endosulfan were initially equal, but α- decreased and β- increased. Both isomers probably moved down into the 25-50mm soil, but the α- dissipated more rapidly. Sulfate concentrations in 25-50mm soil increased throughout the study. While the concentrations of endosulfan in 25-50mm soil were reasonably small, they represented a progressively increasing percentage of the total in 0-50mm soil (Table 3.1), indicating that dissipation was slower in the deeper soil layer. This had significant consequences for calculated half-lives (discussed below). At day 62, after 148mm of rain and an addition input of endosulfan in drift on day 41, the 25-50mm layer contributed ~20% of the total endosulfan and ~30% of the sulfate in 0-50mm soil.

Table 3.1. Distribution of endosulfan in surface soil at four times after application (Jondaryan). An unknown amount of endosulfan was added on day 41 by drift. (n.d. not determined).

<table>
<thead>
<tr>
<th>Depth (mm)</th>
<th>Day after application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>Pesticide</td>
<td>Rain (mm):-</td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
</tr>
<tr>
<td>α + β</td>
<td>0-25</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0-25</td>
</tr>
<tr>
<td></td>
<td>25-50</td>
</tr>
<tr>
<td></td>
<td>50-100</td>
</tr>
</tbody>
</table>

Percent of total (0-50mm) in 25-50mm soil

|           | 1.2 | 3.6 | 11  | 17  |
| Sulfate   | --- | 100 | 13  | 31  |
| Total     | 2   | 5   | 12  | 22  |
On day 62, 73% of total endosulfan was in 0-25mm soil, 21% in 25-50mm and 6% in 50-100mm soil (Fig. 3.8). Thus 94% of endosulfan residues were in the surface 50mm (in close agreement with Kimber et al. 1994 and Kennedy et al. 1997b), with the proportion of sulfate increasing with depth, β-decreasing slightly and α-decreasing significantly. From this and other data, endosulfan appears reasonably immobile in clay soils from the perspective of contamination of the subsoil and groundwater, however this limited downward movement may still have a significant effect on dissipation and runoff potential, as discussed in the next section.

Fig. 3.8. Distribution of endosulfan concentration in soil on day 62 after spraying at Jondaryan, after 148mm of rain. Some additional endosulfan drifted onto the plot on day 41.

The downward movement of endosulfan was probably due to a combination of advection (mass flow with water) and diffusion. While rates of diffusion are generally considered slow, the amounts of rainfall/infiltration seem too small to cause large advective movement, especially as endosulfan is moderately strongly sorbed. Most rainfall events were too small to contribute more than a few pore volumes of water movement below the 25mm depth. Based on soil moisture and bulk density data, the 0-25mm layer had a moisture deficit of 10-15mm initially, and within a few days after each rainfall event due to evaporation. Ideally 10-15mm of infiltration is required to cause water movement below 25mm. Some displacement of ‘old’ water (containing dissolved endosulfan) by ‘new’ water would occur in fine pores with each of the larger rainfall events (Warren Bond, CSIRO, pers. comm.). Displacement even within the 0-25mm layer reduces the travel distance into the 25-50mm layer.

However, an important effect of the small rainfall events may have been to increase the rate of diffusion, by increasing soil moisture content and its continuity. Solute flux by diffusion in the liquid phase is much greater in moist soil than in dry soil. Diffusion flux is the product of concentration gradient in the liquid phase with soil depth ($\delta C_l/\delta z$) and effective diffusion coefficient (Dp[θ]), where θ is volumetric moisture content (Wagenet and Rao 1990). Kemper and van Schaik (1966) found
Dp[θ] can be estimated as \[D_0 \cdot a \cdot \exp[b \cdot \theta]\], where \(D_0\) is the diffusion coefficient in a pure liquid phase and \(a\) and \(b\) are empirical coefficients with values of 0.005-0.01 and 10, respectively (Wagenet and Rao 1990). Thus diffusion flux in liquid phase is approximately a function of \[\exp[10 \cdot \theta]\], which increases from: 1.65 at \(\theta=0.05\), 7.4 at \(\theta=0.2\), 20 at \(\theta=0.3\), 148 at \(\theta=0.5\). Thus the flux of solute moved by diffusion is much greater with increasing moisture content. Diffusion in the gas phase would also occur, given that endosulfan has high volatility (according to rankings of Gerritse et al. 1991 for Henry coefficient \(K_H = 0.326\)). Also some upward flow of water into the surface to satisfy losses to evaporation would occur and therefore advective displacement of endosulfan may occur simultaneously with downward diffusion.

(b) Effect of soil layer depth on half-life

Endosulfan in the 0-25mm soil at Jondaryan dissipated from 6.45 mg/kg to 1.5 mg/kg on day 39 (i.e. 4.95 mg/kg lost), while concentration increased from 0 to 0.20 mg/kg in 25-50mm soil. Downward movement appears to have been only a small component (e.g. 2-12%) of dissipation from the surface 0-25mm. However, including the endosulfan in the 25-50mm soil had a reasonably large effect of calculated half-lives (Table 3.2), e.g. almost doubling the half-life for \(\alpha\)-endosulfan. This is because the deeper soil layer includes endosulfan that has dissipated from the surface layer via downward movement. Also the half-life for total endosulfan (including sulfate) is considerably longer than for the total of \(\alpha+\beta\).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Half-life (days) for</th>
<th>Ratio of half-lives for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-25mm</td>
<td>0-50mm</td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha</td>
<td>8.3</td>
<td>14.8</td>
</tr>
<tr>
<td>Beta</td>
<td>26.9</td>
<td>37.1</td>
</tr>
<tr>
<td>Alpha + Beta</td>
<td>14.3</td>
<td>22.5</td>
</tr>
<tr>
<td>Total</td>
<td>19.8</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Downward movement of endosulfan in the soil appears to be a small component of overall dissipation from the surface soil (0-25mm), based on measured concentrations, but it still makes a considerable contribution to reducing the apparent half-life in the surface layer. From the point of view of pesticide runoff potential, dissipation is more rapid when the shallower soil layer is considered. Using half-lives for the deeper soil (0-50mm) overestimates the persistence and runoff potential.
Half-lives for endosulfan in 0-25mm soil are summarised in Table 3.3. Referring to these half-lives and the preceding results, the following conclusions can be made.

**Form of endosulfan.** Dissipation was consistently more rapid for α-endosulfan than for other forms of endosulfan, with half-lives typically 5-11 days after a single application (excluding rapid initial losses discussed below). Half-lives of β-endosulfan were typically 9-27 days and varied from 1.3 to 3 times those of α-endosulfan. That is, dissipation of the two isomers was affected differently by site and/or environmental factors. The longer half-life for β-endosulfan is consistent with its higher partition coefficient (Chapter 5). Dissipation was well represented by single-phase first-order equations in all studies except at Emerald, where temperatures were highest (discussed below).

Approximate half-lives of endosulfan sulfate, for dissipation after the peak concentration, were comparatively consistent at 7-12 days, including first and second sprays, on dry soil. However, the time to the peak concentration varied widely (4.5-34d) and in about half of the plots endosulfan sulfate concentrations increased throughout the study period, especially when rain occurred. Results for the sulfate represent short-term ephemeral behaviour and do not provide definitive half-lives. Soil concentrations of endosulfan sulfate are a balance between dissipation of the sulfate and formation from the parent isomers, which are themselves dissipating without necessarily converting to sulfate. At longer times, when the remaining parent isomers are more completely sorbed into soil aggregates, conversion to sulfate may lead to a more tightly sorbed and persistent form of sulfate (Hugo 1999 and Chapter 5). Kennedy et al. (2001) found a half-life of 90±47 days for seasonal accumulations of ‘aged’ endosulfan sulfate in soils (0-50mm) in Australian irrigated cotton fields.

**Initial losses and effects of temperature.** Dissipation was more rapid at two sites where spraying occurred in the morning when temperatures were approaching 30°C and daytime temperatures exceeded 35°C, compared with sites where the temperature was 20-24°C at the time of spraying and the endosulfan had a few hours of these lower temperatures to diffuse into the soil matrix. Higher temperatures resulted in initial half-lives of 2-3 days for both α- and β-endosulfan, with dissipation slowing after 3 days at Emerald (2-phase dissipation) and proceeding for 6 days at Gatton. At Emerald, the site with the highest temperatures, these rapid initial half-lives equated to 35-50% loss of the sprayed amounts of both α- and β-endosulfan by the start of the slower second phase. Volatilisation appears a likely pathway for dissipation of the parent isomers of endosulfan during this time (Kennedy et al. 2001, Raupach et al. 2001ab). A notable feature is the rapid dissipation of the β-endosulfan as well as the α-endosulfan under these conditions, whereas Kennedy et al. (2001) generally found the α-isomer more prone to volatilisation than the β-isomer. The large initial losses and effects of temperature for α-endosulfan are also consistent with the laboratory studies of Ghadiri et al. (1995, 1996). However they found no such effects for β-endosulfan, possibly because the endosulfan was mixed into the soil and was more tightly sorbed than occurs with application to the soil surface.
Table 3.3. Summary of half-lives for dissipation of endosulfan from bare soil (0-25mm) and under cover.
初始损失是距离应用速率和拟合等式截取的差，作为一个应用速率的分数，并且因此包括了任何以前的阶段。

<table>
<thead>
<tr>
<th>Site</th>
<th>Phase</th>
<th>Period</th>
<th>α-endosulfan</th>
<th>β-endosulfan</th>
<th>sulfate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial loss (fraction)</td>
<td>½-life (days)</td>
<td>Initial loss (fraction)</td>
<td>½-life (days)</td>
</tr>
<tr>
<td>Emerald (Oct 1994)</td>
<td>1st spray</td>
<td>(7 am 28°C, ULV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bare plot (mean of hill and furrow)</td>
<td>First</td>
<td>0-2.5 d</td>
<td>~0A</td>
<td>2.3</td>
<td>~0A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Second</td>
<td>2.5-16 d</td>
<td>0.52</td>
<td>11.2</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>Wheat plot</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bare hills</td>
<td>Second</td>
<td>0.5-10.5 d</td>
<td>0.36</td>
<td>7.7</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Under stubble</td>
<td>Second</td>
<td>0.5-10.5 d</td>
<td>0.22B</td>
<td>8.7</td>
<td>~0B</td>
</tr>
<tr>
<td></td>
<td>2nd spray</td>
<td>(7 am 28°C, ULV, 3d after 1st spray)</td>
<td>Bare plot</td>
<td>10hr-13 d</td>
<td>0.51</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rain 65mm on day 4</td>
<td>4-13 d</td>
<td>---</td>
<td>8.6</td>
<td>---</td>
</tr>
<tr>
<td>Warren (Nov 1994)</td>
<td>Bare plot (mean of hill and furrow)</td>
<td>First</td>
<td>0.6-8 d</td>
<td>~0A</td>
<td>5.0</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>Bare EC banded plot</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hill 30cm band</td>
<td>First</td>
<td>0.6-6 d</td>
<td>~0</td>
<td>4.0</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>Furrow (drift)</td>
<td>First</td>
<td>0.6-6 d</td>
<td>~0</td>
<td>5.7</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>Cotton trash plot</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soil under trash</td>
<td>First</td>
<td>0.7-6 d</td>
<td>~0B</td>
<td>6.7</td>
<td>~0B</td>
</tr>
<tr>
<td>Gatton (April 1994)</td>
<td>Bare plot (mean of hill and furrow)</td>
<td>First</td>
<td>0.3hr-6 d</td>
<td>~0</td>
<td>3.0</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>1st spray</td>
<td>(9:45am 19°C, EC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd spray</td>
<td>(9:00am 20°C, EC)</td>
<td>6d after 1st</td>
<td>2hr-11 d</td>
<td>~0</td>
<td>29</td>
</tr>
<tr>
<td>Jondaryan (Oct-Dec 1996)</td>
<td>Bare blanket (17-Oct)c</td>
<td>First</td>
<td>0-40 d</td>
<td>~0</td>
<td>8.3</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>Bare band hill (17-Oct)c</td>
<td>First</td>
<td>0-34 d</td>
<td>~0</td>
<td>8.1</td>
<td>~0</td>
</tr>
<tr>
<td></td>
<td>Bare blanket (31-Oct)c</td>
<td>First</td>
<td>0-26 d</td>
<td>~0</td>
<td>6.0</td>
<td>~0</td>
</tr>
</tbody>
</table>

A - "~0" - negligible initial loss after application, as indicated by initial loss for total endosulfan.
B - assuming spray interception equal to % cover (see Table 3.4). C - separate plots; spray date. D - rate.

Effects of rainfall wetting. Dissipation of α- and β-endosulfan was slightly more rapid where soil was temporarily wetter (at Emerald, Warren and Jondaryan), but dissipation of total endosulfan was not enhanced, due to formation of more sulfate. Little sulfate was formed in dry soil while considerably more formed after single rainfall events (Emerald and Warren) and a series of natural rainfall events (Jondaryan). Soil movement during rain also physically relocated endosulfan from the hills into the furrows, negating the distribution of endosulfan created by band spraying on the hills.

Repeated applications. In the two cases where plots were sprayed twice (Emerald and Gatton), half-lives for α-, β- and total endosulfan were longer after two applications than after a single

82
application. This may be partly due to adverse effects on endosulfan-degrading soil microbes (El Beit et al. 1981). This response was particularly strong at Gatton, where as other pesticides (dimethoate and prometryn) were applied at the same spray times. This site did not have a history of pesticide use and may therefore not have had a population of soil microbes adapted to the presence of pesticides. The aged and more sorbed (Chapter 5) and stable residues from the first application (about 1/3 of the total after the second spray) also ‘dilute’ the dissipation after the second application, leading to somewhat longer half-lives.

EC verses ULV formulation. There appears to be no systematic difference in dissipation rates for EC and ULV formulations, or at least they are small compared with differences between sites and environmental conditions (e.g. temperature). Half-lives were similar for EC and ULV, for α, β and total endosulfan, at Warren where they were compared directly.

Effects of cover. Half-lives of endosulfan in soil under wheat stubble or cotton trash were reasonably similar to those in bare soil at Emerald and Warren. Banks and Robinson (1982) found that presence of straw mulch on the soil surface did not significantly affect the persistence of metribuzin (a basic triazine herbicide) in the soil. In the limited studies reported here, the main effect of cover was to intercept sprayed endosulfan, rather than greatly change its dissipation in the soil, as discussed in the next section. As cover can influence moisture, temperature and organic matter regimes in soil, further study of the influence of cover on pesticide behaviour in soil is warranted.

Distribution in soil. Downward movement of endosulfan was slow in a clay soil (Jondaryan), with 73% in 0-25 mm soil, 21% in 25-50 mm soil and 6% in 50-100 mm soil after 62 days and 145 mm of rain after spraying. The proportion of sulfate increased with depth. Concentrations below the 25 mm depth were relatively small, but had a large effect on reducing the half-lives compared with half-lives for 0-50 mm soil, which still contains most of the endosulfan that has moved down.

Effects of soil layer depth. Calculated half-lives were significantly less for 0-25 mm soil than for 0-50 mm soil; almost half for α-endosulfan and reduced by about one third for β-endosulfan. This reflects the greater exposure of the surface to volatilisation and climatic extremes, and losses to downward movement in the soil. Half-lives for the shallower layer should be more relevant for assessing runoff potential, which would be over estimated using the half-lives for the deeper soil.

Dissipation of total endosulfan. Half-lives for total endosulfan in 0-25 mm soil were typically 6-20 days (after initial losses), depending on the conditions and time period considered, due to the progressive change in the ratio of α:β:sulfate. This is consistent with initial half-lives from NSW cotton soils (7.1±3d for 0-7d Kennedy et al. 2001) and from deeper soil layers in India (4-5d Rao and Murty 1980, 10-11d Agnihotri et al. 1996, 5-7d Kathpal et al. 1997), but considerably more rapid than reported in North America (Stewart and Cairns 1974, Spencer et al. 1985). A half-life of 5 days, or even 10 days, presents a considerably different environmental risk than a half-life of 50 days, the ‘selected value’ from Wauchope et al. (1992). However, half-lives would increase at longer times after spraying (Kennedy et al. 2001) and for deeper soil. Half-lives of total endosulfan are also longer than for the sum of α- and β-isomers, due to formation and persistence of sulfate. Equally important,
but less predictable, are the rapid losses observed at two sites. These differences in half-lives and initial losses highlight the need for environmental assessment of pesticides under local conditions. Dissipation studies for assessment of runoff potential should concentrate on the soil surface approximating the runoff-mixing layer, where dissipation is more rapid, rather than the bulk soil.

3.6 Part B. Endosulfan dissipation from crop residues

(a) Emerald

Soil under wheat stubble contained one fifth of the endosulfan found in bare soil 11 hr after spraying (Fig. 3.9). The cover intercepted more than 80% of the spray but contained only 130 g/ha of endosulfan (~1000 g/ha applied). The mass of endosulfan in stubble and soil under the stubble was 324 g/ha, or about 30% of the applied amount. That is, a large proportion of the endosulfan applied to the wheat stubble plot (~70%) dissipated rapidly (Table 3.4). A greater proportion of the more volatile α-isomer was lost (80%) by 11 hr, with 58% of the β- lost and only 2% of endosulfan converted to new sulfate. Of the amount reaching each surface, 88% was lost from stubble and 8% from the soil. Little sulfate formed on the wheat stubble (1-2 g/ha) throughout the study period, while concentrations in soil were similar to bare plots. By 2.5 days after spraying, total endosulfan on wheat plots (stubble plus soil) declined by a further 100 g/ha, mainly due to further losses from the stubble.

![Fig. 3.9. Total endosulfan in wheat stubble and soil (0-25mm) under wheat stubble, compared with bare soil, after one application of endosulfan ULV at Emerald.](image)

After the initial rapid loss, total endosulfan on stubble dissipated with a half-life of 7.9 days (Table 3.4), somewhat more rapidly than on bare soil at Emerald. In particular, β-endosulfan dissipated reasonably rapidly ($t_{1/2} 7.0d$) compared with α- ($t_{1/2} 10.5d$).

2 Half-lives for endosulfan are collected in Table 3.4 at the end of the results, to allow discussion across sites.
Endosulfan sulfate in the stubble trended downwards throughout the study. Dissipation of $\alpha$- and $\beta$-endosulfan in soil under stubble was similar to in bare soil (Table 3.4) ($t_{1/2}$ of 8.8d and 17.6d, respectively). Dissipation of the total endosulfan in the stubble and soil ($t_{1/2}$ 12.3d) was similar to that for bare soil. The important difference is that the wheat stubble greatly increased the initial loss and did not inhibit continuing dissipation, resulting in considerably lower levels of endosulfan throughout the study, reducing the mass available for runoff.

On rainfall simulator plots at Emerald, with cover ranging from 0-60%, interception of sprayed endosulfan on cover resulted in a decrease in endosulfan in soil (0-25mm) with increasing cover (Fig. 3.10). By comparison, concentrations of sulfate (mainly carried over from the previous season) and DDE (from historic applications of DDT) in soil were similar across the range of cover. The consequences of this direct interception of sprayed endosulfan on runoff are presented in Chapter 7.

![Fig. 3.10. Endosulfan and DDE in soil (0-25mm) on simulator plots with a range of cover, 4-7 days after the second, at Emerald. (10% and 50% cover - cotton trash, 20-35% cover wheat stubble).](image)

*(b) Warren*

Dissipation of endosulfan from both wheat stubble and cotton trash at Warren involved a large initial loss followed by dissipation at about the same rate as observed in soil (Fig. 3.11), similar to wheat stubble at Emerald. Wheat stubble resulted in an 80% initial loss of endosulfan in 16 hrs after spraying, with a greater proportion of $\alpha$- lost than $\beta$- (Table 3.4). After the initial loss, dissipation on wheat stubble was slightly more rapid than for bare soil. Dissipation of $\beta$-endosulfan on wheat stubble was more rapid relative to $\alpha$- than would be expected for soil, also similar to Emerald. (No data were collected for soil under wheat stubble in this case).
Fig. 3.11. Dissipation of endosulfan (after application in the evening) on soil (0-25mm), and (a) standing wheat stubble, (b) cotton trash and (c) soil under trash and total on trash and soil, at Warren.
Spraying endosulfan on cotton trash resulted in a 74% initial loss in 18 hrs, again with a greater proportion of \(\alpha\)-lost than \(\beta\)-. Soil under cotton trash exhibited more or less no initial loss of endosulfan (Table 3.4, Fig. 3.11c), similar to behaviour observed on bare soil at this site. The rapid initial loss from the cotton trash resulted in the cotton mulch plot (soil plus trash) having about half the level of endosulfan on bare soil (Table 3.4, Fig. 3.11c). After the initial loss, dissipation from the cotton trash was slightly slower than from bare soil and wheat stubble, though the differences are small compared with the variation in dissipation rates from the various sites. The cotton trash was not as efficient as the wheat stubble at dissipating \(\beta\)-endosulfan, possibly because the cotton trash was more decomposed and contaminated with soil. Little sulfate formed on wheat stubble (0.4 g/ha) and cotton trash (2 g/ha) while the soil underneath contained levels similar to bare soil (10-20 g/ha).

The rapid initial losses of endosulfan on crop residues, and the half-live thereafter, imply that considerable volatilisation occurred, and are consistent with behaviour measured in foliage of cotton plants by Kennedy et al. (2001). They also observed that, after 2-3 days, the \(\beta\)-isomer dissipated in foliage as rapidly as, and sometimes more rapidly than, the \(\alpha\)-isomer, consistent with results on wheat stubble. The low formation of sulfate on crop residues indicates absence of suitable microorganisms. Results may differ on older, more decomposed crop residues and for wetter moisture regimes.

Table 3.4. Summary of half-lives for dissipation of endosulfan (ULV, one spray) from covered soils (0-25mm) and crop residues. Application rates were split between soil and cover using the % cover. Initial loss is the difference between the application rate and the intercept of fitted equation, as a fraction of application rate. Data for nearby bare plots (from Table 3.3) are repeated for comparison.

<table>
<thead>
<tr>
<th>Site &amp; treatment, (period)</th>
<th>Application</th>
<th>(\alpha)-endosulfan</th>
<th>(\beta)-endosulfan</th>
<th>Sulfate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial loss</td>
<td>(1/2)-life (days)</td>
<td>(1/2)-life (days)</td>
<td>From peak</td>
<td>(1/2)-life (days)</td>
</tr>
<tr>
<td><strong>Emerald (7 am 28°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare hills (0.5-11d)</td>
<td>0-11 hr</td>
<td>0.36</td>
<td>7.8</td>
<td>0.34</td>
<td>16.1</td>
</tr>
<tr>
<td>Wheat stubble plot (0.5-11d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total soil &amp; stubble</td>
<td>0-11 hr</td>
<td>0.80</td>
<td>9.0</td>
<td>0.58</td>
<td>10.2</td>
</tr>
<tr>
<td>Soil under stubble</td>
<td></td>
<td></td>
<td></td>
<td>Steady</td>
<td></td>
</tr>
<tr>
<td>Wheat stubble (80% cover)</td>
<td>0.22</td>
<td>8.7</td>
<td>(-0^A)</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>10.5</td>
<td>0.74</td>
<td>7.0</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Increasing</td>
<td></td>
</tr>
<tr>
<td><strong>Warren (8:20pm 20°C)</strong></td>
<td></td>
<td></td>
<td></td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Bare plot (0.6-8d)</td>
<td>0-15 hr</td>
<td>(-0^A)</td>
<td>5.0</td>
<td>(-0)</td>
<td>8.5</td>
</tr>
<tr>
<td>Wheat stubble plot (0.7-6d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total soil &amp; stubble, Soil under wheat</td>
<td>No data</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>0-16 hr</td>
<td>0.86</td>
<td>4.2</td>
<td>0.67</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Increasing</td>
<td></td>
</tr>
<tr>
<td>Cotton trash plot (0.7-6d)</td>
<td>0-18 hr</td>
<td>0.54</td>
<td>6.7</td>
<td>0.39</td>
<td>10.0</td>
</tr>
<tr>
<td>Soil under trash</td>
<td></td>
<td></td>
<td></td>
<td>Increasing</td>
<td></td>
</tr>
<tr>
<td>Cotton trash (65% cover)</td>
<td>0.78</td>
<td>6.7</td>
<td>0.68</td>
<td>9.2</td>
<td></td>
</tr>
</tbody>
</table>

\(A - \sim0\) – negligible initial loss after application, as indicated by initial loss for total endosulfan.
Retention of crop residue cover was effective in reducing runoff, sediment and pesticide movement during storm rainfall (Chapters 6 and 7). However, washoff from crop residue cover is also a possible source of pesticides in runoff. Therefore the behaviour of pesticides in such materials is of interest. The reduction in mass of pesticide lost in runoff has generally been attributed to the reduction in the amount of runoff (containing soluble pesticides) and amount of sediment (containing sorbed pesticides) (Walter et al. 1979). The data for endosulfan dissipation indicate that an additional benefit of retaining crop residues on the soil surface is that they intercept the pesticide during spray application, preventing it from reaching the soil, and dissipate it rapidly. Thus if a storm occurs greater than one day after spraying, a field with stubble retained on the surface will contain much less endosulfan (in both the soil and stubble) than a similar bare field, as well as having a lower potential for runoff and sediment movement.

While this is useful for managing pesticide runoff, it is not known whether such a response can be expected for all pesticides. Indeed it would create problems for weed control if such rapid dissipation occurred for soil-residual herbicides sprayed over crop residues. Washoff of herbicides directly from crop residues is often suggested where greater runoff concentrations of herbicide are found for conservation tillage (Baker et al. 1978, Blevins et al. 1990, Gaynor et al. 1995), although in some cases it may also be related to less tillage/incorporation (Baker and Johnson 1983) and does not occur when even a small amount of rain (e.g. 5mm) occurs between spraying and the first runoff event (Baker et al. 1979). The main processes involved in pesticide behaviour on crop residues are interception, volatilisation (or other rapid losses), dissipation, and washoff by rain, the last three of which would be expected to vary for different pesticides. However, data relating to these processes on crop residues are sparse.

Interception. Banks and Robinson (1982) found increasing the amount of straw on the surface greatly decreased the soil reception of metribuzin, that is, increased the interception. Their results, and results from Emerald and Warren, indicate that the percent cover provided by on-ground crop residues gives a good first approximation the percent interception. Standing crop residues have a vertical profile and may enhance interception of spray droplets, which do not necessarily fall vertically.

Initial loss, volatilisation and dissipation. Few (if any) studies have measured pesticide persistence on crop residues through time. Dissipation of pesticides on plant foliage may be the best available analogue for behaviour on crop residues. Plants, like crop residues, have a high surface area per unit area. Dissipation of most insecticides on plant foliage is much more rapid than in soil, with half-lives mostly 1-7 days (Willis and McDowell 1987). Limited data for herbicides (mainly knockdown products on grasses at 20-26°C) indicate half-lives are generally less than 10 days. Willis and McDowell (1987) also indicate that initial losses often occurred before the first sample taken to calculate these half-lives. These initial losses and rapid half-lives probably involve considerable loss by volatilisation. Taylor (1978) considers that volatilisation rates from plants can be very large, with losses approaching 90 % in 3 days for more volatile compounds. However, not all insecticides
dissipate rapidly from foliage and these compounds will probably persist on crop residues. For example, chlorfluazuron is reasonably stable and persistent on cotton foliage and cotton trash (Kennedy et al. 1997a), consistent with its low vapour pressure.

Endosulfan on surfaces is volatile, with the rate of loss greater for α- than β-isomer than the sulfate (Beard and Ware 1969, Gorbach 1982). Half-life of endosulfan on cotton plants was 1 day in Australia (28°C) (Wilson et al. 1983) and 0.9 and 1.3 days for α- and β-endosulfan in Arizona (30°C) (Willis and McDowell 1987 after Estesen et al. 1979). Kennedy et al. (2001) found initial half-lives (over 2-3 days) of 0.9±0.3 and 2.0±0.8 days for α- and β-endosulfan in foliage of cotton plants in Australia, for multiple fields, years and applications, and confirmed the large volatilisation losses using vapour sampling. Dissipation occurred in two phases and was slower after 2-3 days. The behaviour of endosulfan on wheat and cotton crop residues presented here is consistent with these observations of endosulfan on foliage.

Martin et al. (1978) found that even ‘non-volatile’ herbicides dissipated at a high rate from maize residues and filter papers in 12-14 hr after application, e.g. 56% loss of alachlor and 65% loss of propachlor. Baker and Shiers (1989) also report significant losses - only 86%, 53% and 36% of the sprayed amounts were recovered (in washoff and in the crop residue after rain) within 24 hr of spraying, for cyanazine, alachlor and propachlor, respectively. Losses were generally, but not consistently, lower for triazines (atrazine and cyanazine) than acetanilides (alachlor and propachlor), which have greater vapour pressure. Volatilisation was the major loss mechanism suggested by these authors. Prueger et al. (1999) interpreted higher measured vapour losses of metolachlor (another acetanilide) were in part due to the presence of 80% corn residue cover, though they did not directly confirm this would not have happened from bare soil. They considered corn residue has a weaker adsorption for metolachlor than soil (Parochetti 1978) increasing volatilisation potential. Banks and Robinson (1982) found, after spraying metribuzin and applying rain more or less immediately, no more than 45% of metribuzin in the soil at the lowest mulch rate (2250 kg/ha) and only 35% at the highest mulch rate (9000 kg/ha). The inference from this is that considerable metribuzin was dissipated from, and/or was sorbed to, the straw mulch, and could not be dislodged by rain. However, no control plots were run to determine what happened with no mulch.

Importantly, while these studies all found large initial losses of herbicides from crop residues, they did not determine if similar initial losses occur if the herbicides are sprayed on soil. In field studies over time, Banks and Robinson (1982) found no differences; after 20 mm of irrigation 10 days after spraying, both mulched and un-mulched soil had about 15% of applied metribuzin at day 14. Based on the finding of Savage (1980) that up to 50% of metribuzin applied to soil surfaces can be lost within 4-5 days of application by photodegradation and/or volatilisation it appears that initial losses of the order of 50% may occur with or without crop residue mulch. Therefore it is unclear whether crop residue cover consistently provides an added advantage in reducing pesticide runoff potential (as seen here for endosulfan), in addition to reducing runoff and sediment losses, or if efficacy is any worse. However, the response appears to be related to each pesticide’s volatilisation potential.
Rapid dissipation of pesticides from crop residues may in some cases be undesirable, for instance if weed control is reduced when soil-residual herbicides are sprayed over crop residues. Using weed control as an indirect measure of dissipation/persistence, it appears that soil-residual herbicides may not dissipate much more rapidly on crop residue mulch than on soil (Crutchfield et al. 1985, Steinsiek and Olivier 1979). However, such indirect evidence is also somewhat confounded as - (a) greater levels of mulch can itself increase weed control and by changing the soil moisture regime, improve herbicidal activity (Crutchfield et al. 1985), (b) among herbicides there is a range in weed control response to mulch level (Steinsiek and Olivier 1979), and (c) it is imprecise, e.g. similar weed control may occur even though considerable herbicide is dissipated from or bound in the crop residues.

Washoff. Washoff from maize residues was measured directly for several residual herbicides (triazines - atrazine and cyanazine, acetanilides - alachlor and propachlor). Rain was applied within 24 hr after spraying and more than 80% of herbicides present were washed off (Martin et al. 1978, Baker and Shiers 1989). Cyanazine washoff from maize residue (in 68mm of rain) was not affected by formulation (liquid, wettable-powder or dry-flowable) or method of application (water or oil-water mixtures), and method of application also did not affect washoff of the liquid formulations of alachlor and propachlor (all at 22 hr after spraying; Baker and Shiers 1989). Herbicide remaining on the maize residues after rain was typically 10-20% of applied atrazine and cyanazine, 3-16% for alachlor and 2-5% for propachlor, in the two studies. Banks and Robinson (1982) applied 12.5mm of rain and found no more than 45% of recently applied metribuzin reached the soil at the lowest mulch rate (2250 kg/ha wheat straw) and only 35% at the highest mulch rate (9000 kg/ha). However, as previously discussed it is unclear whether the metribuzin not accounted for was dissipated or was still present in the straw.

Baker and Shiers (1989) considered there is little interaction between crop residues and the herbicides, presumably meaning little sorption occurs – the herbicide is simply sitting on the residue surfaces and is easily washed off. In contrast, Dell et al. (1994) found that sorption coefficients of three fungicides (of a wide range in solubility) were about nine times greater in turf-grass thatch (decomposed and undecomposed root and stem) than in soil. Live grass and soil was removed by washing and the thatch was ground, making it more open to sorption. However, the study does indicate that sorption and therefore washoff may vary with the type and condition of crop residue.

Concentrations of herbicides in washoff water decreased exponentially with accumulated amount of washoff (Martin et al. 1978, Baker and Shiers 1989), similar to washoff from crop canopies (Willis and McDowell 1987). Thus the first increment of washoff produces a large proportion of the final washoff - 20-40% in 14.5mm (Baker and Shiers 1989), 45-65% in 10mm (Martin et al. 1978) and almost 100% in 6 mm (Banks and Robinson 1982). The difference between these studies may relate to the time between spraying and rainfall (22hr, 12-14hr and ‘immediately’, respectively). The fraction of the pesticide load on foliage washed off by rain generally declines with time after application (Willis and McDowell 1987, Willis et al. 1994). The implication of the exponential-decay washoff pattern is that much of the washoff should occur before runoff commences and infiltrate into
the soil rather than contribute to runoff. Silburn et al. (1996) found this occurred when endosulfan in canopy washoff and in runoff from soil under the crop were measured simultaneously.

At least for more volatile compounds, rapid dissipation on crop residues appears to provide an additional reduction in pesticide runoff potential. However, further research is needed on dissipation and washoff of pesticides on crop residues, relative to that on soil, through time after spraying.

3.7 Part C. Other pesticides

Dissipation of pesticides other than endosulfan is presented in this section. Pesticide runoff at various times during dissipation of these pesticides is considered in Chapter 4.

3.7.1 Organophosphates

(a) Dimethoate

Soil concentrations of dimethoate were more than an order of magnitude lower than those for endosulfan, due to 75-80% lower application and more rapid dissipation (Fig. 3.12). Dissipation of dimethoate was quite variable between the three sites (Gatton, Warren and Jondaryan, Fig. 3.12, Table 3.5). In particular, initial losses appear to vary with the time of day when spraying occurred. At Gatton and Jondaryan (sprayed at 9am and 5:30am, respectively), initial losses were 61% and 55%, respectively, while at Warren (sprayed 8-9pm) no initial loss occurred for either the ULV or EC applications. However, after the second spray at Gatton, also at 9am, the initial loss was small (29%), possibly non-existent, and dissipation was slower overall.

![Fig. 3.12. Dissipation of dimethoate in 0-25mm soil, (a) at Gatton, sprayed twice (6 days apart) at 9am, resulting in large initial losses and 2-phase dissipation, and at Warren sprayed at 8-9pm, with ULV and EC treatments, with no initial loss and single phase dissipation, (b) Jondaryan, sprayed at 5:30am, with large initial loss (55%) compared with endosulfan with no initial loss (6%). Data are means of hill and furrow samples. Error bars are ±1 std error.](image-url)

91
Two phases of dissipation are plotted in Fig. 3.12a for the Gatton data. Samples at 20min, 2hr and 24hr after the first spray indicate an initial loss of 31% and a half-life of 0.78 days. In reality multiple phases of first-order dissipation (or a greater than first-order process) occurred, but the data appear to follow a first-order process after 24hr. Samples at 0.5d and 2.5d at Jondaryan had similar concentrations, indicating that the initial loss occurred in the 12 hrs (during daylight) after application. Thus, where initial losses occur they appear to occur more or less within the first day.

The rapid initial loss of dimethoate at Gatton and Jondaryan (sprayed in the morning) may be due to a combination of spray losses/error, volatilisation, hydrolysis and photochemical degradation by sunlight. Dimethoate has a photolysis half-life of 12 days (USDA-ARS 1995) or 7-16 days (Tomlin 1995) and a hydrolysis half-life in water of 4.5d at pH9, indicating some contribution to dissipation is possible. Barrett et al. (1991) state “Dimethoate ... evaporation from soil may contribute to losses of 20-40% (Howard 1991)”. Dimethoate has a relatively low Henry’s coefficient (<0.0001) and high solubility in water (Table 2.4), indicating less volatilisation than for endosulfan. However, the observed behaviour of dimethoate and endosulfan is inconsistent with their Henry’s coefficients. Endosulfan, though more volatile, had low initial losses at all three sites. Sorption to the soil may have competed less strongly with volatilisation for dimethoate, which has a much lower sorption coefficient than endosulfan. The absence of initial loss of dimethoate at Warren (sprayed in the evening) is consistent with lower temperatures reducing volatilisation and the absence of photochemical degradation. Contact with soil overnight appears to prevent the initial loss.

Table 3.5. Initial losses and first-order half-lives for organophosphorus pesticides in soil (0-25mm). Initial loss is the difference between the applied rate and the intercept of the fitted equation at day 0, thus initial loss for second phase includes first phase. Half-lives for 0-50mm soil at Jondaryan were the same as for 0-25mm soil as these pesticides were <DL in 25-50mm soil.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Treatment</th>
<th>Period (hrs or days)</th>
<th>1st phase</th>
<th>2nd phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial loss (fraction)</td>
<td>Half-life (days)</td>
<td>Initial loss (fraction)</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>Spray 1</td>
<td>0.3-24hr/1-6d</td>
<td>0.34</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Spray 2</td>
<td>2-24hr/1-11d</td>
<td>0.09</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>Blanket ULV</td>
<td>1-6d</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>EC band - hill</td>
<td>1-6d</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Jondaryan</td>
<td>Single phase</td>
<td>0.5-62d</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Two phaseB</td>
<td>0.5-5.4d, 2.5-62d</td>
<td>0.24</td>
<td>4.4</td>
</tr>
<tr>
<td>Chloryprifos</td>
<td>Jondaryan</td>
<td>0.5-5.4d, 5.4-62d</td>
<td>0.74</td>
<td>2.0</td>
</tr>
<tr>
<td>Profenofos</td>
<td>Jondaryan</td>
<td>0.5-5.4d, 5.4-62d</td>
<td>0.68</td>
<td>1.9</td>
</tr>
</tbody>
</table>

A – was 0.18. Correct for 13% drift into furrows, estimated from concentration in furrow soil.
B – alternative models for the same data.

Half-lives after the initial loss (after 1day) were reasonably consistent at 8-13 days, except for the first spray at Gatton (Table 3.5), and comparable to the half-life of 11 days measured over 2
months in outdoor soil for incorporated granular dimethoate by Bro-Rasmussen et al. (1970) and the ‘selected value’ of initial half-life of 7 days given by Wauchope et al. (1992).

Dissipation after the first spray at Gatton was more rapid for dimethoate ($t_{1/2}=2.6$ days, Table 3.5) for no obvious reason (e.g. temperature, soil moisture being the same after the second spray). This half-life is closer to observed ‘aerobic DT50 of 2-4.1d’ of Tomlin (1994) and 2.4d half-live in sandy loam (Roberts and Hutson 1998) than the other data. This may reflect the short period of measurement after spraying (1-7d). Samples for 0.5-5.4d at Jondaryan similarly indicated a shorter half-life of 4.4d. Bro-Rasmussen et al. (1970) observed progressively slower dissipation of incorporated OP’s from outdoor soil. The reason for the large difference in dissipation between the two sprays at Gatton is not clear. Dissipation of endosulfan was also slower after the second spray (Table 3.3) and inhibition of soil microbes by the pesticides is suggested (El Beit et al. 1981).

(b) Chlorpyrifos and profenofos

Chlornyrisos and profenofos dissipated rapidly at Jondaryan (Fig. 3.13), even more so than dimethoate. Chlorpyrifos and profenofos concentrations decreased by an order of magnitude in less than 5 days after spraying, while dimethoate took about 25 days. A large proportion of these losses occurred in the first half day. At the first sampling (0.52 days), less than one third of the application rate of chlorpyrifos and profenofos was detected in 0-25mm soil. Errors in application rate or depth of sampling are unlikely, as other pesticides applied in the same mix (e.g. endosulfan) and measured in the same soil samples (i.e. herbicides) were found at concentrations similar to their spray rate.

![Fig. 3.13. Concentrations in 0-25mm soil (a) chlorpyrifos, (b) profenofos, from main plot ('6 wk blanket') and other data from Jondaryan. Data are means of hill and furrow samples. Error bars are ±1 std error. Concentrations were <DL in 25-50, 50-100mm soil, and 0-25mm after day 40.](image-url)
Data from other treatments (samples from simulator plots at 5 and 2 days after spraying), which involved new mixes and applications on different days, are also consistent with these results (Fig. 3.13). Thus a large proportion of the initial losses are probably due to real losses from the soil.

McEwen and Stephenson (1979) list chlorpyrifos among compounds with marked evidence of volatility. Gerritse et al. (1991) rank chlorpyrifos volatility as significant according to its Henry's coefficient. Volatilisation half-lives of 1.9-6.8d were found on three moist soils (Racke 1993). In comparison, profenofos has a lower Henry’s coefficient than chlorpyrifos (USDA-ARS 1995). Unfortunately, published values of vapour pressure and Henry’s coefficient vary. Indeed if volatility were responsible for the large initial losses of the OP’s, large losses of endosulfan would presumably also be expected (Kennedy et al. 1997b, 1998), but did not occur. All three OP’s are considered ‘unstable in alkaline conditions’ (Tomlin 1994) (Jondaryan soil pH=8.1) and OP’s in general are considered susceptible to hydrolysis. Profenofos in particular has a rapid hydrolysis half-life in soil (4.5d at pH9), while chlorpyrifos is generally considered more stable (USDA-ARS 1995). However, in air-dry soil clay-catalysed hydrolysis of chlorpyrifos occurs very rapidly, resulting in short half-lives (1.9-7.8d), especially at higher temperatures (0.75-3d) (Racke 1993). Profenofos has a photolysis half-life of 3.6 days (USDA-ARS 1995). Photolysis of chlorpyrifos on soil surfaces is considered less significant (Racke 1993), although rapid photolysis has been observed (Roberts and Hutson 1998). The significance of each of these processes is unpredictable, but combined they apparently resulted in rapid losses during the first day after surface application.

After the initial losses (after 0.5d), dissipation of chlorpyrifos and profenofos had two distinct phases, with an apparent change in rate at 5.4 days (Fig. 3.13). In reality, it is a continuous multi-order process, depending on several processes. Several studies have found dissipation of chlorpyrifos and other OP’s in soil did not follow simple first-order assumptions, with dissipation slowing with time (Bro-Rasmussen et al. 1970, Racke 1993). Half-lives for the first phase were about 2 days for both chlorpyrifos and profenofos (Table 3.5). For profenofos this is consistent with hydrolysis half-life in soil of pH 9 of 4.5 days and a photolysis half-life of 3.6 days (USDA-ARS 1995), whereas for chlorpyrifos losses may be more related to volatilisation (indicated by Henry’s constant, Kennedy et al. 1997b). During the second phase (5.4-40d), the half-life for profenofos (7d) is similar to values of 8 and 7 days suggested by Wauchope et al. (1992) and Tomlin (1995). The second phase half-life for chlorpyrifos (13d) is considerably shorter than found in many studies (e.g. 30d Wauchope et al. 1992, 81d Kookana et al. 1995, 60-120d Tomlin 1995). However, it is closer to the half-life of less than 7 days found in non-sterile, moist soil held at 28°C, with pH 8 (similar to Jondaryan soil), by Miles et al. (1979). Miles et al. (1979) found rapid microbial degradation of chlorpyrifos can occur under more or less ideal conditions and when photolysis and volatilisation were excluded.

Dissipation of the OP’s was not influenced by the pattern of rainfall (Fig. 3.13). Chlorpyrifos and profenofos were below the DL at 62 days. Concentrations of the three OP’s in deeper soil layers were below the DL from 2.5-62 days, indicating that downward movement did not contribute greatly to dissipation. Overall, dissipation of the OP’s from the surface soils was very rapid, had large initial
losses and multiple phases, and would not be predicted well using standard ‘book values’ for dissipation rates. In contrast, dimethoate sprayed at night (at Warren) showed no initial loss.

3.7.2 Herbicides

(a) Prometryn

Prometryn in 0-25mm soil at Gatton (Fig. 3.14) and Jondaryan (Fig. 3.15) exhibited low initial losses and followed first-order dissipation. Half-lives were 19 and 16 days for the first and second application at Gatton, and 20 days at Jondaryan (Table 3.6). Thus dissipation for 0-25mm soil was considerably more rapid than generally reported for prometryn, e.g. 60 and 40-70 days (Wauchope et al. 1992, Tomlin 1994), although USDA-ARS (1995) reports values of 6-360 days. These differences may relate in part to the shallow depth of soil considered, which is discussed below. However, leaching is not required to enhance dissipation, as at least in the Gatton study, there was no rain. Prometryn in soil is considered reasonably stable with respect to hydrolysis and photolysis (USDA-ARS 1995), and of negligible volatility (Table 2.4). The action of microorganisms in soil is important to breakdown (Extoxnet 1997) and differences in dissipation rates would be expected, depending on factors that affect microbial activity (soil moisture, temperature, organic matter etc). However, it is curious that microorganisms would be particularly active given that the 0-25mm soil at Gatton was reasonably dry throughout (0.046±0.005g/g c.f. air-dry (40°C) moisture content of 0.028±0.007g/g) and the 0-25mm soil at Jondaryan was ephemerally dry (approaching air-dry) much of the time.

Fig. 3.14. Prometryn in soil (0-25mm) at Gatton during a sequence of two applications. Data are means of hill and furrow samples. Error bars are ±1 std error. The last concentration after the first spray (day 6) was based on a single sample and appears erroneously low. An alternative first-order equation is fitted without this value and is preferred.
Table 3.6. First-order half-lives for herbicides in 0-25mm and 0-50mm soil. Initial loss is the difference between the applied rate and the intercept of the fitted equation for 0-25mm soil at day 0. All data are blanket sprayed, mean of hill and furrow, unless otherwise indicated.

<table>
<thead>
<tr>
<th>Site</th>
<th>Pesticide (common name)</th>
<th>Period (days)</th>
<th>Initial loss (fraction)</th>
<th>Half-life (days)</th>
<th>Ratio of Published field half-lives (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gatton</td>
<td>Prometryn - Spray 1B</td>
<td>0.3hr-4d</td>
<td>0.17</td>
<td>19.1</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>- Spray 2</td>
<td>2hr-11d</td>
<td>-0.07</td>
<td>16.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>Jondaryan</td>
<td>Diuron</td>
<td>0.5-62d</td>
<td>0.18</td>
<td>20.3</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>Fluometuron</td>
<td>0.5-62d</td>
<td>-0.27C</td>
<td>14.9</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>Metolachlor</td>
<td>0.5-62d</td>
<td>-0.08</td>
<td>28.7</td>
<td>36.4</td>
</tr>
<tr>
<td></td>
<td>Pendimethalin</td>
<td>0.5-62d</td>
<td>0.03</td>
<td>32.8</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>Prometryn</td>
<td>0.5-62d</td>
<td>-0.02</td>
<td>20.0</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>Pyrithiobac sodium</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Blanket</td>
<td>0.5-62d</td>
<td>0.25</td>
<td>13.1</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>- Banded – hill</td>
<td>0.5-34d</td>
<td>0.30</td>
<td>14.4</td>
<td>No data</td>
</tr>
<tr>
<td></td>
<td>- Blanket 2wks</td>
<td>0.5-25d</td>
<td>0.63</td>
<td>9.8</td>
<td>No data</td>
</tr>
</tbody>
</table>

A – Initial field dissipation from Wauchope et al. (1992) and (in brackets) range from Tomlin (1994).
B – data for last sample at day 6 discarded - appeared to have an erroneously low prometryn concentration.
C – negative initial loss indicates an intercept above the nominal spray rate. A large negative value (e.g. >0.2) indicates a likely error in the spray rate.

(b) Other herbicides (Jondaryan)

The six herbicides studied at Jondaryan all exhibited approximately first-order dissipation from 0.5-62 days with $R^2$ from 0.87-0.96 (Fig. 3.15). Initial losses were generally small, except for (a) diuron, which is considered stable to hydrolysis and photolysis (USDA-ARS 1995) and to have negligible volatilisation (Table 2.4), (b) pyrithiobac sodium, which is considered stable to hydrolysis, moderately resistant to photodegradation (t1/2 43d, USDA-ARS 1995) and to have negligible volatilisation. Thus in both cases the initial losses may simply be an error in spray rate (although all were in the same tank mix). Dissipation of pyrithiobac sodium appears to be more rapid during the period 30-35 days after application, when the greatest amount of rain occurred over the shortest time (Fig. 3.15), consistent with movement into the 25-50mm soil (Table 3.7). Dissipation of the other herbicides, which had less movement into 25-50mm soil, is not clearly related to the pattern of rainfall. Dissipation of pyrithiobac sodium was reasonably consistent for blanket and banded application on the same day, but was more rapid when sprayed 2 weeks later, closer to the period of rainfall on 20-35d (Table 3.6).

Half-lives in 0-25mm soil (Table 3.6) were shortest for pyrithiobac sodium (Py_Na) and fluometuron (~14d), about 20 days for diuron and prometryn, and longest for metolachlor (29d) and pendimethalin (33d). Dissipation ranked more or less in reverse order of $K_{oc}$ (Py_Na <fluometuron <metolachlor <prometryn <diuron <pendimethalin), with the exception of metolachlor. Arguments have been made both for sorption slowing degradation (e.g. protection from microbial degradation)
and in some cases increasing it (Graham-Bryce 1981). All these herbicides are stable to hydrolysis (USDA-ARS 1995), reasonably stable to photolysis in soil, except for metolachlor and fluometuron ($t_{1/2}$ ~9d), and volatilisation is rated as negligible or low (pendimethalin) (Table 2.4), although vapour measurements in the field indicate some volatilisation (e.g. for metolachlor, Prueger et al. 1999). All are susceptible to microbial degradation though pendimethalin may be more resistant (Extoxnet 1997).

Dissipation also ranked more or less in order of increasing downward movement to 25-50mm soil (Py_Na > fluometuron > metolachlor > prometryn > diuron = pendimethalin) (Table 3.7), again with the exception of metolachlor. However, while downward movement contributed to dissipation from the 0-25mm soil, particularly for pyrithiobac sodium, other processes (e.g. in-situ degradation, surface losses) probably caused by far the greatest proportion of dissipation.

Half-lives in 0-25mm soil for pyrithiobac sodium are similar to published values for soil of similar pH (Table 3.6). Half-lives for the other herbicides are considerably shorter ($1/3^{rd}$ - $1/6^{th}$) than published values of 60-90 days (Table 3.6) and are often shorter than the lowest values reported by Tomlin (1994), though similarly low values have been reported (USDA-ARS 1995). The more rapid dissipation observed here is probably related to surface application without incorporation, resulting in exposure to climatic extremes, including rainfall, the warm climate (20-35°C), and the pH and low
organic carbon content of the soils, although the characteristics of the microorganisms present may have contributed.

(c) Effects of soil depth on half-life

Half-lives were consistently lower for 0-25mm soil than for 0-50mm soil (Table 3.6), although half-lives in 0-50mm soil were still considerably lower than published values, as they are still exposed to surface losses and exposure. The difference in half-lives for the two layers related reasonably well to sorption coefficients – less sorbed herbicides experienced greater downward movement from 0-25mm soil into 25-50mm soil (Table 3.7) and thus had lower half-lives for 0-25mm soil. The least sorbed herbicide (pyrithiobac sodium $\text{K}_{OC}<50$) had the greatest reduction in half-life (0.57 ratio of half-lives Table 3.6), fluometuron and metolachlor ($\text{K}_{OC} 100-200$) half-lives were 25-30% lower, and for pendimethalin, prometryn and diuron ($\text{K}_{OC} \geq 400$) half-lives were only 5-13% lower.

Similarly, observed pesticide amounts in 25-50mm soil (Table 3.7) related to sorption coefficients, with least movement for pendimethalin ($\text{K}_{OC} 5000$) (24% in 25-50mm soil by day 62), similar to endosulfan, whereas for pyrithiobac sodium ($\text{K}_{OC}<50$) a much greater proportion moved into the 25-50mm soil (e.g. 72% of total by day 62). Most herbicides were found at concentrations greater than DL in 50-100mm soil on day 62, but concentrations were considerably lower than in upper layers.

Table 3.7. Distribution of herbicides and endosulfan in surface soil at four times after application (Jondaryan) – concentration in 25-50mm soil as a percent of total in 0-50mm soil. Concentrations for the three OP’s were always <DL in 25-50mm soil.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Koc (KOC)</th>
<th>2.4</th>
<th>25.4</th>
<th>39.3</th>
<th>62.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain (mm)</td>
<td></td>
<td>5</td>
<td>24</td>
<td>48</td>
<td>71</td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td>1.2</td>
<td>3.6</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>Sulfate</td>
<td>---</td>
<td>100</td>
<td>13</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12,400</td>
<td>2</td>
<td>5</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>5,000</td>
<td>5</td>
<td>9</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Diuron</td>
<td>480</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>Prometryn</td>
<td>400</td>
<td>0</td>
<td>0</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>200</td>
<td>4</td>
<td>17</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>Fluometuron</td>
<td>100</td>
<td>0</td>
<td>14</td>
<td>27</td>
<td>63</td>
</tr>
<tr>
<td>Py-Na</td>
<td>11</td>
<td>13</td>
<td>34</td>
<td>68</td>
<td>72</td>
</tr>
</tbody>
</table>

As described previously for endosulfan, half-lives for 0-50mm soil are greater than for 0-25mm soil mainly because pesticide that moves below 25mm is recovered in the deeper layer, and use of half-lives for the deeper layer will overestimate the runoff potential.

3.7.3 Comparison of soil concentrations (runoff potential) between pesticides

Concentrations of the various pesticides in the soil surface, and therefore their potential concentrations in runoff, differed markedly (Fig. 3.16), depending on application rate and dissipation rate. There is a large contrast between, on the one hand, endosulfan and most herbicides, applied at
the equivalent of 6-9 mg/kg and dissipating with a half-lives of 20-30 days, and the OP’s (dimethoate, chlorpyrifos, profenofos) which dissipated much more rapidly. In fact, the OP’s dissipated so rapidly their quite different application rates made little difference to soil concentration by five days after spraying. Pyrithiobac sodium was applied at a much lower rate than the other herbicides and therefore has much lower soil concentrations despite having only a slightly lower dissipation half-life. Similarly, herbicides applied at about half the rate (prometryn and pendimethalin) of others have lower soil concentrations until about 40 days after spraying.

![Diagram](image)

**Fig. 3.16.** Concentrations in soil (0-25mm) of (a) four insecticides, and (b) six herbicides, at Jondaryan.

It is notable that soil concentrations of all of the pesticides studied declined significantly during the 62 days, reflecting half-lives of 33 days or less. This relative lack of persistence contrasts with that of DDE, derived from DDT used some 15 or more years ago, but detected at three of the sites, and at concentrations of 1-2 mg/kg at the sites with the longest history of cotton growing (Emerald and Warren). Concentrations for most pesticides declined by at least an order of magnitude within the 62 days. Runoff potential, as indicated by surface soil concentrations, can vary by about an order of magnitude due to the application rates used for various pesticides, and can decline by more than an order of magnitude in 5 days (e.g. OP’s), 35 days (e.g. pyrithiobac sodium) or 60 days (others). At the extreme of rapid dissipation, the OP’s declined by three orders of magnitude in 35 days (Fig. 3.13). Thus application rate and dissipation (and repeated applications) create quite a transient pattern of runoff potential.
3.8 Conclusions

In this chapter, dissipation of pesticides from the surface soil 0-25 mm layer, which contributes to pesticide runoff, was studied in typical cotton growing conditions at four sites. Considerable detail was obtained about soil concentrations, initial losses and dissipation for the period immediately after spraying, generally covering one to three half-lives, relating to the period of potential for high runoff concentrations rather than to longterm persistence. While the major emphasis was on dissipation of endosulfan from soil and crop residues, several other insecticides (OP’s) and a range of herbicides (fluometuron, metolachlor, prometryn, diuron, pendimethalin) were also studied, to provide a contrast in pesticide properties.

In most cases, dissipation from 0-25 mm soil followed first-order dissipation, with half-lives of 6-20 days for endosulfan, 8-13 days for OP’s, and 13-32 days for herbicides. However, in several cases, larger initial losses (within day 1) and more rapid dissipation, extending out to 2.5-5 days, were observed. In terms of being able to predict pesticide concentrations in surface soil, and therefore pesticide runoff, the greatest uncertainty is probably related to the occurrence or otherwise of these large initial losses and early very rapid dissipation. One consolation is that models using more general medium term half-lives that missed this early rapid dissipation would be conservative, in the sense that they would over-predict pesticide runoff, which is probably for the best if the early rapid dissipation does not occur consistently. Most current models lump such losses in an ‘application efficiency’ term with few physical processes (e.g. effects of temperature) considered due to lack of data.

Dissipation in 0-25mm soil was more rapid than in 0-50mm soil, but varied from no effect for the most rapidly dissipated OP’s to 1.6 times faster for endosulfan, and varied according to KOC for herbicides. Herbicides with lower KOC values dissipated faster in the shallower soil than those with higher KOC, due to greater downward movement of the less sorbed herbicides. For example, the most mobile herbicide, pyrithiobac sodium, dissipated 1.7 times faster in the shallower layer.

Half-lives in 0-25mm soil were generally considerably lower than published ‘selected’ values. Endosulfan half-lives were generally much lower, particularly for α-endosulfan, but were closer to values determined in India and recent studies in cotton in Australia. (This simply reflects the limited data available when the selected values were compiled). Only for dimethoate and profenofos were selected values similar to values observed here, but only when more rapid early losses were ignored. Chlorpyrifos dissipated much more rapidly than generally observed elsewhere, though still within the range of published data. The herbicides dissipated at 2-3 times the rate of selected values, although pyrithiobac sodium’s dissipation was consistent with data for soil of similar pH. The surface application of all pesticides studied, without incorporation, and the resulting exposure to climatic extremes and the shallow depth of soil studied is considered to have contributed to more rapid dissipation. However, it is of interest that the relative dryness of the surface soil most of the time did not appear to prevent losses by processes such as microbial degradation, volatilisation and abiotic losses (e.g. hydrolysis).
3.8.1 Endosulfan in soil

Initial losses of α- and β- endosulfan from 0-25mm soil were large (e.g. 50% of applied) in one study (Emerald) where endosulfan was applied in the morning when the air temperature was ~30°C and was exposed to high daytime temperatures (up to 38°C). In contrast, little initial loss occurred when endosulfan was applied in the morning when temperatures were 20°C (Gatton and Jondaryan) and at night when temperatures were 20°C (Warren). Dimethoate (which is poorly sorbed compared with endosulfan) also exhibited large initial losses, except when sprayed at night. A few hours of contact with soil at moderate temperatures appears adequate to allow sorption to soil.

This response to temperature, the properties of endosulfan (low solubility, high vapour pressure, high $K_H$) and direct measurements of vapour (Kennedy et al. 2001, Raupach et al. 2001ab) indicate these initial losses are more likely related to volatilisation rather than other processes such as photochemical degradation. Field trials have shown that photodegradation of endosulfan in soil and on foliage is probably insignificant (Southan 1996 cited by Kennedy et al. 1997b) while volatilisation is rapid, particularly for α-endosulfan. While volatilisation is retarded when the soil is dry (often the case for surface soil), volatilisation rate increase rapidly at relatively low moisture content and then remains high (Taylor and Spencer 1990). The degree of dryness required to suppress volatilisation may be greater than in these studies and that typically experienced in cotton fields. This is supported by measured volatilisation-soil moisture relationships (Taylor and Spencer 1990) and the volatilisation results of Kennedy et al. (1997b) for endosulfan on soil at only slightly above air-dry moisture content (10g/g). Spencer et al. (1969) observe that only a monolayer of water is required on soil surfaces to support volatilisation. Air-dry soil still contains 1-2 L of water per square meter.

Dissipation of α- and β- endosulfan from soil proceeded as a single-phase first-order process at all sites where initial losses were low (Gatton, Warren, Jondaryan) but had two phases at Emerald where large initial losses occurred. α- endosulfan consistently dissipated more rapidly than β-endosulfan, with half-lives of 5-11 days and 9-27 days, respectively. The rate of dissipation of α-endosulfan varied from 1.3 to 3 times that of β-, indicating that dissipation of the two isomers was affected differently by site and/or environmental factors. Dissipation of β-endosulfan was fastest relative to α- when temperatures at the time of application (and soon after) were highest. Half-lives of α-, β- and total endosulfan were longer after two applications than after a single application. Dissipation rate appeared similar for EC and ULV formulations. Half-lives of endosulfan in soil under wheat stubble and cotton trash were reasonably similar to those in bare soil. Half-lives were 30-40% shorter for 0-25mm soil than for 0-50mm soil.

Dissipation of α- and β-endosulfan was slightly more rapid where soil was temporarily wetter after rain, but dissipation of total endosulfan was no faster, due to greater formation of the sulfate metabolite. Comparatively little sulfate formed in dry soil while considerable amounts formed after rainfall. Approximate half-lives for recently formed endosulfan sulfate (1-2 weeks after application) in dry soil, for dissipation after the peak concentration, were 7-12 days. However, in about half the plots studied concentrations of sulfate in dry soil continued to increase throughout the two weeks after
application. Half-life was longer (23 days) where the parent isomers were in the soil for 20-30 days prior to formation of the sulfate during a wetter period. Half-life of the sulfate appears to increase with time of contact with the soil; Kennedy et al. (2001) found half-lives of 92±47 days.

The other effect of rain was to physically move soil and endosulfan from the hill into the furrow, sufficient to remove differences created by band spraying on the hills. Little leaching of endosulfan occurred during 65 mm of rainfall, with less than a 5% reduction in concentrations in 0-25mm soil (at Gatton). Progressively greater concentrations of α-, β- and sulfate endosulfan were observed in 25-50mm soil over 62 days and low concentrations were found in 50-100mm soil at 62 days (at Jondaryan). These results are consistent with other studies of endosulfan (Kimber et al. 1995, Kennedy et al. 2001). Downward movement of endosulfan in clay soils appears insubstantial although it does contribute to lower half-lives for 0-25mm soil than for deeper soil as discussed above.

The behaviour of the parent isomers and of the sulfate is sufficiently different that they should be reported and modelled separately. For example, half-life was 38% greater for total endosulfan than for the sum of α- and β-, due to formation of sulfate.

3.8.2 Endosulfan on crop residues

When endosulfan was applied to wheat stubble and cotton trash, large losses occurred in the first 24 hr, with 75-90% dissipated from crop residues and 50-70% from the plot (i.e. soil and cover), depending on percent covered and temperature. A greater proportion of α-endosulfan (up to 95%) was dissipated from crop residues than β-endosulfan (up to 75%). Initial losses were lower when spraying occurred at night (at Warren), with cooler temperatures, but were still large considering that no initial losses occurred from bare soil under these conditions. These rapid initial losses are consistent with rapid losses from cotton plants (Wilson et al. 1983, Silburn et al. 1996, Kennedy et al. 1998, 2001). Crop residues intercepted sprayed endosulfan in proportion to their percent cover. Little initial loss occurred for endosulfan that reached the soil under crop residues. These losses presumably occur through volatilisation, which would be enhanced by the large surface area of crop residues and poor or slow sorption into the crop residues.

Half-lives for endosulfan on crop residues after the initial loss (>1 day) were generally similar to those on soil at the same site, except that half-lives for β-endosulfan were considerably shorter on wheat stubble than on soil (67% at Emerald and 31% at Warren), reducing the half-lives for total endosulfan by 20-30%. This did not occur on cotton trash, possibly because it was more decomposed and contaminated with soil. Little sulfate was formed on either wheat stubble or cotton trash. The net effect of interception and dissipation by cover, on plots with a range of cover at Emerald (rainfall simulator studies Chapters 6 and 7), was that plots with more cover had lower soil concentrations of α-, β- and total endosulfan.
3.8.3 Consequences for pesticide runoff

In this chapter, the time patterns of concentration in the soil surface after application of various pesticides were determined. This time pattern of concentration is determined by the amount applied and the dissipation rate. In some cases, rapid initial losses occurred, particularly for endosulfan at higher temperatures and for organophosphorus insecticides, significantly reducing the ongoing soil concentrations. Aside from these initial losses, dissipation rates observed for insecticides and herbicides commonly used in the Australian cotton industry were more rapid than generally reported, in part because only the surface soil (0-25mm), which interacts with runoff but is exposed to climatic extremes, was considered. The concentration of a pesticide in the surface soil (0-25mm) when a runoff event occurs defines the amount of that pesticide potentially available for extraction in runoff during that event. Relationships between these soil concentrations and the resulting concentration in runoff are determined in Chapter 4. Dissipation of endosulfan on crop residues was more rapid than on soil, and the resulting impact on runoff concentrations is examined in Chapter 7.
CHAPTER 4.
PESTICIDE EXTRACTION FROM SOIL INTO RUNOFF
CHAPTER 4. PESTICIDE EXTRACTION FROM SOIL INTO RUNOFF

4.1 Introduction

Estimation of pesticide runoff is a poorly understood aspect of the environmental behaviour of pesticides. Wauchope et al. (1992) considered that assessment of pesticide runoff is one of the weakest areas of our understanding of environmental fate, indicating 'the need for a better index of runoff potential'. Holland (1998) identified this as an area where further information is needed for environmental assessment in Australia. A major reason for this poor level of understanding is that the literature on pesticide runoff presents a seemingly random collection of runoff concentrations. Most studies involve only a few pesticides (often just one) so it is difficult to know if the responses observed are due to the properties of the pesticide(s) or the conditions of the study, for instance the timing of the event after spraying.

There are many different pesticides, with a wide variety of chemical properties (Wauchope et al. 1992, Hornsby et al. 1996). Hornsby et al. (1996) list properties of 343 active ingredients of pesticides, however many more compounds, metabolites and other potential soil contaminants exist. These chemical properties can impact on a variety of processes involved between application and runoff arriving at the edge of a field. With so many pesticides, an important issue for their management and regulation is how they behave relative to each other and to their properties. Measurement of pesticide runoff losses from agricultural fields and plots indicate differences in concentrations and total losses between various compounds (Wauchope 1978, etc Chapter 1). However, these studies do not always separate out (quantitatively) the contribution of various causative factors behind these differences and even when they do, it is difficult to compare between sites/studies or between pesticides, or relate their runoff to their properties.

This difficulty arises because runoff transport of a pesticide is the outcome of a series of processes, many of which may be affected by the properties of the pesticide (Chapter 1):
- application→dissipation→loss by leaching→runoff extraction→runoff transport,
- operating on several compartments or surfaces (e.g. plant canopy, crop residues, soil), and
- involving soil/sediment-water partitioning at several stages.

Because of dissipation, timing of the runoff event after application is important. When runoff does occur, the runoff extraction process is affected by the hydrologic and erosion characteristics of the runoff event, as discussed in Section 4.2.1.

Wauchope and Leonard (1980) found that 'edge-of-field' pesticide concentrations in individual runoff events reported in the literature could be related (to within about one order of magnitude) to application rate, time of the event after application and an 'availability index'. The availability index was grouped into four classes according to pesticide formulation (EC, wettable powders, granules, etc), solubility class (i.e. soluble/insoluble) and placement (on foliage, soil surface or incorporated),
and ranged over about an order of magnitude. The variation in runoff concentrations not accounted for by the model includes all other sources of variation such as those related to soil, field and storm characteristics, but also includes some errors from using the same concentration-time decay rate for all data. Though simple, the model shows the relative importance of several factors, however, many other factors (e.g. pesticide and site-specific factors) are lumped together in the availability index.

To simplify the analysis and focus on the data available, only sprays applied to the soil surface (i.e. ignoring non-sprayed formulations, foliage washoff etc.) will be considered. By comparing pesticide runoff to the concentration in the soil at the start of rainfall, one set of factors (i.e. those that occur before rainfall starts - application and dissipation, Chapter 3) can be separated from those that occur during the rainfall event. Pesticide concentration in runoff should then be a function of (a) the concentration and distribution with depth in the soil, (b) desorption and leaching in the soil surface and extraction into runoff in solution, and (c) extraction into runoff with sediment, which depends on detachment, deposition (sorting) and transport of the sediment, as discussed in Section 4.2.1.

Leonard et al. (1979), Baker (1980) and Spencer et al. (1985) found strong relationships between pesticide concentrations in runoff and in soil, within individual studies, as discussed in Chapter 1. However, the approach does not seem to have been taken further, even though Baker (1980) pointed out the similarity of the relationship for the data of Leonard et al. (1979) and Baker and Laflen (1979). The approach taken in this Chapter, outlined in the conceptual framework below, is reasonably simple and (mostly) empirical – what can be learned from the available data? Deriving the best model is a separate issue. While not necessarily leading to a predictive model for pesticide runoff the approach offers a framework for interpreting pesticide runoff studies, by separating key processes that should relate more or less to specific pesticide properties.

This chapter specifically focuses on the relationship between pesticide concentrations in runoff and in the soil, that is, the runoff extraction process, and how different pesticides behave. Data for a range of pesticides from simulated rainfall events on hill-furrow systems (Chapter 2) are used. These data are then contrasted with data from the literature.

4.1.1 Aims

The aims of this chapter were to:

1. Investigate processes of pesticide runoff extraction from soil by determining the relationship between pesticide in runoff and in soil, for pesticides of contrasting properties.

2. Determine how runoff extraction is affected by management practices.

---

\(^{A}\) Equations from Leonard et al. (1987) used in the GLEAMS model, for event average pesticide leaching and runoff in the water and sediment phases predict the rainfall simulator data presented here very well, with the same optimised ‘extraction coefficient’ for all pesticides, in the controlled environment of a spreadsheet.
4.2 Conceptual framework

4.2.1 Runoff extraction from soil

The transfer of chemicals from soil into runoff during a rainfall event is the outcome of several processes. Firstly, leaching of the chemical downwards in the soil with infiltrating water, which depends on the amount of water infiltrated and the sorption properties of the chemical and the soil. The second process involves extraction of the chemical from the soil into runoff, in solution into the water phase in runoff, and by entrainment of sediment into the sediment phase in runoff. These processes act continuously and simultaneously; however leaching is active before runoff commences.

The amount of chemical available for extraction into surface runoff and movement downwards in the soil depends on the concentration in the soil surface, in a layer termed the ‘runoff-mixing layer’. Concentration in the surface 0-10 mm layer provided reasonable empirical relationships for runoff concentrations of several pesticides (Leonard et al. 1979) and for soluble P (Sharpley et al. 1982) and was adopted as a pragmatic compromise in some models (Leonard et al. 1987). In reality, extraction of soluble chemicals from a soil surface into runoff is greatest at the soil surface and decreases exponentially with depth, with some extraction from as deep as 20-25 mm (Ahuja et al. 1981, Ahuja and Lehman 1983). To allow comparison with a depth of uniform extraction, Ahuja et al. (1981) defined an effective depth of interaction (EDI) within which the concentration was uniform and equal to that at the soil surface. EDI values are generally less than 10 mm (e.g. 2-3 mm Ahuja et al. 1981) and vary with soil conditions (density, tilth, roughness, cover, slope etc.), chemical and rainfall characteristics (Leonard et al. 1987, Sharpley 1985).

As discussed in Chapter 1, the relationship between the concentration of a chemical in the soil surface and the concentration extracted into runoff is complex, not least because, for pesticides, it involves extraction partly as a solute and partly sorbed to sediment (Chapter 5). Both the solute and sediment extraction may exhibit similar responses to factors such as rainfall intensity and energy, surface cover, infiltration rate, slope and shear stresses generated by water flowing across the soil surface, although sometimes they may have contrary responses (e.g. clods on the soil surface) (Ahuja 1986, 1990). Thus, for example, there tends to be a positive correlation between solute extractions and soil loss (Sharpley 1985).

Solutes are transferred into runoff by raindrop-accelerated diffusion in the mixing layer; chemicals in soil pore water may mix directly with runoff on the soil surface but are also brought to the soil surface by a pumping action or turbulence associated with raindrops (Ahuja and Lehman 1983, Ahuja 1986, 1990). If complete mixing of the solute in the soil pore water and in the runoff water occurred, the concentration in runoff could be calculated reasonably simply from the soil concentration (while applying suitable leaching and partition). However, complete mixing with a particular soil depth probably does not occur (Ingram and Woolhiser 1980). Also the distribution of the chemical with depth within the surface 0-25 mm will be important, but will generally be unknown.
The processes can be defined mathematically (Ahuja 1986, 1990), however measured data are needed to determine the relevant coefficients, e.g. to describe the incomplete mixing. Leonard et al. (1987) avoided assuming complete mixing by introducing an ‘extraction coefficient’, wherein the effective mass of soil involved in mixing was defined by model calibration.

For the component of chemical extracted into runoff in sediment, the concentration in runoff equals the concentration of pesticide in sediment (mg/kg) multiplied by the sediment concentration (kg/L) in runoff. As a first approximation, the concentration of pesticide in sediment would equal the concentration in the soil surface, after considering desorption. In reality, measured concentrations of strongly sorbed chemicals in sediment are generally found to be 1-10 times soil concentrations (Leonard et al. 1979, Willis et al. 1983) because of size-selective erosion processes (enrichment, Chapter 1). Thus concentrations of chemicals in sediment are related to the concentration in the soil surface, but will vary (from being of equal concentration) due to (a) desorption into the water phase, (b) differences in the concentration in the soil layer sampled and the actual depth of erosion, (c) sediment enrichment. The concentration in the sediment phase in runoff (µg/L) will depend on the mass of this sediment entrained per L of runoff (i.e. the sediment concentration).

The concentration of pesticide extracted in runoff is also affected by the concentration profile within the soil surface (Baker 1980), which would presumably change through time after application. This is a topic that has received little attention in the literature. Both water and sediment phase extraction may mostly be interacting with soil concentrations in the top few mm of soil on average (e.g. typical EDI’s 2-3mm or 10 t/ha soil loss equals ~1mm soil depth) but the actual depth may vary spatially, especially when rill erosion occurs.

Leaching through the runoff-mixing layer continues throughout a rainfall event. Thus chemicals that are weakly sorbed will have decreasing concentrations with time in the soil surface layer. Dilution of a soluble chemical in a volume of water with inflow and outflow, with complete mixing such that concentration in the outflow equals the concentration in the volume, dictates that the concentration in the volume will decline exponentially with time, i.e. \( C(t) = C_0 \exp\left(-\frac{\text{flow}}{\text{volume}} \times t\right) \) (Baker 1980, Steenhuis and Walter 1980). Concentration in the soil surface will also decline exponentially with time for a sorbed chemical, but the rate of decline is mitigated by the sorbed component, and this equation can be formulated to account for this using the sorption coefficient (see discussion). Truman et al. (1998a) confirmed the exponential decline in soil surface concentration under rain experimentally for several pesticides. Progressive loss of the chemical from the soil surface, via leaching and runoff, results in an exponential decline in runoff concentration through time (Ahuja and Lehman 1983), producing progressive depletion/dilution that is frequently described as a ‘first flush’ response in runoff. Chemicals that are more strongly sorbed to soil will be unaffected by this process but their concentration in runoff may change through time where their concentration profile with depth in the runoff-mixing layer is not uniform.
Where leaching is restricted for any reason (poor infiltration, surface sealing or a restriction in the subsoil), dilution of the surface concentration into the rainfall volume still occurs but is transferred into runoff rather than leachate and concentrations in runoff can be one to two orders of magnitude higher than where leaching proceeded unrestricted (Ahuja and Lehman 1983). Where leaching does occur but water flows laterally and exfiltrates (rejoins overland flow), i.e. ‘interflow’, the situation is more complex and less well understood. Snyder and Woolhiser (1985) observed significant exfiltration on sloping flumes, which increased the removal of dye in runoff. They suggest that on sloping land with topsoil overlying less permeable subsoil, dissolved chemicals in runoff may be contributed by interflow exfiltrating as well as by surface exchange processes. Indeed, Barnett et al. (1972) found concentrations in runoff were highest for all (presumably dissolved) nutrients when runoff was interflow (through the tilled layer) rather than overland flow, on slopes of 26-46%. However, Edwards et al. (1980) observed lower concentrations of glyphosate in runoff from an interflow dominated event than from overland flow dominated events on a 15% slope, which they suggest is due to the topsoil ‘filtering’ the glyphosate (i.e. adsorption). Hillslope lateral flow studies in South Australia also found soluble phosphorus concentrations in interflow were typically lower than in overland flow (N. Fleming, SARDI pers. comm.). Thus it appears chemicals may need to be very weakly adsorbed to soil to be efficiently transported in interflow. Restricted leaching in the saturated part of the landscape created by lateral flow may actually be more influential.

In summary, the main processes that can affect runoff extraction are leaching and dilution of solutes (increasingly for weakly sorbed pesticides) and erosion (increasingly for strongly sorbed pesticides), which should be affected by the pesticide sorption properties and the hydrology, and the concentration profile of the pesticide in the soil. Within a rainfall/runoff event these processes are transient, whereas the data considered here are averaged for the entire event, that is, conceptually the integral of the process. If the transient hydrologic or erosion behaviour differs significantly between plots, sites/soils or pesticides, it may be manifested as a difference in the apparent runoff extraction.

### 4.2.2 Runoff extraction ratios

Simple and convenient equations for relating pesticide concentration in runoff ($C_{RO} \mu g/L$), integrated over a runoff event to soil concentrations, are (Leonard et al. 1979, Baker 1980):

\[
C_{RO} = E (C'_{SOIL})^{P_1} \quad \text{for poorly sorbed chemicals, or} \\
C_{RO} = E (SC.C'_{SOIL})^{P_1} \quad \text{for sorbed chemicals, which is} \\
C'_{SED} = (E .1000) C'_{SOIL} = E'_{SED} . C'_{SOIL} \quad \text{when } P_1 = 1.0
\]

where

- $C'_{SOIL} =$ concentration in surface soil (mg/kg)
- $C'_{SED} =$ concentration in sediment (mg/kg)
- $SC =$ sediment concentration in runoff (kg/L)

$E$ and $P_1$ are fitted coefficients.
Leonard et al. (1979) conceptualised $E$ as an ‘extraction coefficient’ for poorly sorbed pesticides and $E'_{SED}$ as an ‘enrichment factor’ for sorbed pesticides (Chapter 1). The exponent $P_I$ represents non-linearity, and tends to be slightly less than 1.0 for sorbed pesticides (e.g. 0.83 Leonard et al. 1979), indicating a changing sediment composition with sediment concentration and is consistent with sediment enrichment through size-selective deposition. That is, enrichment is already built into such a model\textsuperscript{B}. $P_I$ is slightly greater than 1.0 for poorly sorbed pesticides (1.2 Leonard et al. 1979, 1.03 Baker 1980), reflecting changing extraction efficiency and distribution of the pesticide in the surface soil layer with time of contact of the pesticides with the soil; higher concentrations in soil tend to be related to more recent applications.

Following this approach, and assuming linearity ($P_I=1$, unless the data shows otherwise), runoff extraction is considered in terms of the following simple ratios:

\begin{align*}
E_{RO} &= \text{extraction ratio for total pesticide in runoff (water and sediment), } C_{RO} \text{ (µg/L)} \\
&= C_{RO}/ C'_{SOIL} \\
E_{WAT} &= \text{extraction ratio for water phase pesticide concentration in runoff } (C_{WAT} \text{ µg/L}) \\
&= C_{WAT}/ C'_{SOIL} \\
E_{SED} &= \text{extraction ratio for sediment phase concentration in runoff } (C_{SED} \text{ µg/L}) \\
&= C_{SED}/ C'_{SOIL}
\end{align*}

where, by definition, $E_{RO} = E_{WAT} + E_{SED}$.

$E'_{SED}$ is equal to 1.0 when the sediment in runoff has the same chemical concentration as the soil surface layer, implying no desorption, no leaching in the soil, a uniform distribution within the soil layer and no sediment-size selective enrichment or depletion.

\textsuperscript{B} An equation similar to the general empirical equation for enrichment ratio (ER) as a function of sediment yield (Y) (Menzel 1980, Smith et al. 1993), $ER = A.(Y^{b})$ can be derived from Eqn. 4-2, i.e. $ER = E.(SC.C'_{SOIL})^{P_I-1}$. 

109
(b) Concepts of potential runoff concentrations

A maximum potential runoff concentration can be defined where the runoff has a concentration equal to the mass of the pesticide in the soil layer divided by the volume of rainfall. Rainfall is used rather than runoff, as the chemical will dissolve in the total volume of water. Strictly speaking this applies only to a dissolved chemical and depends on the soil bulk density and rainfall amount. However, it does define an upper bound for runoff extraction. For example, for 50 mm of rain, the maximum potential runoff extraction ratio is 300 for 0-10 mm soil and 30 for 0-2 mm soil (bulk density = 1500 kg/m³), and is 500 for 0-25 mm soil using a bulk density of 1000 kg/m³ (more suitable to the rainfall simulator plot conditions).

For sediment bound chemicals, the maximum potential runoff concentration would equal the mass of the pesticide in the soil layer divided by the volume of runoff. However, this is conceptually less appealing as the runoff event would need to erode the entire soil layer. A more useful concept is the potential concentration in sediment or the no-enrichment runoff concentration, where the pesticide runoff concentration equals the sediment concentration in runoff multiplied by the pesticide concentration in the soil, as if the sediment mass was eroded with a concentration equal to the soil concentration with no enrichment or desorption into the water phase; if sediment enrichment occurs, observed pesticide runoff concentration will be greater than this value; if pesticide is desorbed from the soil/sediment, observed pesticide runoff concentration will be less than this value in accordance with the partitioning described by the equation presented below.

(c) Water and sediment runoff phases using simple-linear partitioning

Mulkey and Falco (1977) developed equations for estimating the fraction of pesticide in runoff in the water and sediment phases, which are re-derived in Chapter 5.

\[
F_{\text{wat}} = \frac{1}{1 + (SC \cdot K_P)} \\
F_{\text{sed}} = \frac{SC \cdot K_P}{1 + (SC \cdot K_P)}
\]

which are Eqn. 5-5 and Eqn. 5-6, respectively, in Chapter 5, where \( F_{\text{wat}} \) and \( F_{\text{sed}} \) are the proportions of pesticide in the runoff in water and sediment phase, respectively, and are theoretically defined for linear partitioning where the partition coefficient is \( K_P \) in a volume of runoff containing a sediment concentration of SC (kg/L).

The runoff extraction ratios in water and sediment phases are related to total runoff extraction ratio by \( E_{\text{wat}} = F_{\text{wat}} \cdot E_{\text{RO}} \), \( E_{\text{sed}} = F_{\text{sed}} \cdot E_{\text{RO}} \) and \( E'_{\text{sed}} = F_{\text{sed}} \cdot E_{\text{RO}} / (1000 \cdot SC) \), thus reflecting linear partitioning and sediment concentration. These equations are useful in interpreting measured concentrations and extraction ratios in water and sediment phases, in particular the extent to which variations in measured data (e.g. between pesticides and/or runoff plots) can be explained by partitioning and sediment concentration.
4.3 Methods

4.3.1 Experimental outline

Data for pesticide concentrations in soil (0-25mm) before rain and in runoff from rainfall simulator plots at three sites were used to investigate relationships between pesticide runoff and soil concentration. All sites included bare plots and various pesticide application and/or cultural treatments. The sites, the rainfall simulator, and pesticide application and analysis methods are described in Chapter 2. Pesticides with a wide range of properties were studied (Table 2.4) over a wide range of concentrations in soil (e.g. four orders of magnitude). A brief summary and methods specific to this chapter are provided here.

4.3.2 Rainfall simulator runoff and soil data

Data were used from rainfall simulator plots on cotton hill-furrow systems at three sites – Gatton, Emerald and Jondaryan (Chapter 2). The Emerald study is described in detail in Chapters 6 and 7. Plot conditions and hydrology are summarised in Table 4.1.

<table>
<thead>
<tr>
<th>Plot</th>
<th>Plot width</th>
<th>Furrow slope</th>
<th>Rainfall intensity</th>
<th>Rainfall amount</th>
<th>Runoff (mm)</th>
<th>Infiltration (mm)</th>
<th>Sediment concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>(m)</td>
<td>(%)</td>
<td>(mm/hr)</td>
<td>(mm)</td>
<td>(%) of rain</td>
<td>(range)</td>
<td>(range)</td>
</tr>
<tr>
<td>Gatton</td>
<td>1.6, 12</td>
<td>0.75</td>
<td>1.5</td>
<td>95</td>
<td>63</td>
<td>38.6 (61%)</td>
<td>25 (22-30)</td>
</tr>
<tr>
<td>Emerald</td>
<td>12</td>
<td>1.0</td>
<td>1.0</td>
<td>95</td>
<td>65</td>
<td>15.7 (24%)</td>
<td>49 (46-53)</td>
</tr>
<tr>
<td>Jondaryan</td>
<td>12</td>
<td>1.0</td>
<td>0.2</td>
<td>67</td>
<td>47</td>
<td>29.7 (64%)</td>
<td>17 (14-20)</td>
</tr>
</tbody>
</table>

The following data were used in this chapter:

(a) Pesticide concentrations in runoff.

A flow weighted mean total pesticide concentration (in sediment and water) was calculated for each runoff event and pesticide, and averaged for the two duplicate plots to be compatible with the data for pesticide concentrations in the soil. Similarly, mean concentrations of pesticides in water and sediment phases were calculated from flow-weighted composite samples taken throughout runoff hydrographs. Concentrations in water and sediment phases were used to calculate partition coefficients, presented in Chapter 5, but used here to support interpretation.
Soil pesticide concentrations were calculated as the mean of hill and furrow samples, for each pair of plots under the rainfall simulator (i.e. soil samples were bulked for the two plots). For the Gatton study, soil concentrations were determined for each pair of plots from dissipation curves (Chapter 3), which included data from the runoff plots and from separate sampling areas, based on the time after spraying for each plot. This method was considered preferable because most plots at Gatton were small (0.75m by 1.6m) and fewer soil samples were bulked for each soil pesticide analysis.

A range in soil concentrations between the plots studied is useful, as it will hopefully be reflected in the resulting runoff concentrations and will provide a more robust test of runoff extraction. A range in soil concentrations was obtained by including a range of times after spraying (Gatton and Jondaryan), two sequential applications (Gatton), banded and blanket sprayed plots (Jondaryan) – banded plots had average soil concentration lower by about the percent of the plot sprayed (Chapter 3). Where pesticides were sprayed over cover (endosulfan at Emerald), soil concentrations were lower due to interception of spray by the cover (Chapter 3). In contrast, pesticides applied as farm operations (e.g. herbicides applied 2-7 week before) and residues from previous years (e.g. DDE) had a narrower range of soil concentrations within each study and generally lower concentrations.

Concentrations of some rapidly dissipated pesticides declined to below detection limits in soil and sometimes in both soil and runoff samples (analysis of runoff samples was more sensitive than for soil samples). In either case, the data could not be used in the comparison of pesticides in soil and runoff. The highest soil concentrations observed on runoff plots were similar to maximum concentrations that might be expected under commercial practice in the cotton industry (Simpson et al. 1998, Kennedy et al. 1998) (Chapter 3). High concentrations of endosulfan sulfate, as sometimes seen in commercial fields (Kennedy et al. 1998) were never achieved, due to short times after spraying, dry soil conditions and lower numbers of applications.

4.3.3 Pesticide and cultural treatments

Gatton. The main treatment variable was time after spraying (2hr–15d) through a sequence of two applications six days apart. Endosulfan, prometryn and dimethoate were blanket sprayed on (a) four pairs of standard plots (EC formulation, bare, 1.6m long, 1.5% slope, 95mm/hr rain), and rain was applied 2 hr after the first spray and 2 hr, 26 hr and 9 d after the second spray, and (b) five pairs of plots of secondary treatments where one plot variable was altered. These were: rained on 2 hr after the first spray - plot length (12m), plot slope (0.9% and 4.3%), and stubble cover (100%); rained on 2 hr after two sprays - formulation (ULV). A second storm was also applied to the 12m plots, 20 min after the first. There was some variation in runoff (30-41mm), infiltration (22-28mm) and sediment concentration (24-57g/L). The stubble covered plot resulted in double the amount of infiltration.

Emerald. This study had plots with a range of crop residue cover (wheat stubble or cotton trash), with and without prior wheel traffic. Rain was applied 4-7 d after two endosulfan applications, 17 d after prometryn (banded) and 50 d after trifluralin application (Chapter 7). Data were averaged
for traffic treatments and pooled as 'bare' (bare and cotton trash mulched plots, cover of 0-10 %, five pairs of plots) and 'covered' treatments (30-50% cover, 3 pairs of plots). There were no significant differences in pesticide runoff concentrations between treatments within these groups, or due to time after spraying for each pesticide (Chapter 7). Thus there was a limited range in soil concentrations for each pesticide, in contrast to the other sites. Data for nutrients (various forms of N and P) in soil and runoff from these plots (Appendix B), particularly nitrate (NO$_3$-N), are presented as a tracer of dissolved chemical behaviour.

Jondaryan. The focus of this study was in creating a range in soil concentrations for a wide range of pesticides. Five rainfall simulations (pairs of plots) were run; three were blanket sprayed at 5, 25 and 34 days before rain and two band sprayed, 2.3 and 34 days before rain. Four insecticides and six herbicides were applied (Table 2.3). Different times after spraying were achieved by staggering spray dates prior to a 2-week period of rainfall simulator studies. The blanket-25 d plot was only sprayed with the insecticides and pyrithiobac sodium, and had low or non-detectable concentrations of other herbicides. The blanket-5d plot was band sprayed with pyrithiobac sodium 25 days before rain (rather than 5d). Trifluralin and DDE, residues from past applications (>1yr), were also studied.

4.3.4 Pesticides studied and their properties

Endosulfan (α- and β-isomers, and endosulfan sulfate) and prometryn were studied at all sites, while a range of other insecticides and herbicides were either applied as experimental treatments or were in the soil from previous farm operations. Pesticides studied are listed in Table 2.3 and 2.4 (Chapter 2). The 12 pesticides and their published properties (Wauchope et al. 1992) were:

- DDE with very low solubility in water (0.003mg/L) and very high K$_{OC}$ (380,000-880,000L/kg),
- Endosulfan, trifluralin, chlorpyrifos and pendimethalin with low solubility (0.3-0.4mg/L) and higher soil sorption (K$_{OC}$ 8,000-12,400), and profenofos (Sol 28mg/L, K$_{OC}$ 5,000),
- The herbicides diuron, prometryn, metolachlor and fluometuron (Sol 33-530mg/L); low sorption (K$_{OC}$ 100-480) – note K$_D$=1 for K$_{OC}=100$ and OC=1% typical of Australian cotton soil.
- Dimethoate (Sol ~40,000, K$_{OC}$ 20) and pyrithiobac sodium (Sol ~700,000, K$_{OC}$ 9-21), i.e. very soluble and weakly sorbed to soil.

That is, 14 compounds including the endosulfan isomers and the sulfate. Total endosulfan is used to describe the sum of α-, β- and endosulfan sulfate. Concentrations of pesticides in sediment are generally presented as μg/L (i.e. per litre of runoff) so they are directly comparable with concentrations in runoff, unless otherwise indicated.
4.4 Results and discussion

Results are presented firstly for the rainfall simulator studies as (A) relationships between total concentration in runoff (i.e. sediment plus water phase) and soil concentrations, that is, total runoff extraction, then (B) for runoff extraction in the water and sediment phases, and (C) to put these results into perspective, results from this study are compared with published data.

4.5 Part A. Total concentration in runoff related to concentration in soil

4.5.1 Study 1 - Gatton

Pesticide concentrations in runoff were closely related to soil concentrations (0-25 mm) at Gatton (Fig. 4.1a), with Cro (µg/L) = 26.1 C’soil (mg/kg) ($R^2 = 0.937$, $N=50$, $P<0.001$) including all bare plot data. The coefficient 26.1 is the extraction ratio for total concentration in runoff ($E_{RO}$). $E_{RO}$ was similar (n.s.d.) for the endosulfan compounds (Table 4.2, Cro=27.59 C’soil, $R^2 = 0.965$, $P<0.001$), including endosulfan sulfate with soil and runoff concentrations 1-2 orders of magnitude lower than the parent isomers (Fig. 4.1b). Prometryn had slightly lower runoff extraction for about half of the plots, resulting in a lower runoff extraction ratio ($E_{RO} = 21.3$) and was more variable than other pesticides.

Dimethoate had significantly lower runoff extraction than the other compounds (Table 4.2, Fig. 4.1b), with $E_{RO} = 11.4$. Results presented later indicate extraction of dimethoate was lower than other pesticides in both sediment and water phases. Thus it appears that the concentration of dimethoate in...
the runoff-mixing layer was lower than indicated by the 0-25mm soil concentrations measured before rain. This may be due to rapid dissipation of dimethoate (Chapter 3) depleting concentrations in the surface, or due to leaching into the soil during the rainfall event, consistent with the lower partition coefficient for dimethoate (Chapter 5). However, if leaching were the cause, it is not clear why prometryn did not behave similarly, given it had a similarly low $K_p$.

The secondary treatments, formulation (EC or ULV endosulfan), plot length (1.6 or 12m) and event number (first or second on 12m plots) did not result in large deviations in runoff extraction (Fig. 4.1). Concentration in runoff was only higher for ULV because soil concentration was greater. For bare plots, formulation, plot length, rainfall intensity (95-125mm/hr), runoff (30-41 mm), infiltration (22-30mm), slope (0.9-4.3%) and event number had no significant effect on $E_{RO}$ (using ANOVA). Barnett et al. (1967) also found no effect of plot length on runoff concentrations of 2,4-D. There was a slight trend for $E_{RO}$ to increase with sediment concentration (24-57 g/L) for the more sorbed endosulfan, which was not statistically significant but is physically expected for the sediment phase (discussed below). Effects of cover on runoff extraction are discussed in a later section.

Table 4.2. Mean concentrations in soil (C' soi l) and runoff (Cro), and runoff extraction ratio ($E_{RO}$) for bare plots at Gatton. Mean values followed by the same letters are not significantly different ($P<0.001$, ANOVA). $E_{RO}$ values calculated by regression, which are preferred, are also given.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Mean C' soil (mg/kg)</th>
<th>Mean Cro (ug/L)</th>
<th>Mean $E_{RO}$ Bare</th>
<th>Regression $E_{RO}$</th>
<th>$R^2$</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alpha</td>
<td>2.30</td>
<td>64.3</td>
<td>27.6 a</td>
<td>28.4</td>
<td>0.890</td>
<td>9</td>
</tr>
<tr>
<td>Beta</td>
<td>1.51</td>
<td>38.0</td>
<td>25.4ab</td>
<td>25.3</td>
<td>0.913</td>
<td>9</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.09</td>
<td>1.85</td>
<td>28.2 a</td>
<td>24.6</td>
<td>0.750</td>
<td>7</td>
</tr>
<tr>
<td>Total</td>
<td>3.82</td>
<td>104.0</td>
<td>26.9 a</td>
<td>27.7</td>
<td>0.919</td>
<td>9</td>
</tr>
<tr>
<td>Prometryn</td>
<td>2.62</td>
<td>57.3</td>
<td>22.6 b</td>
<td>21.7</td>
<td>0.640</td>
<td>8</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>0.44</td>
<td>5.2</td>
<td>12.6 c</td>
<td>11.3</td>
<td>0.846</td>
<td>8</td>
</tr>
<tr>
<td>All data</td>
<td></td>
<td></td>
<td></td>
<td>26.4</td>
<td>0.921</td>
<td>55</td>
</tr>
<tr>
<td>All bare</td>
<td></td>
<td></td>
<td></td>
<td>26.3</td>
<td>0.942</td>
<td>50</td>
</tr>
<tr>
<td>All bare endo</td>
<td></td>
<td></td>
<td></td>
<td>27.6</td>
<td>0.967</td>
<td>34</td>
</tr>
</tbody>
</table>

Within the data in Fig. 4.1, $E_{RO}$ decreased with days since the last spray (DSS2) for $\alpha$, $\beta$- and total endosulfan (from about 27 at 2 hr to 21 at 9 days) and for prometryn (from about 23 to 18), was constant for dimethoate and increased for endosulfan sulfate ($P=0.008$, $R^2=0.819$). The $\alpha$, $\beta$- and total endosulfan were similar (n.s.d.) with $E_{RO} = 28.1 - 0.791$.DSS2. Prometryn had a similar slope (n.s.d.) but a lower constant due to overall lower extraction. The lack of response to DSS2 for dimethoate may simply reflect measurement error in the low concentrations in both soil and runoff. The reduction in $E_{RO}$ with time after spraying is probably due to changes in the distribution of the compounds in the soil surface layer over time. Similarly, the increase in $E_{RO}$ with DSS2 for endosulfan sulfate ($E_{RO} = 26.55 + 0.787$.DSS2) may be related to increases over time in concentration.
of this breakdown product in the surface few mm of soil relative to the measured soil layer (0-25mm). Similar trends were found when $E_{RO}$ was related to days since first spray (DDS1) but was only significant for prometryn; much of the pesticide from the first spray dissipated by the time of the second spray (Chapter 3), which is therefore more influential. An effect of 'aging' on runoff extraction is evident but is complicated by having two ages of each pesticide in the soil – a clearer example is presented below for the Jondaryan data after only one spray.

In summary, soil and runoff concentrations for the Gatton plots, summarised in Fig. 4.2, indicate a high degree of consistency between pesticides, especially for endosulfan compounds and prometryn, which have contrasting properties. Dimethoate had lower runoff extraction than the other pesticides. Runoff extraction from bare soil was not sensitive to factors such as plot size, slope or sediment concentration, in the ranges studied, but was less efficient at longer times after spraying.

![Fig. 4.2](image)

**Fig. 4.2.** Mean concentration in runoff against mean concentration in soil for rainfall simulator plots at Gatton. Best fit equations for bare plots ($C_{ro} = 26.1 \times C_{soil}$, $R^2 = 0.937$, $N = 50$) and means ($N = 6$) are shown.

### 4.5.2 Study 2 - Emerald

Total concentrations in runoff from the bare Emerald plots were related to soil concentrations (0-25mm) before rain (Fig. 4.3). Runoff extraction ratios for bare plots were similar for all endosulfan compounds and for prometryn (n.s.d Table 4.3) even though prometryn has a much lower $K_P$ (Chapter 5) and was applied in a band on the hills. Average soil concentration on the plots adequately accounted for band spraying, consistent with results from Jondaryan presented below. The data for each pesticide covers a limited range, as time since spraying was reasonably consistent across plots for each pesticide (Table 4.3 and Chapter 7).
Fig. 4.3. Total runoff concentration of pesticides from bare Emerald plots against soil concentration (0-25mm), (a) linear plot, (b) log-log plot. Lines are for (1) all endosulfan and prometryn, (2) DDE, (3) trifluralin, which had significantly different runoff extraction ratios (Table 4.3).

Er0 values were significantly lower for DDE and trifluralin than for endosulfan and prometryn (Table 4.3). DDE and trifluralin have high partition coefficients and were dominantly transported in the sediment phase; DDE - Kp=10,000, 99% in sediment, trifluralin - Kp=720, 92% in sediment (Chapter 5). Their concentrations in runoff would be related to the sediment concentration in runoff. Thus if more sediment was transported, Er0 values for DDE and trifluralin would increase relative to other pesticides (their Er0 values would also increase somewhat due to partial transport in sediment). However, if sediment concentration in runoff was the sole factor limiting their Er0, runoff extraction of DDE would be as low, or lower, than that of trifluralin. Concentrations of DDE and trifluralin in sediment (mg/kg) were lower than in 0-25 mm soil, particularly for trifluralin (Section 4.6(c)). This suggests that concentrations were lower in the surface few mm of soil that interacts with runoff than in the 0-25 mm soil that was sampled, which would decrease the apparent Er0.

Table 4.3. Mean extraction ratios (Er0) for total concentration in runoff, for bare plots at Emerald, and differences between pesticides, using (a) ANOVA and (b) linear regression. Values followed by the same letter are n.s.d. between pesticides (P<0.002).

<table>
<thead>
<tr>
<th></th>
<th>Endosulfan</th>
<th>Prometryn</th>
<th>Trifluralin</th>
<th>DDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days since spray:</td>
<td>Alpha</td>
<td>Beta</td>
<td>Sulfate</td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td>4-7</td>
<td>4-7</td>
<td>4-7 &amp; &gt;9mths</td>
<td>4-7</td>
</tr>
<tr>
<td>(a) Means Er0 (Cro/C'soil) (ANOVA)</td>
<td>30.2 a</td>
<td>31.7 a</td>
<td>35.3 a</td>
<td>30.9 a</td>
</tr>
<tr>
<td>(b) Regression (Cro= Er0 C'soil)</td>
<td>All endosulfan &amp; prometryn (n.s.d.)</td>
<td>Er0</td>
<td>27.9 a</td>
<td>6.72 c</td>
</tr>
</tbody>
</table>
Time since spraying varied between pesticides (Table 4.3) and $E_{RO}$ decreased with time after spraying in the other studies. Trifluralin is reasonably volatile and was exposed for 50 days since spraying. It was also incorporated during application, which combined with vapour loss from the surface, would lead to a decrease in concentration towards the soil surface. In contrast, the more recently applied endosulfan had concentrations in sediment 1-2 times those of the 0-25mm soil and probably had an increasing concentration towards the soil surface.

Trifluralin had more variable runoff extraction that the other pesticides (Fig. 4.3b) – regression analysis indicated no relationship between trifluralin runoff and soil concentrations (Table 4.3). This may be related to incorporation of the trifluralin being a somewhat haphazard process and creating spatial variability in concentration gradients in the soil. Leonard et al. (1979) noted that trifluralin had a lower extraction coefficient than the four water-transported herbicides in their study, but do not give a value, and that its runoff behaviour was less consistent than for other pesticides, as observed here.

The results for the Emerald study are summarised in Fig. 4.4 using mean runoff concentrations plotted against mean soil concentrations for bare plots. The best-fit regression for these mean concentrations is similar to that fitted for the individual plot data for endosulfan and prometryn (Table 4.3): $C_{ro} = 27.9 C_{soil}$ ($R^2=0.94$).

The average runoff extraction for the endosulfan compounds and prometryn is very similar, while DDE and particularly trifluralin had lower runoff extraction.

![Fig. 4.4](image-url)  
**Fig. 4.4.** Mean concentrations in runoff and soil for pesticides from bare plots at Emerald, with the regression line for all individual plots that had similar mean extraction ratios. DDE2 and DDE5 refer to Block 2 and 5. ESS – endosulfan sulfate.
Contrast with nutrients (N and P). Broadly speaking, concentrations of N and P in runoff had a similar relationship to soil concentrations as the pesticides, even though N and P concentrations were much larger (Fig. 4.5). The relationships are not entirely comparable as the methods used for analysis of soil and runoff samples do not always measure exactly the same components of N and P. For instance, total P in runoff may underestimate P compared with total P in soil (P_{xrf}) (Heather Hunter pers. comm.). Oxidised N is directly comparable as both soil and runoff analysis is dominantly NO$_3$-N. While the NO$_3$-N runoff concentrations vary, their relationship to soil concentrations is not that different from the pesticides. NO$_3$-N is easily leached and its presence in runoff indicates that leaching of chemicals from the runoff-mixing layer was not particularly significant or that leached chemicals return to the surface due to ponding and exfiltration. The sum of sediment N and dissolved total Kjeldahl-N (TKN) in runoff relate well to soil TKN, with similar runoff extraction to pesticides.

Fig. 4.5. Comparison of runoff extraction of N and P with pesticides, Emerald bare plots. NO$_3$-N in runoff plotted against soil NO$_3$-N, sediment-N (Sed-N) plus total dissolved Kjeldahl-N (TKNw) in runoff plotted against soil total Kjeldahl-N (TKN), NH$_4$-N in runoff (NH$_4$-N_{water}) plotted against soil NH$_4$-N, total P in runoff (P_{tot}) plotted against soil total P(xrf).

4.5.3 Study 3 - Jondaryan

Pesticide concentrations in runoff at Jondaryan were largely determined by concentration in soil (0-25mm) before rain (Fig. 4.6), Cro=30.4 C'soil ($R^2$=0.910, P<0.001) for all data. Pesticides applied at higher rates and/or more recently had higher soil concentrations and corresponding higher runoff concentrations. Thus soil and runoff concentrations of herbicides such as metolachlor, fluometuron, diuron and prometryn were 1-2 orders of magnitude greater than for pyrithiobac sodium (applied at $\sim 1/10^{th}$ lower rate) and trifluralin (applied in previous seasons), but runoff extraction was similar (Fig. 4.6a). Similarly, concentrations of endosulfan in soil and runoff were considerably higher than those of organophosphate (OP) insecticides (dimethoate, chlorpyrifos and profenofos), which dissipate much more rapidly (Chapter 3), or for DDE, present at low concentrations, but runoff extraction was similar.
Rapidly dissipated pesticides also have a wider range of concentrations. Effects of the three main experimental variables, pesticide type, days since spraying and band spraying, are discussed below.

Runoff extraction ratios ($E_{RO}$) were not significantly related to plot variables (furrow slope, rainfall intensity, runoff amount or sediment concentration). $E_{RO}$ decreased with increasing infiltration amount ($R^2=0.294$), by 5.9 on average across the range of infiltration values (15-20mm). This was due to a similar decrease in the extraction ratio for pesticides in the water phase with increasing infiltration ($R^2=0.591$), with no effect on extraction ratio for sediment phase. There was no relationship between $E_{RO}$ and sediment-water partition coefficients ($K_P$) in runoff samples (Chapter 5).

Contrast of herbicides and insecticides. On average, herbicides had higher runoff extraction ($Cro=31.9$ C'soil) than insecticides ($Cro=21.7$ C'soil) ($R^2=0.927$, $P<0.001$ for difference in slope). Thus for a soil concentration of 1 mg/kg, concentration in runoff would be $\sim 32 \mu g/L$ and $\sim 22 \mu g/L$ for the herbicides and insecticides, respectively. However, the herbicides included significantly different runoff extraction groups$^C$, (a) trifluralin with the highest $E_{RO}$ (37.1), followed by (b) diuron (30.6), prometryn (28.6) and metolachlor (27.0), and (c) the other herbicides (fluometuron, pyrithiobac sodium and pendimethalin) grouped around $E_{RO} = 20-22$ (similar to the insecticides). These $E_{RO}$ values do not relate to $K_P$ e.g. trifluralin (highest $E_{RO}$) and pendimethalin (lowest $E_{RO}$ group) had the highest $K_P$ values, while diuron (second highest $E_{RO}$) and pyrithiobac sodium (lowest $E_{RO}$ group) had the

---

$^C$ Determined from regression analysis of $E_{RO}$ against DSS presented in the next section. Even though $E_{RO}$ values range from 37.1 (trifluralin) to 16 ($\alpha$-endosulfan), ANOVA was not particularly useful in revealing differences between individual pesticides, because $E_{RO}$ decreased with time since spraying (discussed below) and increased the variance, leading to an l.s.d. of $\sim 10$. For example, when trifluralin was excluded from the ANOVA, differences in $E_{RO}$ between pesticides are not significant.
lowest \( K_P \) values. Among insecticides \( E_R^O \) was higher for the OP's (24-26), compared with endosulfan sulfate (23.1), total endosulfan (19), \( \beta \)-endosulfan (18), DDE (17) and \( \alpha \)-endosulfan (16). Again the \( E_R^O \) values did not relate to \( K_P \), e.g. the OP's had \( K_P \) values 13-130 but had similar \( E_R^O \).

**Time since spraying.** Runoff extraction was less efficient with greater time since spraying (Table 4.4), that is, \( E_R^O \) declined with days since spraying (DSS) between 2-34 days. Trifluralin and DDE were excluded as they were applied in previous years and DSS is unknown. When pesticides were sorted into groups (pesticides n.s.d. within groups; regression by group \( R^2=0.594, P<0.001 \)):

\[
E_R^O = 23.07a - 0.2103a \text{DSS} \quad (R^2 = 0.338, P=0.005) \quad \text{endosulfan compounds}
\]

\[
E_R^O = 25.73a - 0.2188a \text{DSS} \quad (R^2 = 0.511, P=0.002) \quad \text{pendimethalin, fluometuron, Py_Na}
\]

\[
E_R^O = 37.05b - 0.590b \text{DSS} \quad (R^2 = 0.584, P<0.001) \quad \text{chlorpyrifos, dimethoate, profenofos}
\]

\[
E_R^O = 35.66b - 0.355a \text{DSS} \quad (R^2 = 0.432, P=0.006) \quad \text{diuron, metolachlor, prometryn}
\]

Subscripts denote that the last two groups had significantly higher constants than the first two groups (P<0.001). The third group (all OP's) had a significantly greater slope (\( P=0.004 \)), consistent with their much more rapid dissipation (Chapter 3). The decrease in \( E_R^O \) with DSS was entirely due to a reduction in runoff extraction in the water phase (\( E_{\text{WAT}} \)) with time (Table 4.4). Runoff extraction in the sediment phase (\( E_{\text{SED}} \)) had no trend with DSS.

**Table 4.4.** Mean extraction ratios for pesticides at Jondaryan, for application treatments (blanket and banded) and days since spraying (excluding DDE and trifluralin). Means followed by the same letter are not significantly different within rows (ANOVA).

<table>
<thead>
<tr>
<th>Runoff extraction ratio</th>
<th>Blanket 5 days</th>
<th>Blanket 25 days</th>
<th>Blanket 34 days</th>
<th>Banded 2 days</th>
<th>Banded 34 days</th>
<th>Fpr (lsd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total (µg/L) ( E_R^O )</td>
<td>28.0 a</td>
<td>21.0 b</td>
<td>17.1 c</td>
<td>29.9 a</td>
<td>20.8 c</td>
<td>&lt;0.001 (5.6)</td>
</tr>
<tr>
<td>Water (µg/L) ( E_{\text{WAT}} )</td>
<td>10.1 ab</td>
<td>10.8 ab</td>
<td>7.0 a</td>
<td>14.9 b</td>
<td>7.8 a</td>
<td>0.05 (?)</td>
</tr>
<tr>
<td>Sediment (µg/L) ( E_{\text{SED}} )</td>
<td>17.9</td>
<td>13.7</td>
<td>11.7</td>
<td>12.6</td>
<td>16.7</td>
<td>n.s.d.</td>
</tr>
<tr>
<td>Sediment (mg/kg) ( E'_{\text{SED}} )</td>
<td>0.77a</td>
<td>0.74a</td>
<td>0.53ab</td>
<td>0.45b</td>
<td>0.77a</td>
<td>0.039 (0.24)</td>
</tr>
</tbody>
</table>

**Effects of band spraying.** Banded and blanket sprayed plots had similar runoff extraction (n.s.d. Table 4.4) once differences in time since spraying are considered. Band sprayed plots had lower average soil concentrations than blanket sprayed plots and corresponding lower runoff concentrations. The soil concentrations used for band sprayed plots were the means of hill (sprayed) and furrow (slight drift input) samples as approximately 50% of the area was sprayed, i.e. the average concentration over the whole area. Use of this average concentration adequately accounted for band spraying.

The relationship between runoff and soil concentrations from the Jondaryan plots is summarised in Fig. 4.7 using mean concentrations for each pesticide. Runoff concentrations are strongly related to soil concentrations with only minor differences between pesticides with a wide range in partition coefficients.
4.5.4 Effects of cover on runoff extraction

Two interactions of pesticides and crop residue cover were investigated: (a) where pesticides were sprayed over the cover, and may contribute to runoff by washoff from the cover and extraction from the soil, and (b) where pesticides were in the soil under the cover, so washoff is not involved.

Where endosulfan was applied over cover and rain was applied 2 hr later (at Gatton), runoff extraction ratios (based on soil concentrations under the cover) were similar to those for bare soil for total, α- and sulfate endosulfan, and was slightly higher for β-endosulfan (Fig. 4.1). A large proportion of the higher extraction for β-endosulfan was associated with sediment and was probably not caused by washoff. This suggests that washoff from cover was not a major source of these pesticides in runoff or that washoff occurred before runoff started and infiltrated without contributing to runoff. The majority of pesticide washoff from crop residues is known to occur in the first 5-15mm of rainfall (Martin et al. 1978, Baker and Shiers 1989), i.e. before runoff started. In contrast to endosulfan, prometryn and dimethoate had higher runoff extraction from covered plots than for bare soil, indicating that washoff from cover may have contributed. Prometryn and dimethoate are more soluble and less strongly sorbed to soil than endosulfan and the same may be true for sorption to the wheat stubble used here. Even so, their higher runoff extraction is not consistent with the expected early washoff, which should infiltrate before runoff starts. Indeed, the greater infiltration with cover (50mm c.f. 22-30mm for bare plots) did not lead to lower runoff extraction as expected if leaching from the runoff mixing layer was significant. Also cover did not reduce runoff extraction in the sediment phase, as occurred at Emerald (see below), because sediment concentrations were similar for bare and covered plots (though total runoff, soil and pesticide losses were less with cover). Even
though runoff extraction was similar or increased with cover, runoff concentrations were considerably lower, with the exception of prometryn, due to interception of spray on the cover.

At Emerald, runoff extraction ratios were lower for covered plots but were only significantly different for endosulfan sulfate and DDE (Table 4.5). For endosulfan sprayed over the cover 4-7 days before rain, a major effect of cover was to reduce soil concentrations by intercepting the spray and dissipating considerable endosulfan before rain was applied (Chapter 3), with runoff concentrations reduced accordingly (Chapter 7). This tended to outweigh other effects of cover, but runoff extraction (based on concentration in soil under the cover) was still about 30% lower than from bare soil, due to reduced transport in the sediment phase (next section).

Table 4.5. Mean extraction ratios for total concentration in runoff compared for bare and covered plots at Emerald, and between pesticides, using ANOVA. Values for bare plots followed by the same letter are n.s.d. between pesticides (P<0.002). Values for bare and covered plots are n.s.d. except for endosulfan sulfate and DDE (indicated by the F(Pr) for cover). Combinations of pesticide and cover that are significantly different from the all others are underlined.

<table>
<thead>
<tr>
<th>Days since spraying</th>
<th>Endosulfan</th>
<th>Prometryn</th>
<th>Trifluralin</th>
<th>DDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean extraction ratios</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare</td>
<td>30.2 a</td>
<td>31.7 a</td>
<td>35.3 a</td>
<td>30.9 a</td>
</tr>
<tr>
<td>Covered</td>
<td>22.1</td>
<td>23.3</td>
<td>12.2</td>
<td>21.5</td>
</tr>
<tr>
<td>F(Pr) for cover</td>
<td>n.s.d.</td>
<td>n.s.d.</td>
<td>0.013</td>
<td>n.s.d.</td>
</tr>
<tr>
<td>Covered/bare</td>
<td>0.73</td>
<td>0.74</td>
<td>0.35</td>
<td>0.70</td>
</tr>
</tbody>
</table>

For the other pesticides at Emerald, which were in the soil under the cover (i.e. interception and washoff were not involved) response to cover depended on the sorption properties of the pesticide – $E_{RO}$ was reduced most for the most sorbed pesticide (DDE) and least for the least sorbed (prometryn) (Table 4.5). Prometryn concentrations were similar between cover treatments in both soil and in runoff (Chapter 7) and $E_{RO}$ was only slightly lower for covered plots (n.s.d.). Because prometryn was transported mainly in the water phase, the effect of cover on sediment loss, and thus on $E_{RO}$, had little impact. $E_{RO}$ values were lower for covered plots for endosulfan sulfate, trifluralin and DDE. For these more strongly sorbed compounds, a large proportion was transported by the sediment phase in runoff. Cover reduced sediment movement, consequently reducing extraction in the sediment phase (see next section) and total runoff extraction.

Cover explained 61% of the variance in $E_{RO}$ for Emerald plots (P<0.001), with similar slopes (n.s.d.) and different intercepts (trifluralin<DDE<others). $E_{RO}$ values were also positively correlated with sediment concentration ($R^2=0.68$) and negatively correlated with infiltration amount ($R^2=0.57$), but were not significantly related to other variables (slope, rainfall intensity, days since spraying) which had limited ranges. Sediment concentration and infiltration amount were closely related to cover (Chapter 6). The effect of infiltration amount on $E_{RO}$ was weakest for prometryn, the least
sorbed pesticide, and stronger for other pesticides (e.g. DDE). Thus the response of $E_{RO}$ to infiltration is probably spurious, reflecting the effect of cover on sediment concentration and thus on $E_{RO}$.

Of the major factors that are affected by cover, that is, infiltration and sediment transport (Chapter 6), and might therefore affect runoff extraction of pesticides, the influence on sediment appears to dominate. Logically, where cover reduces sediment concentration in runoff, the runoff extraction in the sediment phase is reduced. Thus the response of total runoff extraction to cover will vary depending on the sorption properties of the pesticide. While it is also logical that greater infiltration (with cover) should decrease runoff extraction in the water phase, this did not occur here. Rather, water phase extraction was not affected by cover, except where more soluble pesticides were washed off cover soon after spraying. Runoff concentrations of NO$_3$-N, a very soluble chemical, from the Emerald plots increased with increasing cover, i.e. increasing infiltration, particularly from wheel track plots. This appears to relate to ponding of infiltrated water and dissolved chemicals above compacted layers a few cm under the surface in the furrows, as discussed elsewhere.

4.6 Part B. Concentrations in water and sediment phases and in soil

In reality, total runoff extraction is the sum of extraction in the water and sediment phases, which are affected by the sediment concentration, sediment enrichment and partitioning. Different processes drive extraction from soil into runoff in these phases. Water phase extraction is essentially a solute process, which should relate to desorption and simultaneous leaching and raindrop accelerated diffusion in the runoff-mixing layer (Ahuja 1986). Sediment phase extraction is essentially a physical soil erosion process where the concentration of sediment in runoff will directly affect apparent extraction, but the concentration in the sediment is subject to desorption and, potentially, changes in composition (sorption capacity) of the sediment (enrichment). Understanding extraction in the two phases is helpful in understanding runoff extraction and why it was generally similar for pesticides of markedly different partition properties. Partition coefficients presented in Chapter 5 are used here to interpret the results.

(a) Concentration in the water phase

Concentrations in the water phase were linearly related to concentration in the soil for each pesticide, or group of pesticides with similar partitioning properties (for example, at Emerald Fig. 4.8). The Emerald data (where the range in pesticide properties was greatest) illustrates typical water phase behaviour (Fig. 4.8). Water phase concentrations of endosulfan compounds were strongly related to soil concentrations, over a two order of magnitude range. Similarly, water phase concentrations of prometryn and Py$_\text{Na}$ were strongly related to soil concentrations, for the three sites. Other pesticides had higher or lower concentrations in the water phase, depending on their partitioning properties. Thus the water phase extraction ratio, $E_{WAT}$, varied for different pesticides/groups, from 21 to 0.1 at Emerald (Fig. 4.8), 26 to 8 at Gatton and 25 to 2 at Jondaryan.
Fig. 4.8. Concentration in water phase and soil concentration (0-25mm) at Emerald (bare and covered (circle)), and for prometryn and pyrithiobac sodium (Py_Na) to illustrate behaviour of less sorbed pesticides. Lines are $C_{\text{wat}} = F_{\text{wat}} \cdot E_{\text{ro}} \cdot C_{\text{soil}}$, with $E_{\text{ro}}$ values from Table 4.3.

Fig. 4.9. Runoff extraction ratio in water phase (concentration in runoff $\mu$g/L /concentration in soil mg/kg) related to partition coefficient ($K_p$) for rainfall simulator plots at Emerald, including bare and covered plots, and other selected data. Lines are theoretical fraction in the water phase ($E_{\text{wat}} = F_{\text{wat}} \cdot E_{\text{ro}}$) for mean sediment concentration (18.4 g/L Emerald, 40g/L Gatton), for $E_{\text{ro}} = 27.9$ (prometryn & endosulfan), 15.1 (DDE) and 6.7 (trifluralin), 26.1 (Gatton).
These differences in $E_{\text{WAT}}$ values were related to $K_P$ values and total runoff extraction (Fig. 4.9), i.e. $E_R$ values derived earlier (e.g. Table 4.3 for Emerald). Thus, $E_{\text{WAT}}$ values are largely explained by normal partitioning, and follow the theoretical relation for fraction in the water phase ($F_{\text{WAT}}$, Eqn. 5-5 using mean sediment concentration) to partition the total runoff extraction, defined by $E_{\text{WAT}} = F_{\text{WAT}}E_R$. Where total runoff extraction was similar (e.g. endosulfan and prometryn), $E_{\text{WAT}}$ values fall on a common relationship with $K_P$. Data from other sites fall on or around this relationship, so long as sediment concentration and $E_R$ are similar (e.g. prometryn and pyrithiobac sodium in Fig. 4.9).

Where total runoff extraction was different, $E_{\text{WAT}}$ falls on a different relationship with $K_P$, but is still defined by $E_{\text{WAT}} = E_R$ $F_{\text{WAT}}$, illustrated in Fig. 4.9 for DDE, which had an $E_R =15.1$, and for trifluralin, $E_R =6.7$ (Fig. 4.3a, Table 4.3). The variability in $E_{\text{WAT}}$ for trifluralin is largely caused by variability in $E_R$. Results similar to Fig. 4.9 were found for all three sites.

Variation in $E_{\text{WAT}}$ also occurs due to variation in sediment concentration between plots or sites. Thus the $E_{\text{WAT}}$ values for endosulfan and prometryn at Gatton were slightly lower than at Emerald, because sediment concentrations were about double (Fig. 4.9). However, where a range of cover was studied at Emerald, $E_{\text{WAT}}$ was similar for all cover levels, even though infiltration increased and sediment concentration decreased with cover. This is because (a) runoff concentration of endosulfan sprayed over the cover was largely accounted for by soil concentration, due to interception, and thus effects of cover on $E_R$ were subdued (discussed above), and (b) increased cover lead to (suspected) interflow rather than greater leaching (Chapter 6, 7). Thus runoff concentrations of the least sorbed pesticide (prometryn) were not affected and of NO$_3$-N increased with increasing cover.

Where time since spraying varied (Gatton and Jondaryan), concentration in the water phase was typically lower for a given soil concentration at longer times after spraying and therefore $E_{\text{WAT}}$ decreases with time after spraying (Table 4.4). For Jondaryan plots, $E_{\text{WAT}}$ decreased significantly with days since spraying ($R^2=0.647, P<0.001$), with $E_{\text{WAT}} = \text{constant}–0.1855$.DSS (slopes n.s.d.). However, this is also accounted for by normal partitioning as $K_P$ increases with time after spraying (Chapter 5), i.e. $E_{\text{WAT}}$ and $K_P$ values fall on the line defined by the aforementioned equations. If a constant $K_P$ value were used for each pesticide, some variation in water phase concentrations would not be correctly predicted, e.g. by a factor of two. The higher $E_{\text{WAT}}$ values and lower $K_P$ values soon after spraying may indicate washoff of a component of the pesticides that has not sorbed far into the soil, or into soil aggregates, i.e. the ‘fast’ desorption phase discussed in Chapter 5.

$E_{\text{WAT}}$ was not significantly related to furrow slope, plot length, rainfall intensity, runoff amount, or sediment concentration (n.s.d. in ANOVA) for all sites/plots (range in these values was not large). $E_{\text{WAT}}$ was not significantly related to infiltration at Gatton or at Emerald. At Jondaryan, $E_{\text{WAT}}$ decreased significantly with total infiltration (slope of $-1.23$ /mm of infiltration). This site had the lowest infiltration, and relative to this low infiltration, the range in infiltration was largest. This indicates that different water phase extraction may be expected if a wider range in hydrologic conditions were encountered.
In summary, differences in concentrations in the water phase in runoff were related to concentration in the soil and partitioning. When soil concentration is accounted for using the ratio of water phase runoff to soil concentration ($E_{\text{WAT}}$), $E_{\text{WAT}}$ values are related to (a) total runoff extraction ($E_{\text{RO}}$) (which are presumed to vary due to concentration gradients in the soil), and (b) partition coefficients ($K_P$), both between pesticides and through days since spraying. Thus observed water phase extraction generally followed normal partitioning and the theoretical relation for fraction in the water phase ($F_{\text{WAT}}$, Eqn. 5-5) based on $K_P$ and SC.

(b) Concentration in the sediment phase

Concentrations in the sediment phase in runoff ($C_{\text{sed}}$ in pg/L) were related to soil concentrations, within pesticides or groups with similar partition coefficient and total runoff extraction. When only pesticides with higher partition coefficients ($K_P<100$) are considered, the relationship is reasonably consistent across the sites (Fig. 4.10). For example, $C_{\text{sed}}$ for endosulfan compounds were closely related to soil concentrations across three orders of magnitude at Gatton ($C_{\text{sed}} = 19.7 C'_{\text{soil}}$, $R^2 = 0.89$, $N=30$), for all treatments (formulation, cover etc.), Emerald ($C_{\text{sed}} = 21.6 C'_{\text{soil}}$, $R^2 = 0.83$, $N=20$, Fig. 4.11a) and Jondaryan ($C_{\text{sed}} = 14.9 C'_{\text{soil}}$, $R^2 = 0.97$, $N=20$). The coefficient is the sediment phase runoff extraction ratio ($E_{\text{SED}}$), which varies slightly between sites due to differences in $E_{\text{RO}}$ and $K_P$.

![Figure 4.10](image-url)
When all pesticides are considered, $E_{SED}$ values varied from about 30 to 2 at each site. Again using the Emerald data as an example because of the wide range in sorption properties, $E_{SED}$ was lower for DDE, prometryn and trifluralin than for endosulfan (Fig. 4.11a). Comparison with partition coefficients (Fig. 4.11b) indicates the lower $E_{SED}$ for prometryn is explained by normal partitioning. Prometryn and endosulfan had similar total runoff extraction ($E_{RO} = 28$, Fig. 4.3) and plot on the same theoretical partitioning line in Fig. 4.11b. DDE and trifluralin also had lower $E_{SED}$ values than endosulfan (Fig. 4.11a), but this is due to lower total runoff extraction alone ($E_{RO}$ values of 15.1 and 6.7, respectively, Fig. 4.3). Similarly, at Gatton and Jondaryan, differences in sediment phase runoff extraction were accounted for by total runoff extraction ($E_{RO}$) and normal partitioning.

For trifluralin at Emerald (Fig. 4.11b), $E_{SED}$ was highly variable, as were total runoff extraction and $E_{WAT}$, and this variation is not explained by partitioning or sediment concentration, but simply reflects the variation in total runoff extraction between plots, discussed above.

![Fig. 4.11.](image)

Fig. 4.11. (a) Concentration in the sediment phase in runoff and in soil (0-25mm) before rain, for bare rainfall simulator plots at Emerald. (b) Runoff extraction ratios from (a) against partition coefficients. Lines are theoretical fraction in sediment phase ($F_{SED}$) for sediment concentration of 18.4g/L, multiplied by total extraction ratios of 27.9 (endosulfan, prometryn), 15 (DDE) and 6.7 (trifluralin).

Where days since spraying varied (Gatton and Jondaryan), $K_P$ and $E_{SED}$ increased with time after spraying, particularly for pesticides with lower $K_P$ values (e.g. <50 L/kg). However, the relationship between $K_P$ and $E_{SED}$ followed normal partitioning. Thus normal partitioning accounted for much of the variation in $E_{SED}$ between pesticides and where $K_P$ increased with time after spraying.

While the partition coefficient and total extraction account for gross differences, e.g. between pesticides, sediment phase extraction varies between plots and sites (Fig. 4.11b) due to differences in sediment concentration and concentration in sediment (mg/kg, Section 4.6(c)). $E_{SED}$ should increase in direct linear proportion with sediment concentration if pesticide concentration in sediment (mg/kg) is constant. Indeed, $E_{SED}$ increased with sediment concentration (Fig. 4.12, Fig. 4.13), especially for the
more highly sorbed compounds and less so for less sorbed pesticides, due to desorption. However, pesticide concentrations in sediment (mg/kg) were not constant and typically decreased with increasing sediment concentration and were influenced by the sizes of sediment transported (Section 4.6(c)). Also the relationship of partitioning to sediment concentration is non-linear (for constant $K_p$); the concentration in the sediment phase increasing less than proportionally as sediment concentration increases. Thus, $E_{SED}$ does not increase in direct proportion to sediment concentration – a doubling of sediment concentration does not lead to a doubling of pesticide concentration in the sediment phase.

Fig. 4.12. Effects of sediment concentration on extraction ratios in sediment phase ($E_{SED}$), at Gatton. Lines: solid - total endosulfan, dashed - dimethoate. Points enclosed: square - ULV others EC, circle - covered others bare, dash - 12m long others 1.6m.

Fig. 4.13. Runoff extraction ratios for sediment phase ($E_{SED}$) related to sediment concentration for Emerald plots. Lower sediment concentrations (5-10g/L) are covered plots.
For Jondaryan plots, $E_{SED}$ increased significantly with sediment concentration (SC) over the range 9-15 g/L: $E_{SED} = \text{constant} + 1.059 \cdot \text{SC} \ (P<0.001, \ R^2=0.711, \ \text{slope} \ P<0.001)$ when all pesticides were considered in ANOVA. The average increase in $E_{SED}$ with SC is close to a direct linear proportion, because for all but four pesticides, sediment enrichment was not affected by sediment concentration. For the other four pesticides, sediment enrichment and concentration in sediment (mg/kg) decreased with increasing sediment concentration (similar to Gatton and Emerald) and did so sufficiently to totally negate the effect of sediment concentration on $E_{SED}$. These pesticides (trifluralin, DDE, endosulfan sulfate and pendimethalin) were the most highly sorbed and aged compounds.

(c) Enrichment ratios in sediment

Concentrations in sediment ($C_{sed}$ mg/kg) were related to soil concentrations, within pesticides or groups with similar partition coefficients. For example, concentrations of endosulfan compounds in sediment and soil were related closely at each site ($R^2=0.85-92$ for linear regressions), for example, at Jondaryan $C_{sed}=0.6 \cdot C_{soil}$ ($R^2=0.92, \ N=20$), where the coefficient (0.6) is the enrichment ratio ($E_{sed}$) (Fig. 4.14a). Concentrations in sediment and soil were closely related for all more sorbed compounds ($K_p>100$), with an average $E_{sed}$ of 0.7 ($R^2=0.86, \ N=30$) (Fig. 4.14a). Pesticides with lower partition coefficients ($K_p<50$, dimethoate, fluometuron, metolachlor, prometryn and pyrithiobac sodium) had lower enrichment ratios (e.g. as low as 0.1) and this is largely accounted for by normal partitioning (Fig. 4.14b). Time after spraying had a large effect on $E_{sed}$ (and $K_p$) for the less sorbed compounds, clearly illustrated by fluometuron, also largely accounted for normal partitioning (Fig. 4.14b). However, enrichment ratios varied by as much as ±50% around theoretical partitioning.

![Fig. 4.14.](image-url)

(a) Concentration in sediment and in soil (0-25mm) before rain, for pesticides with $K_p>100$, on bare rainfall simulator plots at Jondaryan.

(b) Enrichment ratios plotted against partition coefficients. Lines are theoretical fraction in sediment phase ($F_{SED}$ for SC=11.6 g/L, multiplied by enrichment ratios of 1 and 1±50%.)
Some of the variation in $E'_{sed}$ values is related to sediment concentration, with lower $E'_{sed}$ values for plots with greater sediment concentration for the more sorbed pesticides. This is consistent with desorption from the sediment during normal partitioning, for example for endosulfan at Gatton where sediment concentration varied 20-60 g/L (Fig. 4.15a), but could easily be misinterpreted as the physical enrichment often observed for sorbed chemicals in sediment (Leonard et al. 1979, Rose and Dalal 1988). In contrast, a decrease in $E'_{sed}$ with sediment concentrations for DDE and other more strongly sorbed and aged pesticides at Jondaryan (Fig. 4.15a) indicates that some physical enrichment may have occurred at that site. For all other pesticides, including endosulfan, desorption was the dominant process and the remaining variation in $E'_{sed}$ is apparently related to factors other than sediment concentration (which only varied slightly between plots), though these are not consistent (Table 4.4). For example, banded application may affect $E'_{sed}$ if a portion of the sediment is sourced from unsprayed soil of low concentrations.

![Diagram](image)

**Fig. 4.15.** Effect of sediment concentration in runoff on pesticide enrichment in sediment ($E'_{sed} = C_{sed}/C_{soil}$), at (a) Gatton and (b) Jondaryan. The calculated $E'_{sed}$ lines represent normal partitioning for two $K_p$ values.

At Emerald, sediment enrichment ratios were also not related to sediment concentrations, but rather were related to the proportion of various sediment sizes in runoff, which were affected by the cover treatments (Fig. 4.16). Possible reasons for this effect of cover treatments on sediment sizes are discussed in Chapter 6. The important points are that (a) variations in the sediment sizes eroded caused a less than two-fold difference in pesticide concentrations in sediment and in sediment enrichment, and (b) that the results in Fig. 4.16 imply that coarser sediment had higher sorbed pesticide concentrations than the finer sediment, opposite to what is generally expected. Coarser sediments eroded from the Emerald soil are aggregated, rather than primary particles (Chapter 6).
For the majority of pesticides studied, concentrations of pesticides in sediment (mg/kg) were generally equal to or less than concentrations in the soil, due to partitioning into the water phase. Even for pesticides with $K_p$ values as high as 100-200, such as endosulfan, average $E_{SED}'$ were about 0.5 at Gatton and 0.7 at Jondaryan, and this was consistent with expected partitioning. However, at Emerald $E_{SED}'$ averaged about 1.2 for bare plots and were as high as 2-3 for some cover treatments. For pesticides that are more tightly sorbed than endosulfan a smaller proportion of desorption is expected. At Emerald, $E_{SED}'$ values averaged 0.80 for DDE and 0.35 for trifluralin. This range in enrichment ratios probably reflects two factors: (a) differences in the concentrations of the various pesticides in the eroded and sampled soil layers, that is, gradients in concentrations in the soil; and (b) selective transport/deposition of sediment sizes of lower or higher concentrations than the bulk sediment. Differences in concentrations in eroded and sampled soil can also result where sediment is eroded from deeper soil (e.g. micro-rilling on the steep sides of the hills) or from soil of higher or lower spray rate (e.g. due to spray variability, shadowing by hills, band spraying). This is a sampling problem as much as a conceptual issue.

**(d) Summary**

Concentrations of pesticides in both water and sediment phases in runoff, and concentrations in sediment (mg/kg), show strong relationships with concentrations in soil prior to rain. However, differences in runoff extraction between pesticides are more apparent in the separate phases than for total concentrations. These differences in runoff extraction between pesticides in the separate phases are related to:
(a) Total runoff extraction ($E_R$), that is, where $E_R$ is increased or decreased for any reason, extraction of the sediment and water phases is also directly affected.

(b) Sediment-water partitioning. Across the range of partition coefficients, the change in extraction in the sediment and water phases is considerable and opposite. $E_R$ can be partitioned into the two phases using $F_{WAT}$ (Eqn. 5-5), based on $K_P$ and sediment concentration, and includes effects of time after spraying on $K_P$.

(c) To a lesser extent to sediment concentration, particularly at higher partition coefficients. This is also accounted for by normal partitioning, so long as the assumption that $K_P$ is constant for all sediment concentrations holds.

(d) Sediment-size selective enrichment processes.

Normal partitioning accounted for much of the observed variation in water and sediment phase extraction, but variation in $K_P$ with time after spraying must be considered.

Extraction in the sediment phase ($E_{SED}$) is theoretically expected to increase in direct proportion with sediment concentration, and sediment concentration should be an important determinant of total runoff for more sorbed pesticides. However, reduced concentrations in sediment (mg/kg) and enrichment ($E'_{SED}$) with increasing sediment concentration partially offset the effect of sediment concentration at Gatton and Emerald, and negated it entirely for Jondaryan plots. That is, increased sediment loads in runoff did not lead to as great an increase in concentrations of sorbed pesticides in runoff as would be expected. Furthermore, at one site where sediment size-pesticide transport interactions were studied, larger sized sediment were believed to have higher pesticide concentrations than finer sediments, contrary to expected behaviour.

### 4.7 Comparison between sites and pesticides

The only pesticides applied at all three sites were endosulfan and prometryn. Runoff extraction ratios for endosulfan were significantly different for the 3 sites, but not different between $\alpha$-, $\beta$-, sulfate and total endosulfan (2-way ANOVA). In particular, $E_R$ was lower for the Jondaryan plots for $\alpha$- and $\beta$- isomers (and therefore total endosulfan), which was probably due to the longer times since spraying for most plots at this site compared to the others and because these plots gave the lowest sediment concentrations (Table 4.6). However, the markedly higher sediment concentrations at Gatton did not result in the greatest $E_R$ as this site also had lower $K_P$ values for endosulfan and a lower proportion of sediment phase transport. $E_R$ for endosulfan sulfate was lower at Gatton and Jondaryan, where it occurred due to breakdown of recently applied endosulfan, than at Emerald where it was mostly carried over from applications in the previous growing season. The mean $E_R$ for prometryn were similar for the 3 sites (Table 4.6) and were not related to the amount of infiltration during the rainfall event. Emerald had the highest infiltration, and the greatest infiltration before runoff began, and had a marginally higher $E_R$.
Table 4.6. Runoff extraction ratios (E_{RO}) compared between sites for bare plots only (using ANOVA). Means followed by the same letter are not significantly different between columns (P<0.05).

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Gatton</th>
<th>Emerald</th>
<th>Jondaryan</th>
<th>Between Sites</th>
<th>Grand mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain (mm)</td>
<td>63</td>
<td>65</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rain rate (mm/hr)</td>
<td>~95</td>
<td>~95</td>
<td>~70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infiltration (mm)</td>
<td>25</td>
<td>49</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infiltration @ RO start</td>
<td>14</td>
<td>28</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment concentration (g/L)</td>
<td>41 (24-57)</td>
<td>18</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slope (%)</td>
<td>1.5 (0.9-4.3)</td>
<td>1.0</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Days since last spray</td>
<td>0.08-9</td>
<td>Varied by pesticide</td>
<td>2-34d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) ANOVA
- All pesticides 23.8 26.1 23.8 n.s.d. 24.8
- All endosulfan 27.0a 32.0b 19.9c
- Total endosulfan 26.9a 30.9a 19.1b
- Endosulfan sulfate 28.2a 35.3b 26.4a
- Prometryn 22.6 29.8 28.6 n.s.d. 26.1

(b) by regression
- All pesticides 26.1 27.2 30.4 n.s.d. 27.6
  (R²) (0.94) (0.85) (0.91) (0.90)
- All endosulfan 27.6 27.4
  (R²) (0.97) (0.92)

When all pesticides are considered, mean runoff extraction ratios were similar across sites (Table 4.6), with a mean of 24.3 (s.e. 1.5), and were similar for insecticides (24.1) and herbicides (24.7) (n.s.d.), using ANOVA. Regression analysis gives higher values, giving more weight to larger values, which is considered preferable. Regression analysis including all sites (bare plots, all pesticides) gives:

- Cro = 27.37 C’soil (R²=0.922) all endosulfan (slopes n.s.d.)
- Cro = 27.18 C’soil (R²=0.934) all insecticides (slopes n.s.d., except for DDE lower)
- Cro = 28.07 C’soil (R²=0.835) all herbicides (slopes n.s.d., except for trifluralin lower)
- Cro = 27.66 C’soil (R²=0.902) all pesticides excluding DDE and trifluralin
  (slopes s.d. for metolachlor P<0.001 & prometryn P=0.03)

In reality, it is splitting hairs to worry which of these runoff extraction ratios is the ‘best’ and a value of 30 is probably adequate. The runoff extraction data for each pesticide for bare plots are summarised in Fig. 4.17, using the mean concentrations in runoff and in soil. This shows that the main outliers were:

- Gatton - dimethoate had a lower E_{RO}. This may be partly because of higher sediment concentrations at this site, which increased the E_{RO} for the more sorbed endosulfan compounds. This is the only case where there is an indication that leaching from the runoff mixing layer may have reduced pesticide runoff proportionately more so than for other pesticides. However, the contrasting behaviour of prometryn, of similar partition coefficient, should be noted.
- Emerald – trifluralin and DDE had lower $E_{RO}$. Extraction was probably limited by the sediment concentration, as these pesticides had the highest $K_p$ at this site, and/or because concentrations were lower in the soil surface than in the 0-25mm soil for these more aged pesticides.

- Jondaryan – DDE had a lower $E_{RO}$, which again is probably limited by the lower sediment concentrations at this site or because concentrations were lower in the soil surface than in the 0-25mm soil. However, the $E_{RO}$ for DDE (16.7) was similar to those for many other pesticides at longer times after spraying (herbicides 20.6, insecticides 17.6, at 34 days after spraying). Trifluralin had the highest $E_{RO}$ (37) in contrast to Emerald where it was lowest.

Concentration gradients in the soil surface, where concentration in the surface few mm of soil differs significantly from the sampled 0-25mm layer discussed below, are a likely source of variation in runoff extraction, as indicated by the variable results for the more aged trifluralin and DDE and the trend $E_{RO}$ to decrease with time after spraying in general. Separation of differences between pesticides, groups or sites in somewhat confounded by differences in time after spraying. However, the main features of the data are (a) the high degree of consistency between pesticides and sites, even though some systematic variation can be expected with time since spraying, (b) the great extent to which concentration in soil explains concentration in runoff. This consistency is illustrated by the similarity in runoff extraction for pesticides of very different properties, for example pyrithiobac sodium, dimethoate and fluometuron of very low sorption and high solubility in contrast with pendimethalin, trifluralin and endosulfan of much higher sorption.
Fig. 4.17. Mean pesticide concentrations in runoff related to mean concentrations in soil, for (a) Gatton, (b) Emerald, and (c) Jondaryan.
4.8 Part C. Comparison with published data

To put the results from this study into perspective, a comparison with published data is presented. Studies where concentrations of pesticides are measured in both soil and runoff, and where runoff extraction ratios can be determined are uncommon.

4.8.1 Rain-fed cropping studies

(a) Leonard et al. (1979)

Leonard et al. (1979) used data from four small cropping catchments in Georgia USA (~3% slope, sandy loam soils), over four years of annual applications of herbicides to summer crops (data from Smith et al. 1978). Annual average sediment concentration was 5.6 g/L and ranged from 1.8 to 18.8 g/L annually in on-terraced catchments, so conditions were not particularly more or less erosive than on the rainfall simulator plots. They investigated relationships between concentrations in runoff and in soil (0-10mm). For four herbicides of reasonably similar sorption (atrazine, cyanazine, diphenamid and propazine, all with $K_{OC}$ of 100-210) and dominantly transported in the water phase, they found a strong relationship ($R=0.93$), with no difference due to herbicide, watershed or year (Fig. 4.18). The rainfall simulator data coincided with this data over much of the range (Fig. 4.18).

![Fig. 4.18. Pesticide soil and runoff concentrations from rainfall simulator plots (this thesis, Cro=30*C’soil), compared with herbicide data from Leonard et al. (1979) from catchments (Cro=50*C’soil^1.2), and potential maximum concentrations for 50mm rainfall. Rainfall simulator sites: DD – Jondaryan, EM – Emerald, Gatton. Py_Na is pyrithiobac sodium.](image-url)
Leonard et al. (1979) derived the following relationship between total concentration in runoff $C_{RO}$ (μg/L) and concentration in 0-10mm soil $C'_{SOIL}$ (mg/kg):

$$C_{RO} = 50 \left(C'_{SOIL}\right)^{1.2}$$  \hspace{1cm} \text{Eqn. 4-3}

The coefficient of 50 was considered an “extraction coefficient”. The data extended over four orders of magnitude and was significantly non-linear (soil concentration to the power 1.2), indicating that extraction is somewhat more efficient at higher soil concentrations and becomes less efficient with time of herbicide contact with the soil. The extraction coefficient of 50 and the (linear) extraction ratios from the rainfall simulator plots are not directly comparable because of this non-linearity. The two relationships coincide at a soil concentration of around 0.1 mg/kg (Fig. 4.18) (or exactly 0.0778 mg/kg). Runoff concentrations from the catchments are twice those from the rainfall simulator plots at a soil concentration of 5 mg/kg.

The higher runoff concentrations from the catchments than for rainfall simulator plots at higher soil concentrations cause both the higher extraction coefficient and the exponent of 1.2 derived by Leonard et al. (1979) (high values being heavily weighted in regression fit). The higher concentrations in catchment runoff were associated with runoff soon after spraying and presumably with higher concentrations in the top few mm of the soil. In contrast, in the rainfall simulator data, lower soil concentrations are not necessarily associated with greater times after spraying but rather may be associated with low applications rates (e.g. pyrithiobac sodium and some OP’s). Leonard et al. (1979) considered the non-linearity reflected less efficient extraction with time after spraying, which was confirmed in the rainfall simulator study, and “inadequacy in using the 0-10mm zone as a reference throughout the growing season”. As time progresses, 0-10mm soil may over-estimate the surface concentration exposed to runoff, with concentrations lower at the soil surface and increasing with depth. Leonard et al. (1979) provide some of the few data on this issue, e.g. at 13 days and 20 mm of rain after spraying, atrazine concentrations were lower in 0-10mm soil than in 10-20mm soil.

Different soil depths were used in the catchment and rainfall simulator studies for measuring soil concentrations, 0-10 and 0-25mm, respectively. The importance of this sample depth depends on the pesticide distribution in the soil. The extraction coefficient/ratio would be independent of soil depth if concentration were uniform with soil depth. Soon after surface spraying, the concentration in 0-10mm soil should be greater than in 0-25mm soil – as runoff concentration would be the same, the apparent extraction ratio would be lower for the shallower soil sampling depth. If the concentration in 0-10mm soil were lower than in 0-25mm soil, the apparent extraction ratio would be higher for the shallower soil sampling depth. It is difficult to determine how important this issue is compared to others factors (e.g. soil and hydrologic conditions), or what is the ‘right’ sampling depth, without a direct comparison and detailed information on the distribution of pesticides in soil over time after spraying. Sampling will never be precise, due to the graininess, clodiness and unevenness of soils.

Both the Leonard et al. (1979) and rainfall simulator data are well below the maximum potential runoff concentration, that is, if runoff had a concentration equal to the mass of the pesticide in the soil
layer divided by the volume of rainfall. Maximum potential concentrations are about an order of magnitude higher than the measured concentrations (Fig. 4.18). They indicate maximum potential values of the runoff extraction ratio for 50mm of rain (for example) of 300 and 500, for 0-10mm and 0-25mm soil depth (depending on bulk density and rainfall amount). Thus both natural rainfall and rainfall simulator are typically extracting less than 10% of the mass of pesticide in these soil layers. This is consistent with observed pesticide losses as a percent of applied amounts (Chapter 1) and with the view that the runoff-mixing layer is shallower than 10mm (Baker 1980, Ahuja 1986). The potential runoff concentration (i.e. with complete extraction) corresponds with the observed runoff data for a soil depth of less than 2mm (Fig. 4.18).

Leonard et al. (1979) also studied paraquat, a compound highly sorbed to clay surfaces and dominantly transported in sediment. They found a good relationship between runoff concentration and concentration in 0-10 mm soil multiplied by sediment concentration (SC) (Fig. 4.19): 

$$C_{RO} (\mu g/L) = 1000 \times 2.16 \times [SC (g/L) \times C_{SOIL} (mg/kg)/1000]^{0.83}, \ (R=0.97).$$

Multiplying soil concentration by sediment concentration gives an estimate of runoff concentration where the sediment mass is eroded with a concentration equal to the soil concentration, i.e. with no enrichment or desorption into the water phase, shown as the ‘no-enrichment’ line in Fig. 4.19.

![Fig. 4.19. Pesticide runoff concentrations related to soil concentration times sediment concentration (SC), from rainfall simulator plots (this thesis), compared with catchment data from paraquat (catchments P1-4, Leonard et al. 1979), and enrichment ratios for the paraquat data. Rainfall simulator sites: DD – Jondaryan, EM – Emerald, and Gatton. Py_Na is pyrithiobac sodium.](image)
Concentration of paraquat in sediment was greater than in the soil. Leonard et al. (1979) identified the coefficient of 2.16 as an enrichment factor due to preferential transport of finer sediments in runoff. Similar sediment enrichment ratios for clay, organic matter and specific surface of sediment compared to the catchment soil were found. The exponent value of 0.83 was interpreted to indicate a changing sediment composition with sediment concentration. This non-linearity results in an enrichment ratio for paraquat of 7.0 at low values of SC.C'SOIL and decline to 1.5 at the highest values of SC.C'SOIL (Fig. 4.19).

The rainfall simulator plots produced runoff concentrations generally lower than for paraquat at the same soil concentrations (Fig. 4.19). At the lowest paraquat concentrations, runoff concentrations were an almost order of magnitude greater than runoff concentrations from the rainfall simulator plots, because of the 7-fold enrichment. Pesticides were transported from the rainfall simulator plots with less enrichment, that is, the pesticide concentrations in sediment (mg/kg) were closer to the soil concentration and thus runoff concentrations were closer to being equal to SC.C'SOIL.

The enrichment ratios for paraquat and their relationship to sediment concentration are similar to relationships typically found for sediment-bound chemical transport from lighter textured soils (Rose and Dalal 1988, Smith et al. 1993), except that in this case the soil concentration is included as well as the sediment concentration. Data for other pesticides that are dominantly transported on sediment (toxaphene, DDT and DDE) from McDowell et al. (1981) and Willis et al. (1983) also plot close to or just above the 'no-enrichment' line in Fig. 4.19 (data not shown) and are consistent with the data from this study. However, data are not given for pesticide concentrations in the soil surface, so interpretation (based on equation given for pesticide concentration as a function of SC) is less certain. Sediment-weighted average enrichment ratios of clay and organic matter were about 2.0, so pesticide concentrations in sediment were probably within a factor of 1-3 of soil concentrations for most events.

(b) Baker (1980) (data from Baker and Laflen 1979)

Baker and Laflen (1979) studied runoff of atrazine, propachlor and alachlor (KOC = 100-200), applied to the surface on wheel tracks and non-wheel tracks, or incorporated into the soil, using a rainfall simulator (Table 4.7). Rainfall intensity was 70 mm/hr and rain was applied 7-11 hours after spraying. Thus the study was typical of many rainfall simulator studies with rain applied soon after spraying at a reasonably high intensity. Baker (1980) found the relationship between event average concentration in runoff and in 0-10mm soil for these plots was \( C_{RO} (\mu g/L) = 45.\left(C'SOIL \text{ (mg/kg)}\right)^{1.03} \), \( R=0.81 \) and that the agreement with the Leonard et al. (1979) data for water-transported herbicides was "surprisingly good". Indeed the data from the two studies are quite similar (Fig. 4.20) and both have slightly greater runoff concentrations than the rainfall simulator plots (\( C_{RO}=30.C'SOIL \), this study) at higher soil concentrations. Simulated rain applied to small plots soon after spraying and at a reasonably high intensity appears to have provided a useful estimate of herbicide runoff concentrations from the catchments, albeit that they were performed in a different location. A direct comparison from White et al. (1976) is given below.
Table 4.7. Description of published catchment and rainfall simulator studies where data were obtained for relating runoff and surface soil concentrations. Only those treatments, pesticides etc. used here are described. Methods for estimating mixing layer soil concentration are described.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Description of study and method for estimating mixing layer soil concentration. (In order of year published).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DRYLAND (RAIN-FED) CROP LANDS</strong></td>
<td></td>
</tr>
<tr>
<td>Trichell et al. (1968)</td>
<td>Measured runoff of three acidic herbicides, picloram, 2,4,5-T and dicamba, at 24 hr and 4 months after spraying, from fallow soil rainfall simulator plots (3.28m x 3.28m, 12.7 mm in 1hr), on a clay loam soil on 3% slope in Texas. Soil concentrations were not measured. Soil concentrations (0-5mm) for 24hr after spraying were calculated from the spray rate assuming no losses.</td>
</tr>
<tr>
<td>Ritter et al. (1974)</td>
<td>Measured atrazine and propachlor (KOC ~100) in soil and in runoff on four small catchments in Iowa USA, silt loam soils, slopes of 10-15%. Herbicides were applied annually at planting, with ‘ridged’ corn compared to ‘surface-contoured’ corn. Detailed soil concentration data were collected. Soil concentrations (0-25mm) interpolated from first-order equation fitted to data measured through time.</td>
</tr>
<tr>
<td>White et al. (1976)</td>
<td>Measured runoff of 2,4-D from a 0.34ha catchment, cultivated (annual Corn, conventional till), on loamy sand (OC=0.29%), 3.2% slope, Tifton Georgia, 1970-1972, and concentrations in soil (0-5mm) after 2,4-D application in 1972. In 1972, simulated rainfall (82.5mm in 30min) was applied to 30.2 m² sub-plots at 1, 8 and 35 days after 2,4-D application. Soil concentrations for storms and for rainfall simulator plots were determined from days after spraying by interpolating between soil concentration data. Event average runoff concentrations were not presented (see text).</td>
</tr>
<tr>
<td>Leonard et al. (1979), data from Smith et al. (1978)</td>
<td>Measured pesticide in soil (0-10mm) and runoff from four small cropping catchments in Georgia USA (~3% slope, sandy loam soils), over four years of annual applications of herbicides to summer crops. Annual average sediment concentration was 5.6 g/L and ranged from 1.8 to 18.8 g/L annually in on-terraced catchments. Four herbicides were of reasonably similar sorption (atrazine, cyanazine, diphenamid and propazine, KOC 100-210) and were dominantly transported in the water phase, while paraquat was strongly bound to sediment. Event average runoff concentrations and soil concentrations (0-10mm) were taken from Fig. 4 and 5, Leonard et al. (1979).</td>
</tr>
<tr>
<td>Baker and Laflen (1979), data from Baker (1980)</td>
<td>Measured runoff of atrazine, propachlor and alachlor (KOC 100-200), applied to the surface on wheel tracks and non-wheel tracks, or incorporated into the soil, from 1.5x9.1m rainfall simulator plots (7% slope, on a sandy loam soil). Rainfall intensity was 70 mm/hr and rain was applied 7-11 hr after spraying. Event average concentrations in runoff and soil (0-10mm) were taken from Fig. 3 in Baker (1980).</td>
</tr>
<tr>
<td>Edwards et al. (1980)</td>
<td>Measured runoff and soil (0-25mm, including overlying vegetation) concentrations of glyphosate (anionic, phosphate-like sorption) on catchments (0.3-3.1 ha, ~15% slope) with reasonably high cover and low sediment loads, in Iowa. Data were derived from equations for soil and runoff concentrations against days since spraying (Table 3).</td>
</tr>
<tr>
<td>Buttle (1990)</td>
<td>Measured metolachlor (KOC 200) in soil (0-150mm) and in runoff during 3mths after one application on natural rainfall runoff plots (23.8 m²) on upslope areas (loam soil, OM=2.7%, slope ~9%), in Canada. Pre-emergence surface broadcast (‘surface’) application was compared with pre-plant incorporated to 150 mm (‘incorp’) for maize. Soil concentrations (0-25mm) - for surface application, estimated by assuming all herbicide in 0-150mm was in 0-25mm depth, - for incorporated, by assuming concentrations in 0-25mm soil equal to 0-150mm soil.</td>
</tr>
<tr>
<td><strong>IRRIGATED CROP LANDS</strong></td>
<td></td>
</tr>
<tr>
<td>Spencer et al. (1985)</td>
<td>Measured runoff, sediment and concentrations of 20 pesticides in runoff from some ten furrow irrigated fields (28-60ha) in the Imperial Valley, California, for 1-3 years each. Soils were silty clay or silty clay loam, 40-50% clay, OC=0.4-0.7%. Insecticides were generally aerially applied, and some was usually intercepted on the crop canopy. Herbicides were generally applied to soil with ground-rigs. Event average (flow weighted) pesticide concentrations were calculated. Sediment concentrations were reasonably low, with an average across fields of ~0.7g/L (season averages of 0.2-1.2g/L for different fields, 0.2-2g/L for individual irrigations). Before some irrigation events, samples of 0-10mm soil were collected from the irrigation furrow. Partition coefficients were measured in runoff for selected events. Runoff and soil concentrations taken from Appendix Tables 1-6.</td>
</tr>
</tbody>
</table>
Data for runoff and soil concentrations are shown in Fig. 4.20 for the catchment/natural rainfall studies of Ritter et al. (1974) for atrazine and propachlor, White et al. (1976) for 2,4-D, Edwards et al. (1980) for glyphosate and Buttle (1990) for metolachlor, and the rainfall simulator plots of Trichell et al. (1968) for three acidic herbicides, with the data for Baker (1980) and Leonard et al. (1979), and the best-fit lines from Leonard et al. (1979) and this thesis. In the interests of brevity these studies are described in Table 4.7. Soil concentrations were derived from the measured data as provided in the papers and varied in quality, quantity and soil depth (Table 4.7). Availability of soil concentrations was the main limitation determining which studies could be used.

![Herbicide data diagram](image)

Fig. 4.20. Pesticide soil and runoff concentrations from North American rainfall simulator and catchment studies in rain-fed crop lands, compared with Leonard et al. (1979) (Cro=50.C’soil^{1.2}) and Cro=30.C’soil (this study), and lines approximating limits of the data.

The herbicide data from these five studies more or less coincided with the other data (Fig. 4.20), though runoff extraction reported by Ritter et al. (1974), Edwards et al. (1980) and Buttle (1990) were often greater at higher soil concentrations. This is probably due to the steeper slopes of the catchment/plots (10-15%, 15%, 9%, respectively). The average extraction ratio for the data of Ritter et al. (1974) was 167, five times the value from the rainfall simulator studies. Runoff concentrations from Ritter et al. (1974) and Buttle (1990) for some events approach the potential for complete extraction from the 0-10 mm soil (for a 50mm rainfall), with an extraction ratio of 200 (Fig. 4.20).
Both studies were under highly erosive conditions and experienced large pesticide losses. Ritter et al. (1974) recorded a storm 7 days after application where 15% of the applied atrazine was lost in runoff.

In the Buttle (1990) study, extraction ratios were highest soon after spraying and declined with time for both the surface and incorporated applications, implying more rapid loss of the metolachlor from the runoff-mixing layer than that measured in the 0-150 mm soil. The soil concentrations used here probably overestimate the actual mixing layer concentrations at longer times after spraying. Runoff concentrations were enhanced by a large contribution by sediment phase transport; 31-46% of metolachlor losses were carried in sediment. This is higher than generally expected for this reasonably soluble herbicide (Chapter 5) because sediment concentrations were high, averaging over 100 g/L and above 200 g/L in some events, compared with 6 g/L on average from the catchments of Leonard et al. (1979). Surface-applied metolachlor gave considerably higher soil (0-25mm) and runoff concentrations than when incorporated into the soil (Buttle 1990) but give about the same runoff extraction (accepting the assumptions made in deriving 0-25mm soil concentrations from the measured 0-150mm soil data, Table 4.7).

The data from Edwards et al. (1980) for glyphosate fitted the relationship $C_{RO} (\mu g/L) = 56.3 [C_{SOIL} (mg/kg)]^{1.6}$, not dissimilar to the relationships from Leonard et al. (1979) and Baker (1980). The catchments apparently had high cover (of sprayed-out meadow?) and the soil concentration data included glyphosate on the cover, so runoff probably included washoff from this cover. The acidic herbicides, picloram, 2,4,5-T and dicamba, (Trichell et al. 1968) and 2,4-D (White et al. 1976) also approximately fit the general trend of the other data. The very high runoff concentrations measured by Trichell et al. (1968) are related to high soil concentrations and are probably not due to inherently greater runoff extraction of these compounds. Acidic herbicides are considered highly soluble and are from a different class of chemicals to the herbicides examined in other studies, which are mostly of somewhat similar properties, i.e. triazine and acetamide herbicides, and therefore might be expected to have similar runoff behaviour.

**Summation.** Concentrations in runoff are strongly related to concentrations in the soil surface, with little systematic difference apparent for different pesticides. The data from US croplands are consistent with the relationship from the rainfall simulator (this study) over much of the range. Still there is a reasonable range in runoff concentrations at any particular soil concentration, with runoff extraction ratios from 10-200 for individual events when the most erosive sites are included (Fig. 4.20). For the data of Leonard et al. (1979) and Baker (1980), 90% of events had an extraction ratio between 15 and 80, or 0.3 to 1.8 times the mean value. Coefficient of variation was 72%. In other words, runoff concentrations varied by less than a factor of two compared with a variation of three-four orders of magnitude due to change in soil concentration over time. Thus the analysis provides a useful but imprecise first approximation.
White et al. (1976) measured runoff of 2,4-D from a small, cultivated catchment in Georgia (annual Corn, conventional till). They present ranges of runoff concentrations on a monthly basis for three years, and ranges of runoff concentrations in a series of storms and concentrations in soil (0-5mm) after 2,4-D application for one year. Actual event average concentrations were not given, so the mean of the range values was used. Simulated rainfall was applied to three 30.2 m² sub-plots at 1, 8 and 35 days after 2,4-D application, at a high intensity (165mm/hr for 30 min). Soil concentrations for storms and for simulator plots were determined from days after application by interpolating between the soil concentration-days since spraying data, similar to Leonard et al. (1979). Total 2,4-D (i.e. including the acid and ester) was determined in runoff, sediment and soil; these forms of 2,4-D have somewhat different properties and their proportions may have changed through time, which may have affected the results. Two aspects of the data are of interest here, namely, comparison of rainfall simulator data with catchment data, and comparison of soil and runoff concentrations.

Mean concentrations of 2,4-D in runoff from rainfall simulator plots and from the catchment fit the same first-order relationship with days after spraying (Fig. 4.21), indicating that the rainfall simulator provides a reasonable estimate of pesticide runoff from the catchment. A more direct comparison is not possible as the two types of data only overlap at 34 days after spraying – concentration from the simulator plot fit between concentrations from the catchment for two storms around this time. The maximum concentrations in runoff observed on the rainfall simulator plots also agree reasonably closely with maximum concentrations measured from the catchments in each year when considered as functions of days after application (Fig. 4.21).

![Fig. 4.21. Comparison of concentrations of 2,4-D in runoff from rainfall simulator plots and from a catchment, through time after application (data from White et al. 1976). Concentrations are event means (symbol), maximum and minimum (error bars), and maximum annual.](image-url)
Mean runoff concentrations for the rainfall simulator plots and the catchment storms relate well
to soil concentrations and cluster around the equation of Leonard et al. (1979) and the results from
this study (Fig. 4.22). Apart from data at one day after spraying the average extraction ratio
\(E_{RO}=25.7\) is similar to that for the rainfall simulator plots in this thesis (mean \(E_{RO}=27.7\)). The lower
runoff extraction at one days after spraying may be related to greater leaching out of the runoff mixing
layer and little contribution from sediment phase transport, as the effective partitioning coefficient was
lower than at later times (Chapter 5). Maximum runoff concentrations for the rainfall simulator plots
and the catchment storms were also correlated with soil concentrations, with a similar relationship for
the two scales, with an extraction coefficient 5-6 times that of the event average.

![Fig. 4.22. Mean and maximum concentrations of 2,4-D in runoff from rainfall simulator plots and from a
catchment related to concentration in soil (0-5mm), from White et al. (1976), compared with Leonard et al. (1979) \(C_{ro}=50\cdot C_{soil}^{1.2}\) and \(C_{ro}=27.7\cdot C_{soil}\) (this chapter).]

4.8.2 Irrigated cropland studies

(a) Spencer et al. (1985)

Spencer et al. (1985) measured runoff, sediment and concentrations of 20 pesticides in runoff
from some ten furrow irrigated fields (28-60ha) in the Imperial Valley, California, for 1-3 years each
(silty clay or silty clay loam soils, 40-50% clay, OC=0.4-0.7%). Insecticides were generally aerially
applied, and therefore there was usually some interception on the crop canopy. Herbicides were
generally applied directly to the soil with ground-rigs. Event average (flow weighted) pesticide
concentrations were calculated. Sediment concentrations were reasonably low, with an average across
fields of about 0.7 g/L (season averages of 0.2-1.2 g/L for different fields, 0.2-2 g/L for individual
irrigations). Before some irrigations, samples of 0-10mm soil were collected from the irrigation
furrow. These pesticide soil and runoff data were used by Spencer et al. (1985) to investigate relationships between pesticide in runoff and in soil prior to irrigation, and are used here to determine runoff extraction ratios. The relationship was poor for methidathion (an OP), and the pyrethroids permethrin and fenvalerate, which were present in runoff at extremely low rates – these data were ignored. Thus data are available for the insecticides chlorpyrifos, diazinon, ethyl parathion, malathion, methyl parathion (organophosphates), endosulfan (organochlorine), methomyl (carbamate), and the herbicides trifluralin, prometryn, DCPA and dinitramine.

Runoff concentrations relate reasonably well to soil concentrations for each pesticide or group of pesticide (Fig. 4.23), though there is a reasonable variation between some irrigation events; not too surprising given the data are from a variety of fields, years, crop stages and irrigation number within a season. The data for prometryn and methomyl coincide reasonably well with the relationship determined for rainfall simulator plots (C_ro=27.7*C_soil). Runoff extraction ratios vary by about a factor of seven, i.e. E_ro = 4 to 31, and are highest for the less sorbed prometryn (31.3) and methomyl (21.7), and decrease to 4-7 for more sorbed compounds.

![Fig. 4.23. Mean concentrations in runoff from furrow irrigation related to concentrations in furrow soil (0-10mm), Imperial Valley, California (Spencer et al. 1985), compared with C_ro=27.7*C_soil (this chapter). Herbicides (Koc 5000) - DCPA and dinitramine. OP's - chlorpyrifos, diazinon, ethyl parathion, malathion, methyl parathion. Koc values are from Wauchope et al. (1992).](image)

The E_ro values for each pesticide or group derived in Fig. 4.23 are plotted against partition coefficients in Fig. 4.24. The trend for decreasing runoff extraction ratio with greater partition coefficient is consistent where partition coefficients measured in the irrigation runoff by Spencer et al. (1985) are used (Fig. 4.24). Measured partition coefficients were about five times ‘selected’ soil sorption coefficients from Wauchope et al. (1992) for chlorpyrifos, endosulfan and trifluralin, 1.6 times for DCPA and about the same for prometryn.
Fig. 4.24. Runoff extraction ratios (ERO, slopes of equations fitted in Fig. 4.23) related to soil sorption coefficients (Kd) from KOC (Wauchope et al. 1992) and OC=0.5%, or, where available, partition coefficients (Kp) in the irrigation runoff of low sediment concentration (Spencer et al. 1985). OP’s are chlorpyrifos, diazinon, ethyl parathion, malathion, methyl parathion.

The lower runoff extraction observed for the more sorbed pesticides is directly related to the low concentrations of sediment in the runoff water. The contribution of pesticides in the sediment phase to the total concentration was low (e.g., <20%), even for highly sorbed pesticides (Fig. 4.25a). For tightly sorbed pesticides, little in transported in the water phase so without sediment movement, little is transported in total.

Fig. 4.25. (a) Fraction of pesticide in the sediment phase (FSED) related to Kp, for actual sediment concentration in irrigation runoff (~0.7g/L) and for sediment concentrations of 25 and 50 g/L. ERO – Kp is shown to indicate the relevant Kp for each pesticide. OC is endosulfan.

(b) Runoff extraction ratios for measured sediment concentration and calculated for sediment concentration of 25 g/L, using the measured Kp values.
Had the sediment concentration in runoff been greater, the proportion of pesticides in the sediment phase would have been considerably greater for the more sorbed pesticides in runoff (e.g. 80-100% for Kp>100, Fig. 4.25a) and the runoff extraction ratio would have been higher (ERO = 25-35), similar to that of prometryn (Fig. 4.25b). Even for DCPA with a measured Kp of 40, the proportion in the sediment phase would increase from almost nothing with sediment concentration of 0.7 g/L to about 50% with sediment concentration of 25 g/L, doubling the ERO to 34. Increased sediment concentration does not affect runoff extraction of prometryn, because little was transported on sediment in any case (Kp = 1.5), and ERO was about 33 for both sediment concentrations.

This interpretation of the data of Spencer et al (1985) indicates that runoff extraction ratios are similar to those in this thesis, once differences in sediment concentrations are taken into account.

4.9 General discussion

There is evidently a high degree of consistency in runoff extraction from soil for pesticides with a wide range of properties, both within the rainfall simulator studies and across rainfall simulator and catchment studies in the literature. This indicates that runoff concentrations, which do vary widely, are mainly determined by the soil concentration at the time of the event (i.e. determined by application and dissipation rate) and to a lesser extent vary with site/event-specific hydrology and erosion factors.

4.9.1 What differentiates runoff extraction between pesticides?

Differences in runoff extraction between pesticides from bare soil would occur if:

(a) Pesticides were differentiated due to leaching, requiring (very) different sorption properties and significant infiltration, particularly before runoff commenced, and requiring that leached pesticides are not returned to runoff by interflow. This is discussed in the next section (4.9.2).

(b) Pesticides were differentiated by sorption to sediment, requiring different sorption properties and (very) low sediment concentrations. With a very low sediment concentration, poorly sorbed pesticides are extracted into runoff, but strongly sorbed pesticides would be almost absent. With higher sediment concentrations, pesticide concentration in runoff will only depend on the soil concentration, with the Kp determining partitioning in the runoff; the extreme case is where all the soil in the mixing layer is eroded into the runoff volume. This discussed in section 4.9.3.

(c) Pesticides have different concentration-depth distributions within the runoff-mixing layer. Ahuja et al. (1981) found the degree of mixing decreased exponentially with soil depth, being highest at the surface and minimal at 20-25mm. A pesticide recently sprayed on the soil has a higher concentration in the upper few mm of soil compared with the average over the sampled depth, and its apparent runoff extraction ratio would be higher. Over time, greater dissipation near the surface and downward movement (leaching and diffusion) leads to lower concentrations in the surface than in deeper soil and a lower apparent runoff extraction ratio. A pesticide that is mixed into the soil (e.g. by injection, tillage, leaching and diffusion) may have a uniform concentration with depth, or if it is volatile, may have a lower concentration towards the surface.
4.9.2 The role of leaching from the runoff mixing zone

Reduction in concentration due to leaching of a partially sorbed pesticide in a soil layer can be calculated using the advection equation (Steenhuis and Walter 1980, Leonard et al. 1987):

\[
C'_{s2} = C'_{s1} \exp \left[ \frac{-(P - Q - AWS)}{D (K_D (BD/1000) + POR)} \right]
\]

where \( C'_{s1} \) and \( C'_{s2} \) = concentration in soil (mg/kg) before and after rain of \( P \) (mm) and runoff of \( Q \) (mm). \( AWS \) = available water storage in the soil layer (mm), \( D \) = soil layer depth (mm), \( K_D \) = sorption coefficient (L/kg), \( BD \) = bulk density (kg/m\(^3\)) and \( POR \) = soil porosity (v/v).

The potential effects of leaching on concentrations in the soil surface (0-25mm) for a range of \( K_D \) values and indicative pesticides, calculated with this equation, are illustrated in Fig. 4.26. For the infiltration observed on bare plots at Emerald, soil concentrations are barely affected for pesticides with \( K_D \) greater than 100 (e.g. endosulfan, trifluralin, DDE), even with 100 mm of infiltration. This agrees with field observations of endosulfan being found mostly in the surface few cm over periods of months (Kimber et al. 1994, Kennedy et al. 2001). Soil concentrations are only slightly reduced for \( K_D = 14 \) (e.g. prometryn), reduced by 10% during 50 mm of infiltration. With \( K_D = 1.4 \) (e.g. atrazine or fluometuron), soil concentration is reduced by about 25% with 30 mm of infiltration (i.e. when runoff started) and is halved with 50 mm. \( K_D \) needs to be about 0.2 for soil concentration to be halved with 30 mm of infiltration. Also, 12-15 mm of infiltration is needed to exceed the storage capacity (AWS) and initiate leaching below 25mm, due to the high water holding capacity typical of clay soils.

![Fig. 4.26. Reduction in concentrations of pesticides in the soil (0-25mm) due to leaching for a range of pesticide \( K_D \) values, using \( K_P \) values measured at Emerald and several lower values. Calculated using Eqn. 4-4 (bulk density = 1000 kg/m\(^3\); moisture content before rain =0.086 g/g).](image-url)
Thus the $K_D$ must be low (e.g. $<2$) for leaching to significantly reduce the concentration in 0-25mm depth of soil during a single large rainfall event, consistent with Briggs (1981). Partition coefficients measured in runoff were generally greater than 10, and were only as low as 2-5 for a few of the pesticides and then only in the first few days after spraying (Chapter 5).

At the other rainfall simulator sites, infiltration amounts were about half those at Emerald, with only 10-15 mm of infiltration before runoff commenced and only 17-25 mm in total (Table 4.6). Thus infiltration only exceeded the storage capacity in 0-25mm soil at about the time runoff commenced, so a considerable proportion of the pesticide would be available to mix with runoff. By the end of the runoff event less than one pore volume of water had leached through the 0-25mm soil, due to the reasonably high amount of runoff (e.g. at Jondaryan 17 mm infiltrated and 30 mm run-off).

Where infiltration was highest (65mm), that is, Emerald runoff plots with cover (Chapter 6), data for NO$_3$-N in runoff indicate that leaching was probably inhibited by subsoil compaction restricting infiltration, particularly for wheel-track plots. NO$_3$-N concentrations in runoff increased with increasing cover, i.e. with increasing infiltration. With greater cover, runoff occurred due to ponding of infiltrated water in the shallow tilled layer in the bottom of furrows, resulting in restricted leaching and more complete mixing. This is consistent with the much greater concentrations in runoff (of Br) where leaching is prevented, observed by Ahuja and Lehman (1983). However, runoff concentrations of prometryn, the least sorbed pesticide studied, only increased slightly on covered wheel-track plots, probably because some of the leached prometryn was sorbed. Thus it appears that pesticides must be very weakly sorbed to respond the same as NO$_3$-N or Br.

A case where leaching may have reduced runoff extraction was for dimethoate at Gatton where runoff extraction was more than halved (Section 4.5.1), which is supported by soil concentrations measured after rain which were 5% of concentrations before rain, whereas endosulfan was not affected (Chapter 3). The lack of effectiveness of leaching was also demonstrated by the no/slight response of water phase runoff extraction ($E_{WAT}$) to infiltration amount (Section 4.6(a)).

In dissipation studies in Chapter 3, downwards movement into the 25-50mm soil was found at Jondaryan under natural rainfall for a small proportion of applied endosulfan and various herbicides. For the herbicides, the proportion that moved down increased for herbicides with lower $K_{OC}$. This occurred over a period of weeks, with 77mm of rain by 39 days and 140mm by 62 days. This is thought to have occurred due to a combination of leaching and diffusion, activated by each wetting event, discussed in Section 3.5.3(a) (Chapter 3). Leaching may have more impact on pesticide runoff by enhancing dissipation from the runoff-mixing layer than during the actual runoff event.

In principle, it is possible to determine the degree of leaching/dilution from the characteristic decrease in runoff concentrations during rain (Ahuja 1986). However, the time-decay in concentrations was not as dramatic as in some studies (White et al. 1967, 1976; Baker and Laflen 1979, Fig. 1.10) and concentrations also decreased during rain for more strongly sorbed pesticides, particularly in the first few days after spraying. This indicates progressive erosion of high
concentrations in the surface few mm of soil, which decline with depth. It would be difficult to separate these two phenomena.

Thus reduction in runoff concentration due to leaching from the soil prior to runoff does not appear to have been particularly influential in the rainfall simulator studies, because the depth of infiltration was small and soil sorption coefficients were generally too high. Depth of infiltration would need to be considerably larger, or \( K_D \) considerably smaller, for leaching to influence runoff concentration. This does not mean that pesticide solute is not being redistributed within the runoff-mixing layer or being diluted in the volume of infiltration and runoff. Indeed the same analysis applied to say the 0-5mm soil indicates considerably more leaching.

The infiltration observed on the rainfall simulator plots, which appears too small to leach a significant proportion of pesticide out of the runoff-mixing layer, is not unusual during storm rainfall on bare cultivated soil used for grain and cotton cropping in Eastern Australia (i.e. north of Dubbo). Infiltration on the black Vertosol at Emerald is actually in the high end of the range of final infiltration rates measured on a wide range of bare soils in this region by Loch and Foley (1994) (Chapter 6). The black Vertosol at Jondaryan had the least infiltration, but most soils in the region used for cropping would have similar or lower infiltration after about six years of cropping (Connolly et al. 1997). This is because these soils develop surface seals rapidly when exposed to rain (Foley and Silburn 1994), which limit their infiltration rate to 10-25 mm/hr or less (Loch and Foley 1994, Connolly et al. 1997), and because of restricted infiltrations through the (rather ubiquitous) compacted soil below the tilled layer (Silburn and Connolly 1995). Thus the hydrologic conditions in the rainfall simulator studies are not atypical of large areas of agricultural land in the region after fallowing or pre-irrigation.

4.9.3 Why pesticides had similar runoff extraction

The concentration of a pesticide in runoff is the total of the water and sediment phases. The distribution between these phases is described by the partition coefficient, which in the rainfall simulator studies varied over 4-5 orders of magnitude between pesticides, and the fraction in either phase varied accordingly (Chapter 5). It is therefore intriguing that a more or less fixed proportion of the concentration in the soil surface was extracted into runoff for all these pesticides. For this to occur the concentrations of poorly sorbed pesticides extracted in the water phase and the tightly sorbed pesticides extracted in the sediment phase must be more or less equal for a given soil concentration. The similarity of runoff extraction ratios across the range of \( K_F \) values therefore depends on sediment concentrations being in a certain range, sufficient to cause this similarity.

However, a number of factors appear to push runoff extraction towards similarity rather than difference between pesticides, so long as leaching is restricted. An important factor is that the mass of soil and volume of water involved in mixing are the same for all of the pesticides on a plot. The consistency of runoff extraction indicates that this is also reasonably similar between plots and sites. Many of the factors that increase extraction of solutes also increase detachment of sediment (e.g. increased rainfall intensity and energy, slope and shear stresses generated by water flowing across the
soil surface or decreased surface cover and infiltration rate) (Ahuja 1986, 1990). Thus there tends to be a positive correlation of solute extraction and soil loss (Sharpley 1985).

Other mitigating factors are that:

- As sediment concentration decreases, (a) physical enrichment of chemicals in sediment generally increases, so that the sediment phase concentration does not decrease in linear proportion with the sediment concentration, and (b) the distribution between water and sediment phases is highly non-linear (i.e. for normal linear partitioning, Eqn. 5-5, Chapter 5) and the effect is similar to physical enrichment. The net effect of these processes is to moderate the expected effects of sediment concentration on runoff extraction, except at very low sediment concentrations. Thus, in the Gatton study, runoff extraction was similar between plots even though sediment concentration varied from 20 to 60 g/L. However, if sediment concentration is low enough (or much higher) runoff extraction will become different for strongly and weakly sorbed pesticides. Thus for Emerald plots, where cover reduced sediment concentration from 20 g/L to 6 g/L, the $E_{RO}$ value for DDE and trifluralin were halved while the $E_{RO}$ for Prometryn was not significantly reduced.

- All pesticides studied had some contribution to runoff concentrations in both the water and sediment phases, except for DDE (Chapter 5). This may involve only 10% in the sediment phase for the most weakly sorbed chemicals very soon after spraying, but was 20-40% after a few days. Thus all pesticides (except DDE) were extracted partly as a solute and partly in sediment.

The decrease in runoff extraction ($E_{RO}$) with time after spraying may be related to:

- an apparent increase in $K_P$ with time (ageing) (see Chapter 5). However, this appears unlikely to be a direct causal relationship, as differences in $E_{RO}$ between pesticides are not related to $K_P$.

- distribution of more of the pesticide deeper in the 0-25mm soil layer with time where it is less involved in mixing with runoff water. Initially after spraying, concentration is probably greater in the surface of the 0-25mm layer (e.g. the few mm most directly involved in mixing with runoff) than averaged over the layer. With time, concentration in the surface will decrease and approach the concentration in the whole layer, due to diffusion and leaching. After some time concentration in the surface may be lower than that in the whole layer, due to volatilisation and greater exposure (e.g. to sunlight, extreme temperatures).

Less efficient runoff extraction at longer time since spraying also means that runoff extraction is lower at lower soil concentrations, as soil concentrations decline with time since spraying. Thus if the data for any pesticide covered a wide range in concentrations (which is not always true for the data here), a non-linear relationship between runoff concentrations and soil concentrations is likely. Thus Leonard et al. (1979) found $C_{ro} = 50 \times (C_{soil})^P$, where $P=1.2$ and was significant.

The similarity of runoff extraction between the three rainfall simulator studies was probably because of similarities across sites in soil factors, hydrology and erosion. All soils had low organic carbon contents (1.1-1.4%); different soil OC would alter pesticide partitioning but, given the lack of
response of runoff extraction to partitioning, this may not change runoff extraction unless other factors such as infiltration (leaching) changed substantially. Infiltration was generally low, due to surface sealing on the bare soil, shallow subsoil compaction and moist subsoil. The sites had low slopes (0.2-2%) with hill-furrow systems, and therefore similar erosion/deposition processes operated, although sediment concentration varied 10-60 g/L. However, these conditions would apply during early season storm events on much of the land used for irrigated cotton production in Australia and most would apply to large areas of dryland cropping on clay soils late during fallows and around planting time.

A factor that warrants further study is runoff extraction for dryer subsoil conditions and/or lower rainfall intensity, i.e. conditions where infiltration before runoff is greater. This may lead to lower runoff extraction of less sorbed pesticides and differences between pesticides.

The higher runoff extraction observed in some studies in the literature (e.g. $E_{RO} \sim 80-200$) are presumably related to maximisation of many of the factors discussed here, i.e. inhibition of leaching (moist soil after spring planting, compaction etc) and highly erosive conditions (where sediment concentrations are high enough to firstly, partition more of the generally weakly sorbed pesticides into the sediment phase, and secondly to transport it).

4.10 Conclusions

Previous studies (Leonard et al. 1979, Wauchope and Leonard 1980) suggested that, to understand pesticide runoff, it is useful in to separate the processes that occur between spraying and the runoff event (application and dissipation) and those that occur during the runoff event, that is extraction of pesticides from soil into runoff. To investigate this process, mean flow weighted concentrations of pesticides in runoff from simulated rainfall events on hill-furrow systems were compared with their concentrations in soil before rain at three sites.

4.10.1 Runoff extraction on bare soil

For bare soil, the total concentration of each pesticide extracted into runoff was closely related to the concentration in the soil (0-25mm) prior to rainfall, irrespective of pesticide properties (e.g. partitioning coefficient). The ratio of runoff concentration to soil concentration, the runoff extraction ratio ($E_{RO}$), was generally similar for pesticides with a wide range in sorption properties and for the three soils. As a first approximation, concentration in runoff ($\mu g/L$) = 28 concentration in soil (mg/kg), (or $E_{RO} = 28$). The 14 pesticides (and their soil sorption coefficients $K_D$) ranged from tightly sorbed (DDE, $K_D \sim 15,000$) to weakly sorbed (fluometuron, dimethoate and pyrithiobac sodium, $K_D < 30$). Runoff extraction was also approximately similar for dissolved N and P, and organic N, at one site where nutrients were also studied, even though concentrations of nutrients were 1-2 orders of magnitude greater than for pesticides.

The total concentration of pesticide in runoff consist of concentrations in the water and sediment phases. Extraction ratios for pesticides in the water phase ($E_{WAT}$) decreased as the partition coefficient increased. Extraction ratios for pesticides in the sediment phase ($E_{SED}$) increased as the partition...
coefficient increased. Both relationships were consistent with normal partitioning. Physical
enrichment due to size-selective sediment sorting was limited, with enrichment ratios often less than
1.0 (due to desorption) and no greater than 2.0, despite considerable deposition in the furrows. This is
because the soils eroded as aggregates (due to low sand and high clay content), and possibly because
coarser sediment had greater concentrations of sorbed pesticides than finer (suspended) sediment.

Both the rainfall simulator data, and data from the literature, indicate that runoff extraction ratio
decreases with time after spraying. This is considered to be due to changes in the concentration profile
in the soil surface with time, a topic that has received little study.

The similarity of runoff extraction ratios between sites was probably due to similarities in soil
factors, hydrology and erosion. However, the conditions studied would apply during early season
storm events on much of the land used for irrigated cotton production in Australia and large areas of
dryland cropping on clay soils around planting time.

The notable similarity of runoff extraction ratio for all pesticides (and N and P) in the rainfall
simulator studies was probably because (a) the main factor that limits runoff of weakly sorbed
chemicals, i.e. leaching from the runoff mixing zone, was ineffective due to low infiltration and
ponding of infiltrated water in the shallow tilled layer in the bottom of furrows, resulting in more
complete mixing, and (b) sediment concentrations were high enough to ensure transport of more
strongly sorbed pesticides. Also all pesticides generally had at least some transport in both the water
and sediment phases. The concentration of pesticide extracted from soil into runoff appears to be
determined by the soil concentration and the mixing and erosion processes, with, in the absence of
significant leaching and the presence of sufficient sediment transport, little differentiation between
pesticides of different partition properties. This is partly because, on any plot, the same mass of soil
and the same volume of water are involved in mixing, independent of the chemical being considered,
and because factors that increase extraction of solutes also tend to increase detachment of sediment.

Where hydrologic and erosion differed markedly from the conditions studied here, due to
cultural practices and/or markedly different soil properties, runoff extraction would also differ and
differentiation between pesticides according to sorption may occur. In particular, runoff extraction of
weakly sorbed pesticides will decrease with considerably greater infiltration and runoff extraction of
tightly sorbed pesticides will decrease when sediment concentrations are considerably lower.

Analysis of published data indicate results from the rainfall simulator studies are not atypical,
although higher runoff extraction occurs under more erosive conditions (e.g. steep US croplands) and
lower runoff extraction occurs under less erosive conditions (e.g. furrow irrigation on low slopes).

The analysis of the rainfall simulator and published data presented here, presents a conceptual
model where the major drivers of observed pesticide runoff can be separated between (a) application
rate and dissipation, described by the soil concentration at the start of rain, which may account for 3-4
orders of magnitude differences in runoff concentration, and (b) runoff extraction during the rainfall
event, which appears to vary over a limited range.
4.10.2 Effects of spray/cultural treatments

**Time since spraying.** Runoff extraction ratio decreased with time after spraying, due to a decline in runoff extraction in the water phase. $K_p$ increased rapidly soon after spraying and more slowly at longer times (Chapter 5). However, this is probably not the cause of decreased runoff extraction with time, as runoff extraction did not differ for pesticides of vastly different $K_p$ values. Rather, the decline in runoff extraction is probably related to changes in the concentration profile in the 0-25mm soil layer.

**Band spraying.** Runoff extraction ratios were similar for banded and blanket spray plots. Band spraying is accounted for so long as average soil concentrations are calculated on a whole area basis.

**Furrow slope.** Within the range of slopes studied, 0.2-2% between sites and 0.6-4% within one study, runoff extraction ratios were similar.

**Cover.** When pesticides were sprayed over on-ground cover, runoff extraction ratios were slightly lower (times 0.7) for more volatile pesticides that apparently do not washoff the cover (e.g. endosulfan). The main effects of cover were interception, binding and dissipation of the pesticide on the cover before rain, reducing the soil concentration available for runoff extraction (Chapter 3). However, runoff extraction was significantly higher where pesticides were washed from the cover, contributing to runoff concentrations directly, or indirectly by increasing the soil concentration. This occurred for dimethoate and prometryn (soluble, weakly sorbed pesticides), two hr after spraying. Behaviour over longer times is uncertain. Where pesticides were in the soil under the cover, and cover reduced sediment concentrations in runoff, runoff extraction ratios were unaffected for a weakly sorbed herbicide, but were significantly lower (one half) for more strongly sorbed and aged compounds. Further study of pesticide dissipation and washoff from crop residue cover over time after spraying is warranted as retaining cover is a key element in conservation farming systems.

In summary, the rainfall simulator studies, and data from the literature, indicate that runoff extraction is reasonably consistent over a range of conditions found in agriculture. Thus runoff concentrations are closely related to soil concentrations at the start of the event. Importantly, runoff extraction of pesticides with a wide range of chemical properties is similar, unless considerable infiltration occurs during the early stages of the event or low sediment concentrations are transported in runoff. These hydrologic and erosion outcomes do not generally occur during large storms on bare soil but may occur in farming systems that retain surface cover.
CHAPTER 5: PESTICIDE DISTRIBUTION IN WATER AND SEDIMENT
5.1 Introduction

Partitioning of pesticides between solid (soil or sediment) and water phases is important in determining both their mobility and persistence. Runoff of more strongly sorbed pesticides is more manageable using erosion control practices (Walter et al. 1979, Silburn and Connolly 1998). However, more strongly sorbed pesticides may have greater potential to be lost in runoff under erosive conditions, because the pesticide remains at or near the soil surface, available for runoff extraction (Zhang et al. 1997). Similarly there is a positive association between sorption and persistence; more strongly sorbed compounds tend to dissipate more slowly (Hornsby et al. 1996).

Distribution of pesticides between water and sediment phases in runoff ($K_F$), or more usually between water and soil ($K_D$) (due to availability of data, discussed below), is often used in describing the environmental fate and behaviour of nonionic pesticides. Environmental risk assessment is based on several considerations. Firstly, pesticides can be ranked using the partition coefficient as an indicator of likelihood of leaching and groundwater contamination, or transport in runoff (Baker and Johnson 1983). Baker and Laflen (1983) grouped chemicals by $K_D$, as follow:

- $K_D$ greater than 100, lost primarily with sediment,
- $K_D$ in the range 0.1–100, lost primarily with surface runoff,
- $K_D$ less than 0.1, lost primarily with subsurface drainage.

As shown in the preceding chapter, a pesticide’s sorption coefficient may not affect the total pesticide loss in runoff under some hydrologic conditions, but it will certainly affect the mode of transport and efficacy of management practices. Also the hydrologic and erosion conditions that lead to this lack of response of pesticide runoff to sorption coefficient may not always prevail. Secondly, pesticides may be less of a problem in off-site water bodies (e.g. are less bio-active) once bound to sediments. Batley and Peterson (1992) used a pesticide runoff risk assessment method to rank pesticides used in the Australian cotton industry, with a risk factor of: mass applied x percent in water x half-life / LC$_{50}$, where percent in water was determined from fugacity principles and LC$_{50}$ is the concentration that results in 50% mortality of aquatic species. That is, they used partitioning (as % in water) as an indicator of risk to aquatic systems, but not necessarily as an indicator of risk of pesticide runoff itself.

The data most commonly available describing pesticide partitioning is the soil sorption coefficient ($K_{OC}$ or $K_D$). Soil sorption coefficients have been measured for many pesticides, often for a variety of soils (Wauchope et al. 1992, Hornsby et al. 1996). However, soil sorption coefficients are generally measured under specific, laboratory conditions, vary with soil properties (to some extent accounted for by soil OC, Chapter 1), and are often measured in North American and European soils. Sorption coefficients have been measured for only a few pesticides in a limited range of Australian soils (Kookana et al. 1998) and little data is available for higher clay soils used by the Australian...
cotton industry. The other data available are sediment-water partitioning, measured at much higher water-solid ratios. As described below, soil-water and sediment-water partitioning observed in the field may differ from laboratory derived sorption data for a variety of reasons.

5.1.1 Relating pesticide partitioning in runoff and soil sorption

Partitioning is affected by properties of the pesticide, the soil/sediment and the non-filterable materials in the water, as discussed in Chapter 1. After application, a pesticide is subject to adsorption to the soil in the presence of low to very low ratios of water-soil, e.g. generally less than 0.5:1 (at a bulk density of 1140 kg/m³, moisture content is 0.5 g/g at saturation). It may then be subject to cycles of desorption and re-adsorption with changes in soil moisture content, and advection and diffusion into the interior of soil aggregates. During the rainfall event when runoff occurs, water infiltrates into the soil and the pesticide is subjected to desorption, approaching a new equilibrium distribution in the soil pore water-soil matrix, while the water phase is simultaneously leached downwards in the soil. Once runoff begins, pesticide in the water phase in pore water is extracted into runoff via raindrop-accelerated diffusion (Ahuja 1986) while soil particles containing sorbed pesticide are detached to become sediment in runoff. This sediment is subjected to continuous size-selective deposition and re-entrainment; depending on the physical conditions, some or all of the originally entrained sediment is transported in the runoff. The runoff has a much higher ratio of water-sediment than in the soil, e.g. 10:1 at 100 g/L sediment concentration or 100:1 at 1 g/L. The distribution of the pesticide in runoff should reflect the masses extracted in the water and sediment phases, after losses due to deposition, and re-partitioning to equilibrate in the water and sediment in the runoff.

Thus partitioning observed in runoff may differ from that in soil, and more importantly the most commonly available partitioning data, from laboratory sorption studies, may not be directly applicable.

(a) Laboratory soil sorption studies

Pesticide partitioning has generally been studied in the laboratory using soil-water mixtures (batch technique), generally measuring adsorption rather than desorption, to obtain a partition coefficient ($K_D$), which may be normalised using organic carbon content (OC) to give $K_{OC}$ (Wauchope et al. 1992). The slurry mixture is generally shaken for 2-48 hr to obtain a near-equilibrium distribution, with a water-soil ratio higher than for in-situ soil pore water and using vigorous shaking, which may disrupt soil aggregates (Kookana et al. 1998). This may create more time for equilibrium, and more physical contact between pesticides and sorption sites, than occur under field conditions during a rainfall event. Rainfall wetting causes limited breakdown of soil aggregates compared with other methods of wetting (Loch and Foley 1994). Kookana et al. (1998) consider that, for estimating parameters relevant to transport of pesticides in soil profiles, flow techniques are preferable over batch techniques. The flow techniques study the leaching-sorption behaviour while allowing a variety of non-ideal processes (non-equilibrium adsorption/desorption) to operate. Truman et al. (1998b) achieved a similar outcome in the context of partitioning in runoff using a rainfall simulator.
Generally, 50% of the final adsorption occurs within the first few minutes (Karickhoff 1980) and a large proportion occurs in the first hour (Talbert and Fletchall 1965, Novak et al. 1994, Hugo 1999). Similarly, desorption rates for some pesticides are sufficiently rapid that much of the equilibrium concentration is achieved within the time of most storm runoff events (Hance 1976). However, both adsorption and desorption appear to approach equilibrium in two or more phases, a rapid component achieved as described above in minutes or hours and a much slower component which continues for weeks (Karickhoff 1980, Brusseau and Rao 1989, Novak et al. 1994). Wauchope et al. (in press) suggest three phases – rapid (in minutes), intermediate (hr-days) and very slow (resulting in the aging phenomena discussed below) (Chapter 1). The slower phases are viewed as diffusion to or from sorption sites that are inaccessible directly to the bulk water. Brusseau and Rao (1989) consider soil physical non-equilibrium (mobile/immobile water domains) may be more important than chemical non-equilibrium although the two are intrinsically linked\(^\text{D}\). Reversibility of sorption may vary from complete (Karickhoff 1981) to partial (Brusseau and Rao 1989, Clay and Koskinen 1990), although it is sometimes difficult to separate irreversibility, kinetics and dissipation.

One consequence of the slower phase(s) is that sorption coefficients will vary with mixing time. Talbert and Fletchall (1965) found \(K_D\) values for five s-triazines attained a large proportion of their final values in just 1 hr, but continued to increase over four days of adsorption. In the most extreme cases, \(K_D\) values for prometryn and propazine increased by a further 40% and 60%, respectively. Note that this result could also be explained by continuing breakdown of soil aggregates during the experiment. Determining whether these slower phases are of practical consequence to pesticide runoff is more difficult – are they out weighed by other uncertainties, as suggested by Pionke and DeAngelis (1980). Models that assume instantaneous linear-equilibrium sorption often give adequate predictions (Leonard 1990). However, more complex sorption models (e.g. two-compartment models with two phases of sorption) often perform better in reproducing results of specific experiments, particularly leaching studies (Boesten and Van Der Pas 1983, Brusseau and Rao 1989, Li et al. 1999) but also in the rare cases where they have been applied to pesticide runoff (Truman et al. 1998a).

Another consequence of bi-phasic sorption is that sorption coefficients will vary with water flow through a soil mass; like a batch study where water is being removed and replaced with clean water. For example, if 90% of a pesticide could be desorbed in one hr and the remainder was very slowly desorbed, after one hr of water infiltration the pesticide remaining in the soil is a more tightly sorbed component. A batch desorption study, or partitioning in a runoff sample, after one hr would presumably reveal a much greater sorption coefficient than for the original soil, so long as desorption was limited to a reasonably short mixing time\(^\text{E}\). Pignatello (1989) performed such an experiment,

\[^{D}\] It has been shown that fast-slow chemical kinetics and immobile-mobile flow lead to the same solution to the convection-dispersion equation (Nkedi-Kizza et al. 1984).

\[^{E}\] Baker et al. (1978b) referred to this phenomenon, from a runoff point of view (discussed in Section 5.2.2), as "selective extraction".
except that the ‘fast’ phase was first removed from the soil by volatilisation, and found the partition coefficient increased over an order of magnitude through successive aqueous extractions.

The magnitude of the increase in sorption coefficient would presumably be greater at longer time of contact of the pesticide with the soil. Because the slower phases are related to desorption of pesticide from the interior of soil aggregates/organic particles, where it arrived by the ‘slow’ process of diffusion during adsorption (assuming no change in soil water content), the duration of prior adsorption should determine the proportion in the slow compartment. Conversely, immediately after a pesticide was sprayed on a soil a proportion may be sorbed, but mostly on the surface of soil aggregates. Increasing intensity of adsorption with duration of prior adsorption, or contact with soil, is referred to as aging.

\( (c) \) Aging in soil

The forgoing discussion mainly relates to processes that occur in a soil-water system within say 24 hr of mixing. However, changes in sorption also occur over time periods of weeks or months after application of a pesticide and in the intervening periods between rainfall and runoff events. Apparent sorption coefficients, based on observed partitioning in runoff, have been observed to increase with time of contact with soil (Smith et al. 1978, Leonard and Wauchope 1980, Leonard 1990, Truman et al. 1998ab). Boesten and Van Der Pas (1983) found that soil-water slurry desorption coefficients measured 56 days after application of cyanazine and metribuzin were 2-3 times those from laboratory slurry adsorption studies. After 121 days, desorption coefficients were six times and eight times laboratory values, for cyanazine and metribuzin, respectively. Pesticide models that do not account for this behaviour will tend to over-predict leaching (Boesten and Van Der Pas 1983). When two-compartment sorption was added to GLEAMS, the model predicted increasing sediment phase partitioning with time, as observed in runoff, and gave improved predictions of pesticide behaviour in soil and runoff (Truman et al. 1998).

Leonard (1990) suggests a possible explanation for the effects of aging is pesticide diffusion into the soil organic matter particles with subsequent desorption becoming kinetically inhibited, that is, dominated by the intermediate to very slow phases of Wauchope et al. (in press). Diffusion into soil aggregates or areas of immobile soil water would result in similar behaviour. The processes that cause \( K_D \) to increase with time would not operate continuously at the same rate, and the rate of increase would slow with time, i.e. \( K_D \) should approach a plateau. Therefore some model, such as CALF/VARLEACH (Walker and Barnes 1981, Cohen et al. 1995) represent time variability of sorption in soil as \( K_D(t) = K_{D1} + S(t^{1/2}) \), where \( K_D(t) \) is the \( K_D \) at time \( t \) (days), \( K_{D1} = K_D \) on the first day, \( S = \) slope of the \( K_D\)-time\(^{1/2} \) dependence (Eqn. 1-3).
5.2 Conceptual framework

5.2.1 Pesticide distribution in runoff

In the literature, the distribution of pesticides in runoff is often reported as the percent or fraction of the total in the water and sediment phases. Measured percentages in the water phase in agricultural runoff studies vary reasonably systematically between pesticides of differing properties, albeit with wide ranges of percent in water (Fig. 5.1 Wauchope 1978). Soluble pesticides are generally transported in the water phase (e.g. picloram, 2,4-D salts). Those with low solubility are dominantly transported in sediment (e.g. DDT). For intermediate solubilities, there is a large change in percent in water phase over a limited range in solubility (~ -0.5-+1.5 logSOL or 0.32-32 mg/L). Pesticides with solubilities in this range may have a ‘foot in each camp’. MSMA and paraquat have other properties (strong sorption to clay surfaces) that cancel out effects of their high solubility. Data used in Fig. 5.1 were mainly from plots or small catchments under cropping, presumably with reasonable high rates of soil erosion. For this relationship to hold in the low solubility/low percent in water range, there must be sufficient sediment in the runoff (as discussed below).

![Partitioning of pesticides between water and sediment in runoff (range reported in literature) as a function of solubility (mg/L). MSMA and paraquat strongly sorbed to clay surfaces, which cancels out effects of their high solubility. The upper values for trifluralin are erroneous (RD Wauchope, pers. comm. 2003). (Source: Wauchope 1978).](image)

Fig. 5.1 provides a useful, simple guide to how certain pesticides behave. However, many of the pesticides used in the Australian cotton industry, and in particular endosulfan, and recently introduced pesticides are not included. Reported values for endosulfan appear to conflict. For example, during studies of endosulfan in the Australian cotton industry, 80-90% was transported in the

160
water phase from irrigated fields near Warren (Kennedy et al. 1998, 2001), 60-70% under simulated rain near Warren (Hugo 1999), 20-30% in major erosion events at the Queensland field study (Simpson et al. 1996, 1998.), 27% based on fugacity (Batley and Peterson 1992), compared with 90-98% in irrigation tailwater in California (Spencer et al. 1985) and 20% based on solubility (Fig. 5.1).

Some of this variation in percent in the water phase may relate to differences in soil properties (e.g. organic carbon) and to time of contact with the soil discussed above. White et al. (1976) found 2,4-D in runoff from rainfall simulator plots 1- and 8-days after application was mostly associated with the water phase, 86% and 73%, respectively (as expected, since 2,4-D is not strongly sorbed to soil), but at 35 days after application more of the 2,4-D was transported in the sediment phase with only 37% in water. However, as will be demonstrated in this chapter, percent in water phase in runoff also varies systematically with the sediment concentration in runoff as well as with properties of the pesticide, resulting in a wide range in responses and apparent inconsistencies of reported values.

(a) An equation for percent of pesticide in runoff in the water phase

Mulkey and Falco (1977) developed equations for estimating the fraction of pesticide in runoff in the water phase, which are re-derived here. Pesticide distribution between solution and solid phases (soil or sediment) can be described with a simple (linear isotherm) partitioning coefficient ($K_P$): -

$$K_P = \frac{C_s'}{C_w}$$

Eqn. 5-1

Where $C_s'$ (mg/kg) is concentration in sediment and $C_w$ (mg/L) is concentration in water, and $K_P$ has units of L/kg. $C_s'$ equates to concentration in sediment per unit of water volume $C_s$ (mg/L) divide by concentration of sediment in runoff (SC, kg/L)

$$C_s' = \frac{C_s}{SC}$$

Eqn. 5-2

Thus, with concentrations expressed per unit of water volume (eg. µg/L or mg/L)

$$K_P = \frac{C_s}{SC C_w}$$

Eqn. 5-3

Or

$$C_w = \frac{C_s}{K_P SC} \quad \text{and} \quad C_s = K_P SC C_w$$

Eqn. 5-4

As the total concentration per unit volume equals the sum of $C_w$ and $C_s$, or $C_W(1 + K_P SC)$, the fraction transported in the water phase ($F_{wat}$) is:

$$\text{Fraction in water phase} = \frac{1}{1 + SC K_P} = \frac{1}{(1 + SC \ K_{OC} (OC%/100))}$$

Eqn. 5-5

Likewise, the fraction in the sediment phase is

$$\text{Fraction in sediment phase} = \frac{SC K_P}{(1 + SC K_P)} = \frac{SC K_{OC} (OC%/100)}{(1 + SC \ K_{OC} (OC%/100))}$$

Eqn. 5-6
K_p is the product of K_{OC} and the fraction of organic carbon (OC). Thus, for a particular pesticide (K_{OC}), the percentage in the water phase is dependent on sediment concentration and organic carbon content. As linear partitioning was assumed, there is no dependence of this equation on pesticide concentrations, which may not always be the case. Also if K_p increases with aging or is greater for desorption than adsorption, the percentage in the water phase will be reduced accordingly.

5.2.2 Partition coefficients observed in runoff studies

To use Eqn. 5-5 or more complex models to estimate distribution of pesticides in sediment and water, appropriate values of partition coefficients are required. One approach to determining partition coefficients (K_p) appropriate for pesticide runoff, as opposed to soil-water partitioning (K_D), is to calculate them from concentrations measured in sediment and water phases in runoff.

**K_p compared to K_D.** Baker and Laflen (1979) found K_p values in runoff from rainfall simulator plots within 12 hr of application, for propachlor, atrazine and alachlor, were 3-4 times their soil-water K_D values. Spencer et al. (1985) found that apparent K_p values in irrigation runoff were greater than generally reported in laboratory studies (i.e. K_D values). This was not explained by enrichment of finer sediment and organic matter, since the sediment had similar composition to the bulk soil. Bowmer et al. (1986) found Freundlich adsorption coefficients (k) for glyphosate in turbid irrigation water several orders of magnitude higher that reported previously for soils (though this may be caused by differences in P concentrations competing for adsorption sites, Chapter 1). Gouy and Belamie (1993) found K_p values in runoff from rainfall simulator plots (4 pesticides on 3 soils) were considerably greater than K_D values from batch studies on the soils. K_p values decreased with increased sediment concentration. Prediction of pesticide runoff using the CREAMS model (Knisel 1980) was improved when the K_p values were used rather than the K_D values. Truman et al. (1998b) found that partitioning coefficients measured in runoff and splash from small rainfall simulator plots were at least 31 times greater than reported K_D values for atrazine, chlorpyrifos and 2,4-D.

In part, these observations may be related to sediment enrichment and to the increases in apparent K_D with time of contact of pesticides with soil noted above – runoff events may occur weeks or months after pesticide application whereas K_D reported in laboratory studies are generally for much shorter contact times. This is illustrated by K_p values calculated from the data of White et al. (1976) for 2,4-D in runoff from rainfall simulator plots 1-, 8- and 35 days after application; K_p values were all much higher than soil-water K_D values (0.2-1.0 at 1%OC, Wauchope et al. 1992) and increased with time after application – 128, 349 and 2000, respectively. Similarly, K_p calculated for atrazine in runoff from the rainfall simulator plots of White et al. (1967) increased from 1.8 at 1 hr after application to 4.5 at 96 hr. K_p values for methoxychlor and endosulfan in runoff, calculated from catchment data of Willis et al. (1987), also increased during 0-20 days after application.

**K_p during a runoff event.** Baker et al. (1978b) found that K_p calculated from concentrations in rainfall simulator runoff increased considerably from the first 1/3 of the rainfall event compared with during the last 2/3. Increase in K_p was greatest for fonofos (4-7 time increase), which was applied
several weeks before, was incorporated and is more sorbed, than for surface applied fonofos (x1.5), and for alachlor (x1.6) and cyanazine (x1.4) applied to the surface only 48 hours before rain. Truman et al. (1998b) found that effective partitioning coefficients for atrazine, chlorpyrifos and 2,4-D measured in runoff from small rainfall simulator plots increased gradually during a rainfall event. They considered that instantaneous equilibrium was not achieved and that non-equilibrium conditions existed during the rainfall event. Baker et al. (1978b) attributed this to "selective extraction", where the less tightly bound component of the pesticide is washed-off (and would also be leached) first; consistent with the view of Wauchope et al. (in press) that sorption is multi-phasic. Explanations for these phenomena will be explored further in the Discussion.

To summarise, pesticide partitioning observed in runoff indicates that, for pesticides used in the cotton industry, (a) distribution (i.e. percent in water phase) should relate to pesticide properties (Fig. 5.1), but (b) will vary depending on sediment concentration in runoff according to Eqn. 5-5, (c) partition coefficients may be considerably greater than soil-water KD values, and (d) that partition coefficients increase with time of contact of the pesticide with the soil. Factors involved in causing Kp values to be greater than KD, and to increase with time, are given in the Discussion.

One way to determine partition coefficients applicable to pesticide runoff is to observe partitioning in runoff, for which rainfall simulators are a useful approach. The rainfall simulator provides an opportunity to calculate partition coefficients relevant to behaviour of pesticides during rainfall, runoff and erosion for the particular field situation. These coefficients relate to desorption of pesticides from soil aggregates that are partially broken down at a wetting rate and with energy inputs appropriate to rainfall. Prior to desorption under rain the pesticides have been applied, moved into the soil and dissipated under field conditions, and had some time, days or weeks, in which to diffuse into the soil matrix and into the interior of aggregates.

5.2.3 Aims

The aims of the research described in this chapter were, for conditions and pesticides used in the Australian cotton industry, to:

1. Determine partitioning between sediment and water under field runoff conditions for various pesticides (as partitioning affects transport processes and efficacy of management options).
2. Assess the utility of simple models for sediment-water distribution of pesticides.
3. Determine the value of small plots/rainfall simulation for providing reasonable estimates of sediment-water distribution of pesticides.
5.3 Methods

5.3.1 Data sources

Data for distribution of pesticides in sediment and water phases in runoff were taken from the three rainfall simulator studies used in the previous chapter – Gatton, Emerald and Jondaryan. Bulk runoff samples were taken to provide a flow-weighted mean concentration during the applied rainfall event. These samples were filtered and used to determine pesticide concentrations in the sediment and water phases. The pesticides studied and methods used for obtaining pesticide concentrations in sediment and water phases are given in Chapter 2. The event average runoff concentrations observed, in total and in the sediment and water phases, are presented in Chapter 4. Data are averaged for the two plots under the simulator, unless otherwise indicated. Event average sediment concentrations in runoff used here were determined by dividing total soil loss by total runoff for the event.

Endosulfan and prometryn were studied at all three sites, dimethoate at two and a number of other pesticides at Emerald and Jondaryan (5 organophosphate insecticides and 7 herbicides), as described in Chapters 2 and 4. Data available varied slightly from that in the previous chapter:
- At Gatton, “bulk” runoff samples were only analyzed from a subset of plots,
- At Emerald, “bulk” runoff samples were not collected for one plot,
- At Jondaryan, concentrations in the sediment and water phases were available for monocrotophos and parathion methyl (not used in the previous chapter as no data were available for soil concentrations). Conversely, DDE and endosulfan sulfate were not detected (<DL) in the water phase, so could not be reported here.

Distribution of pesticides in sediment and water phases in runoff are presented in two ways:
(a) Percent of total loss in the water phase, allowing comparison with similar data from the literature, and
(b) Sediment-water partition coefficients (\(K_P\) and \(K_{OC}\)). \(K_P\) values (L/kg) were calculated for the “bulk” runoff samples as concentration of pesticide in sediment (mg/kg) divided by concentration of pesticide in water (mg/L). \(K_{OC}\) values were calculated by dividing \(K_P\) by the fraction of organic carbon in the surface soil (Table 2.1).

The term partition coefficients or \(K_P\) is used to refer to sediment-water partitioning (i.e. in runoff) whereas soil sorption coefficient or \(K_D\) is used to refer to soil-water partitioning.
5.4 Results and discussion

5.5 Part A. Percent of pesticide losses in the water phase

Results from the three sites, including any effects of treatments, follow. Comparison between pesticides and their relationship to pesticide properties are then considered jointly in section 5.5.3.

(a) Gatton

Percentages of pesticide in the water phase in runoff decreased with time after spraying for all pesticides, based on limited data from bare plots at Gatton (Table 5.1). This is consistent with partitioning coefficient ($K_p$) increasing with time after spraying (see below), as both percent in water phase and $K_p$ are calculated from the same data. Endosulfan compounds had lower percent in the water phase than prometryn and dimethoate. Percentages of pesticide in the water phase were similar for bare and covered plots at two hr after spraying, because sediment concentrations were similar, although total runoff and soil losses were one third of those from bare plots (Chapter 4). Covered plots produced greater concentrations of prometryn and dimethoate in runoff (Chapter 4), however this occurred in both the water and sediment phases, with the distribution more or less similar.

Table 5.1. Percent of total pesticide transported in the water phase in runoff, for rainfall simulator plots at 2 hr and 9 days after spraying at Gatton. Values are means of two or more plots. (<DL - not detected in water phase).

<table>
<thead>
<tr>
<th>Time after Spraying</th>
<th>Percent in water phase in runoff</th>
<th>Endosulfan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>Bare</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hr</td>
<td>46</td>
<td>24</td>
</tr>
<tr>
<td>9 days</td>
<td>29</td>
<td>15</td>
</tr>
<tr>
<td>Covered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hr</td>
<td>42</td>
<td>25</td>
</tr>
</tbody>
</table>

(b) Emerald

Percent of pesticide in the water phase was significantly greater for covered plots (wheat stubble and cotton mulch retained) than for bare and cotton trash mulched plots, for all pesticides except DDE (Table 5.2). Percent of DDE in the water phase was so low (<1%) that differences between treatments were not detectable. The increase in percent in water with cover reflects the lower concentrations of sediment in runoff from covered plots (Chapter 6). Logically, with less sediment in runoff, the proportion in the water phase will approach 100%. Percent in water depends on sediment concentration and $K_p$ as expressed by Eqn. 5-5. The increased percent in the water phase with cover (Table 5.2) is fully accounted for by the lower sediment concentrations with higher cover, for all pesticides, as described by Eqn. 5-5, as discussed in Section 5.5.2. This is reinforced by the fact that, for each pesticide, $K_p$ did not vary with cover (see below).
Table 5.2. Percent of loss in the water phase in runoff for cover treatments and Blocks 2 and 5, on rainfall simulator plots at Emerald. Wheel traffic was n.s.d. for all pesticides. Values were also calculated with Eqn. 5-5 and solubility (Wauchope 1978). (CT- cotton trash; WH – wheat).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sediment Concentration (g/L)</th>
<th>α</th>
<th>β</th>
<th>Sulfate</th>
<th>Total</th>
<th>Trifluralin</th>
<th>Prometryn</th>
<th>DDE Block 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Days since spraying :-</td>
<td>4-7</td>
<td>4-7</td>
<td>---</td>
<td>4-7</td>
<td>50</td>
<td>15-18</td>
<td>~17 yrs</td>
</tr>
<tr>
<td>Comparing cover treatments</td>
<td>Bare</td>
<td>19.4</td>
<td>27.6a</td>
<td>17.7a</td>
<td>23.7a</td>
<td>20.4a</td>
<td>8.2 a</td>
<td>78.7 a</td>
</tr>
<tr>
<td></td>
<td>CT mulched</td>
<td>17.0</td>
<td>29.8a</td>
<td>19.0a</td>
<td>23.0a</td>
<td>21.7a</td>
<td>7.6 a</td>
<td>81.6 a</td>
</tr>
<tr>
<td></td>
<td>WH stubble</td>
<td>6.4</td>
<td>50.9b</td>
<td>34.4b</td>
<td>47.3b</td>
<td>38.5b</td>
<td>15.1 b</td>
<td>91.8 b</td>
</tr>
<tr>
<td></td>
<td>CT retained</td>
<td>5.6</td>
<td>63.0b</td>
<td>41.7b</td>
<td>27.9a</td>
<td>44.2b</td>
<td>20.0 b</td>
<td>92.5 b</td>
</tr>
</tbody>
</table>

Significance P=0.001 P=0.005 P=0.002 P=0.004 P=0.011 P=0.016 n.s.d.

Plots with < 10 % cover (Bare and cotton trash mulched)

<table>
<thead>
<tr>
<th></th>
<th>Days since spraying :-</th>
<th>4-7</th>
<th>4-7</th>
<th>---</th>
<th>4-7</th>
<th>50</th>
<th>15-18</th>
<th>~17 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare</td>
<td>19.6</td>
<td>25.5 a</td>
<td>15.7 a</td>
<td>19.5 a</td>
<td>18.4 a</td>
<td>6.7 a</td>
<td>80.8 a</td>
</tr>
<tr>
<td></td>
<td>CT mulched</td>
<td>16.7</td>
<td>35.7 b</td>
<td>24.3 b</td>
<td>33.3 b</td>
<td>27.2 b</td>
<td>11.1 b</td>
<td>78.4 a</td>
</tr>
</tbody>
</table>

Significance P=0.009 P=0.004 P<0.001 P=0.006 P=0.02 n.s.d. n.s.d.

Estimate from Eqn. 5-5 and Wauchope (1978)

<table>
<thead>
<tr>
<th></th>
<th>Days since spraying :-</th>
<th>4-7</th>
<th>4-7</th>
<th>---</th>
<th>4-7</th>
<th>50</th>
<th>15-18</th>
<th>~17 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eqn. 5-5</td>
<td>20</td>
<td>27</td>
<td>16</td>
<td>22</td>
<td>19</td>
<td>10</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Wauchope (1978)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>20</td>
<td>8</td>
<td>80</td>
<td>5</td>
</tr>
</tbody>
</table>

Taking cases with greater sediment loads (15-25 g/L), that is, bare and cotton trash mulched plots, percent of pesticide in the water phase varied, from 0.5% of DDE, to 80% of prometryn, with endosulfan 18-27% and trifluralin 7-11% (Table 5.2), consistent with Wauchope (1978) based on solubility (Table 5.2), discussed further in a later section. The percentage in water increases in order of increasing solubility and decreasing soil sorption (Table 2.4), except that endosulfan in the water phase was higher than trifluralin, which has a lower published sorption coefficient. This also occurred at Jondaryan and may be because the trifluralin was more aged in the soil than endosulfan at both sites. Discrepancies are not surprising considering the soil sorption values in Table 2.4 are selected from a wide reported range (Wauchope et al. 1992).

The percentage in the water phase was not significantly different for wheel and non-wheel tracks – runoff, soil loss, pesticide losses and concentrations were all higher for wheel tracks (Chapter 6 & 7), but sediment concentrations and pesticide partitioning were not. The percentage in water for the endosulfan compounds and trifluralin was significantly higher for Block 5 than Block 2 (Table 5.2), even though concentrations in the water and sediment phases were not significantly different (Chapter 7). This is explained by 15% lower average sediment concentration and slightly more cover on average for plots in Block 5, as described by Eqn. 5-5 (Section 5.5.2). Prometryn did not respond in this way as it is much less sorbed to sediment, while the response of DDE in confounded by low levels in water. This variation between Blocks is indicative of how percent transported in water is variable, due to differences in sediment-water ratio.
The percentage in the water phase in runoff at Jondaryan was similar for blanket and band-sprayed plots (at the same times after spraying) but was affected by time after spraying and ranged from 10 to 90% for the various pesticides (Table 5.3). At longer times after spraying, percentage in water ranked in decreasing order: trifluralin, pendimethalin, diuron, endosulfan=20%, 50%, prometryn=metolachlor, fluometuron, Py_Na. The organophosphates, at 1-5 days after spraying (after which they were no longer detected), ranked: chlorpyrifos, parathion-methyl, 50%, profenofos, monocrotophos=dimehotox. For endosulfan, α-, sulfate and total endosulfan typically had a slightly greater percentage in the water phase than the β-isomer, though they were all similar at 34 days.

Table 5.3. Summary of percentage of pesticide in the water phase in runoff from bare rainfall simulator plots, at various days since spraying at Jondaryan, and at Gatton and Emerald.

<table>
<thead>
<tr>
<th>Pesticide (common name)</th>
<th>Percent in water phase</th>
<th>Days since spraying:--</th>
<th>Gatton</th>
<th>Emerald</th>
<th>Jondaryan</th>
<th>Jondaryan</th>
<th>Jondaryan</th>
</tr>
</thead>
<tbody>
<tr>
<td>INSECTICIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-</td>
<td>29</td>
<td>29</td>
<td>40</td>
<td>28</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>β-</td>
<td>15</td>
<td>18</td>
<td>24</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Sulfate</td>
<td>&lt;DL A</td>
<td>24</td>
<td>16</td>
<td>26</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>Total</td>
<td>22</td>
<td>21</td>
<td>32</td>
<td>24</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>DDE</td>
<td>---</td>
<td>0.5 [17yr]</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organophosphates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>--- B</td>
<td>---</td>
<td>27</td>
<td>22</td>
<td>&lt;DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parathion methyl</td>
<td>---</td>
<td>---</td>
<td>37</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profenofos</td>
<td>---</td>
<td>---</td>
<td>55</td>
<td>27</td>
<td>&lt;DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>---</td>
<td>---</td>
<td>95</td>
<td>49</td>
<td>&lt;DL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethoate</td>
<td>64</td>
<td>---</td>
<td>95</td>
<td>70</td>
<td>71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HERBICIDES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trifluralin</td>
<td>---</td>
<td>8 [50d]</td>
<td>39</td>
<td>41</td>
<td>7 (&gt;1yr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>---</td>
<td>---</td>
<td>25</td>
<td>18</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diuron</td>
<td>---</td>
<td>---</td>
<td>45</td>
<td>29</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>---</td>
<td>---</td>
<td>77</td>
<td>50</td>
<td>59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prometryn</td>
<td>72</td>
<td>80 [17d]</td>
<td>89</td>
<td>83</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluometuron</td>
<td>---</td>
<td>---</td>
<td>90</td>
<td>79</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrithiobac sodium</td>
<td>---</td>
<td>---</td>
<td>92</td>
<td>---</td>
<td>68 (25d), 72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A - <DL = concentration in water phase, and sometime total concentration in runoff, below detection limit, e.g. organophosphates at > 5d after spraying.
B - '---' = pesticide either not applied, not present or not analysed.

Thus the pesticides tend to fall into two groups, with lower values (i.e. <50%) for endosulfan, pendimethalin, diuron, trifluralin, chlorpyrifos, profenofos and parathion-methyl, and higher values (i.e. >50%) for pyrithiobac sodium, fluometuron, metolachlor, prometryn, dimethoate and monocrotophos. However, the more water-transported group still had 30-40% in sediment at longer times after spraying (e.g. after 10 days) while the more sediment-transported pesticides still exhibited a significant proportion in the water phase, particularly in the first few days after application, declining
to 10-20% in water at longer times. That is, none of these pesticides can be expected to have only minute concentrations in the water phase in runoff (like e.g. DDE at Emerald; paraquat, Leonard et al. 1979), rather concentrations would be at least one tenth of total concentration. Similarly, all pesticides had some component transported in sediment, which should be manageable using erosion control practices. Thus all these pesticides tended to have a foot in each camp to some extent.

The percentage in the water phase decreased with time after spraying (Table 5.3), consistent with the increase in $K_p$ reported below. Time after spraying was significant in regression analysis for all pesticides (generally with $R^2>0.85$), except $\beta$-endosulfan and endosulfan sulfate (excluding five organophosphates, with data for only one or two plots). The decline in the percentage in water with time after spraying appears non-linear, decreasing more rapidly during the first five days after spraying and approaching a plateau at longer times (Fig. 5.2). A power function gave a better fit to the limited data than an exponential or log function. This behaviour is consistent with the non-linear relationships found between partition coefficients and time after spraying (presented below).

![Fig. 5.2](image_url)

**Fig. 5.2.** Percentage in the water phase in runoff with time after spraying, from rainfall simulator plots at Jondaryan. Only selected pesticides are shown for clarity. Other endosulfan compounds, trifluralin and parathion-methyl more or less plot with the low percent in water group, while pyrithiobac sodium, metolachlor, dimethoate and monocrotophos plot with the higher group.

The poor relationship of percent in water and time after spraying for $\beta$-endosulfan (for no apparent reason) and endosulfan sulfate resulted in a poor relationship for total endosulfan, though an overall decrease still occurred. No relationship would be expected for the sulfate, which was not applied as such, and would be of variable age within and between plots.

Other plot variables (furrow slope, rainfall intensity, infiltration amount, runoff amount and sediment concentration) were not significant in regression analysis on percent in the water phase.
These variables only varied over a small range for the Jondaryan plots. Percent in the water phase is related to sediment concentrations for some individual pesticides, for example endosulfan, as discussed in the next section. However, the differences between pesticides and the more extreme times after spraying had a greater effect on percent in the water phase.

5.5.2 Endosulfan runoff in the water phase

Endosulfan was studied at all three sites, and in a number of studies mentioned in Section 5.2.1, providing an opportunity to compare its behaviour in various situations. For the simulator studies, percent in the water phase varied between 15-45%. Fig. 5.3 shows that most of this variation is related to differences in (a) sediment concentration, and (b) time since spraying, or more directly, increase in the partition coefficient with time since spraying. The three sites, coincidentally, had reasonably similar soil OC (1.1-1.3%, Table 2.1) removing some potential variation in partitioning.

The data for endosulfan for the three sites, for longer times after spraying, fall on and around a single theoretical relationship with sediment concentration, derived using Eqn. 5-5 with $K_{OC}=12,400$ ($K_{P}=161$ for longer times after spraying and $K_{P}=50$ for 2hr after spraying at Gatton. The data for 2 days after spraying at Jondaryan, which sits between the two lines in Fig. 5.3, would fit on a line using $K_{P}=75$, the partition coefficient for runoff from these plots.

Thus the observed variation in percent in the water phase for endosulfan (15-45%) is mainly related to differences in sediment concentration and time after spraying. Once these factors are considered partitioning was reasonably similar between the sites. At longer times after spraying, the
soil-water partition coefficient, $K_{OC}=12,400$, given by Wauchope et al. (1992), describes partitioning at the three sites well. The analysis also shows that when data are available to calculate the percent of a pesticide in the water phase and the sediment concentration is known, a partition coefficient can be calculated and Eqn. 5-5 can be used to provide useful insights into how that pesticide might behave if variables such as sediment concentration and organic carbon content were different.

The utility of Eqn. 5-5 is illustrated for the percentages in the water phase for endosulfan observed in the USA and in Australian cotton studies over the past decade. Field observations of endosulfan in the water phase in runoff varied from:

- 90-98% for irrigation tail-water in the Imperial Valley, California (Spencer et al. 1985),
- 80-90% in a NSW cotton field near Warren (Auscott field 4) (Kennedy et al. 1998, 2001),
- 60-70% in a rainfall simulator study (Auscott field 34) near Warren (Hugo 1999)
- 20% in major erosion events, reducing to 90% for more minor events (e.g. sediment concentration ~1 g/L) in irrigated fields at Emerald (Simpson et al. 1996, 1998).

All of these observations are consistent once differences in sediment concentration and OC% are taken into account using Eqn. 5-5 (Fig. 5.4). A $K_{OC}$ value of 12,400 was used for the Australian studies with their soil OC values, resulting in different $K_P$ values for each site. For Imperial Valley, a $K_{OC}$ value of 40,000 and OC=0.62%, reported by Spencer et al. (1985), were used. Thus each site has its own relationship between percent in water and sediment concentration (Fig. 5.4).

![Fig. 5.4. Percent endosulfan in water phase in runoff as a function of sediment concentration for data from other studies. Lines are calculated with Eqn. 5-5, using $K_{OC}=12,400$ for Australian sites and $K_{OC}=40,000$ for Imperial Valley, California (Spencer et al. 1985).](image-url)
The reported average percentages of endosulfan in the water phase and average sediment concentrations are close to the theoretical line for each site. Thus the large variation in reported values of percent in the water phase are explained by differences in sediment concentration and soil organic carbon at the sites, using (for Australian sites) a single value of $K_{OC}$. Even for the California site, this $K_{OC}$ value would have given a reasonable estimate, because at low sediment concentrations the percent in the water phase approaches 100% for all values of $K_{OC}$.

Thus for endosulfan in runoff, there is a wide range of percentages in water possible, e.g. 10–95%, due to the range in sediment concentration than might occur from cotton fields (1-40 g/L). Also, the soil organic carbon has a reasonably large effect, with much higher percent in the water phase for the lower OC soils. On soils with OC of 0.5% (not uncommon after some years of cultivation), the majority of endosulfan in runoff will be in the water phase. Increasing the soil OC will improve the potential for erosion control practices to manage endosulfan runoff. Ironically, these erosion control practices will reduce the sediment concentration and increase the percent of endosulfan in the water phase, but the total loss and concentration in runoff would be substantially reduced (Chapters 6 & 7).

Of the components of endosulfan, percent in the water phase was 1.5-2 times greater for $\alpha$-endosulfan than for $\beta$-endosulfan at shorter times after spraying (e.g. <10 days), consistent with their sorption coefficients (Table 2.3), but becoming similar at longer time after spraying (Table 5.1, Table 5.3). Percentages for endosulfan sulfate and total endosulfan were generally intermediate between those of the parent isomers. Total endosulfan in the water phase depends on the proportions of the $\alpha$-, $\beta$- and sulfate present. Thus it may be elevated for a time after spraying while $\alpha$-endosulfan is most prevalent (due to its higher proportion in applied endosulfan, 70:30 $\alpha$-:$\beta$-) then decrease as $\beta$-endosulfan becomes relatively more prevalent (as $\alpha$-endosulfan dissipates more rapidly, Chapter 3) and trend towards the behaviour of sulfate at longer times as it becomes the predominant form.

Endosulfan in the water phase may not be truly in solution and may be associated with particulates not removed during sediment-water separation. Peterson and Batley (1993a) found percentages desorbed from sediment into water of up to 18%, 12% and 14% for $\alpha$-, $\beta$- and sulfate endosulfan, respectively. They considered these proportions greater than expected for such an apparently hydrophobic compound and suggest this was due to high concentrations of colloidal particles in the water produced by shaking the sediment and water. Similarly, Karickhoff and Brown (1978) found a large proportion of paraquat (a compound highly sorbed to clay surfaces) in the water phase was in fact still sorbed to particulates not removed by the sediment-water separation. They point out that sediment-water separations are not absolute and that “solution” phase measurements do not necessarily measure only dissolved or “free” compound. However, from the point of view of transport off-site in runoff, it is probably the component that acts like a dissolved compound that matters, whether it is truly dissolved or not. The data presented above indicates high percentages of endosulfan in the water phase can occur in runoff; the solubility of endosulfan would allow concentrations of up to 320 $\mu$g/L in water in the absence of enough (competing) sorptive material.
5.5.3 Comparison between pesticides and with other data

(a) Relationship to solubility

The percent in the water phase in runoff from bare plots for many of the pesticides related reasonably well to solubility as described by Wauchope (1978) in Fig. 5.1, for shorter times after spraying (Fig. 5.5). These include data for 2 hr at Gatton and 2 days at Jondaryan, and endosulfan at Emerald (4-6 days after spraying). Total, \( \beta \)- and sulfate endosulfan and the more soluble compounds fits the general relationship well. However, \( \alpha \)-endosulfan at 2 hr (Gatton) and 2 days (Jondaryan) after spraying had 40-45% in the water phase compared with 20% estimated from Wauchope’s curve. Profenofos and metolachlor also had about 20% less in the water phase of than estimated from the curve, but are within the typical range of some of the data (e.g. see fonofos). Diuron and parathion methyl had 36% and 47% less in the water phase than estimated from solubility; their sorption does not appear to be well described by their solubility in this case. Parathion methyl has a sorption coefficient more than an order of magnitude higher than generally found for non-ionic compounds of similar solubility (see Fig. 5.7 and the relationship between solubility and sorption below). This is not the case for diuron – rather its sorption at Jondaryan was much stronger than generally reported.

![Graph showing pesticide loss in water phase vs. log of solubility](image-url)

**Fig. 5.5.** Comparison of percent pesticide loss in water phase in runoff from bare rainfall simulator plots at three sites, at shorter times after spraying against their solubility (from Wauchope et al. 1992), overlayed on the data reviewed by Wauchope (1978).
At longer times after spraying, percentages in the water phase in runoff were lower than at earlier times. These data coincided closely with the relationship with solubility (Wauchope 1978) for pesticides with solubilities less than 1.0 (Fig. 5.6). This included trifluralin (7-8% in water phase) and DDE (< 1% in water phase) for which no data were available at short times after spraying. Percent loss in water for DDE was in the bottom of the range for DDT, probably because the DDE was considerably aged in the soil. The endosulfan compounds were more tightly grouped than at shorter times after spraying, with α-endosulfan no longer present in the water phase at higher levels, and were more consistent with the relationship with solubility.

At longer times after spraying, pesticides with solubilities greater than 10 had considerably lower percentages in the water phase than at shorter times after spraying and than the 90-100% in water found by Wauchope (1978) (Fig. 5.6). Only 60-70% was found in the water phase for all the more soluble compounds, with the exception of prometryn at Emerald, which still had only 80% in the water phase. The distribution of 2,4-D in runoff from the rainfall simulator plots of White et al. (1976) also indicates large reductions in percent in water with time after spraying (Fig. 5.6).

Fig. 5.6.  Comparison of percent pesticide loss in the water phase in runoff from bare plots at three sites, at longer times after spraying, overlayed on the data reviewed by Wauchope (1978) (the upper values for trifluralin are erroneous). Data are from: Gatton 9 days, Emerald >14 days, Jondaryan 34 days after spraying.
Profenofos and diuron, with intermediate solubilities (10-100), had much lower percent in the water phase than the relationship with solubility predicts, even more so than at shorter times after spraying. Percent in the water phase could not be calculated for parathion methyl five days after spraying as concentrations in water were below the detection limit. However, the concentration measured in the sediment phase (µg/L) was slightly greater than that in total in runoff (sediment and water), indicating that the parathion methyl remaining at five days after spraying was fairly strongly sorbed and that percent in water was probably declining similar to the other pesticides (Fig. 5.2).

The results in Fig. 5.5 and Fig. 5.6 indicate that (a) the relationship with solubility (Wauchope 1978) provides a useful indication of distribution in runoff of recently applied pesticides under conditions found in Australian cotton fields, (b) a number of pesticides not originally included fit the relationship, and (c) percent in the water phase decreases with time after spraying, particularly for less soluble compounds. This should improve the effectiveness of erosion control in controlling runoff of these pesticides. In general, estimates of percent in water from the relationship in Fig. 5.5 will be more prone to inaccuracy for log solubilities between 0 and 2 (solubilities of 1-100), that is, in the steeply rising part of the curve. Above and below this range, sorption is either so weak or so strong that reasonably distinct behaviour is likely. However, this relationship will only hold where the runoff contains sufficient sediment; as sediment concentration decreases the percent in the water phase will increase systematically according to Eqn. 5-5, as illustrated for endosulfan above (Fig. 5.3, Fig. 5.4). Some of the range in percent in the water phase found by Wauchope (1978) is probably related to differences in sediment concentration.

(b) Relationship with soil sorption coefficients

Wauchope (1978) used solubility as the predictive pesticide property, however this is presumably a surrogate for more direct measures of partitioning. Solubility and soil sorption are correlated for many groups of non-ionic compounds (Chiou 1990, Wauchope et al. 1992). Solubilities for the pesticides used by Wauchope (1978) in Fig. 5.1, and those studied here, have a reasonably strong (though imprecise) inverse relationship to soil sorption (Fig. 5.7). Wauchope et al. (1992) found a strong inverse relationship for all non-ionic pesticides in their database, approximated by \( K_{OC} = 3000/\sqrt{SOL} \). The majority of \( K_{OC} \) values in the database were within a factor of three of the estimate from the equation and all values were within a factor of 10. Even so, there is quite a range in \( K_{OC} \) values for pesticides with solubilities of 1-1000, that is, in the range where percent in water phase in runoff increases rapidly. Solubility is a property of the compound in water, whereas \( K_{OC} \) will vary (e.g. over an order of magnitude) depending on the properties of the soil. Paraquat and MSMA are examples of pesticides with particular properties that would not be expected to fit such a relationship. Properties other than solubility may better capture the distribution in runoff of such compounds.

The ranges for percent in water phase in runoff from Fig. 5.1 are shown in Fig. 5.8 plotted against the “selected” soil sorption (\( K_{OC} \)) values from Wauchope et al. (1992). The relationship is more or less the inverse of the solubility-percent in water phase relationship. Pesticides with low and
high $K_{OC}$ values have high and low percent in the water phase, respectively. A large change (decrease) in percent in the water phase occurs for $K_{OC}$ in the range 500 to 5000, which relate to $K_D$ values of 5–50 for OC=1%. Paraquat and MSMA now fit the general relationship, as hopefully will other such tightly sorbed ionic pesticides. Parathion-methyl does not fit the general relationship.

![Graph showing inverse relationship between solubility and soil sorption $K_{OC}$ values.](image)

**Fig. 5.7.** Inverse relationship between solubility and soil sorption $K_{OC}$ values from Wauchope *et al.* (1992), for the pesticides in Wauchope (1978) and this study. The equation for non-ionic pesticides $K_{OC} = 3000/\sqrt{\text{SOL}}$ (Wauchope *et al.* 1992) is also shown. MSMA and paraquat are strongly sorbed to clay surfaces.

The data from the rainfall simulator plots in the first few days after spraying coincide with the data of Wauchope (1978) when plotted against the $K_{OC}$ values Fig. 5.8. This includes profenofos, diuron and parathion methyl, which did not fit so well when related to solubility. At longer times after spraying (data not shown), percent in water from these plots was lower as discussed above. For more tightly sorbed compounds, i.e. those around endosulfan, this improved the fit to Wauchope's data. For the more poorly sorbed compounds, percent in water was 20-30% lower, around the bottom of the range of data from Wauchope (1978). This reflects the increase in partition coefficients away from the "selected" $K_{OC}$ values, as discussed below. If the actual partition coefficients were used, these data would move to the right in Fig. 5.8, closer to the general relationship.

The rainfall simulator data indicate that the high values of percent in water for parathion methyl, given by Wauchope (1978), which did not fit the general relationship, are somewhat anomalous. The original studies from which they were derived presumably involved conditions that were significantly different from those in the other studies, such as very low sediment concentrations and/or sediment of very low organic carbon content. The data of Spencer *et al.* (1985) and Kennedy *et al.* (1998, 2001), with high percentages in the water phase for endosulfan (discussed above), from irrigation runoff with
low sediment concentrations and low organic carbon contents, would similarly not fit with the other data when compared with either solubility or KOC. The high values of percent in water for trifluralin, given by Wauchope (1978), which do not fit the general relationships with solubility or KOC (Fig. 5.8) are in error (RD Wauchope, pers. comm., 2003).

These empirical relationships between percent in the water phase and either solubility or KOC only hold where sediment concentrations are similar to those in the original studies. Where sediment concentration is low the percent in the water phase will increase as shown by Eqn. 5-5 in Fig. 5.3 and Fig. 5.4. In reality, these empirical relationships, while providing a useful guide to differences in behaviour of various pesticides for reasonably erosive field conditions, are only a sub-set of possible outcomes defined by Eqn. 5-5. The curve shown in Fig. 5.8 is just one of a family of curves, depending on the sediment concentration and organic carbon, as illustrated below.

Leonard (1988, 1990) illustrated Eqn. 5-5 and used it to show the relationship between erosion control and pesticide runoff (Fig. 5.9, Fig. 5.10). For a pesticide of a given KP there is a wide range in percent transported in water i.e. from 0-100%, depending on the concentration of sediment in runoff. A pesticide with a very low KP (e.g. <5) will mainly be transported in water (80-100%) so long as sediment concentration is not very high (e.g. >100g/L), while pesticides with very high KP (e.g.
50,000) will be mainly transported in sediment so long as there is some sediment in the water. However, pesticides with intermediate $K_p$ (e.g. 10-10,000) can occur over a wide range of percent in water or sediment. Thus erosion control (i.e. reducing sediment concentration) will have some useful effect in reducing runoff transport of a wide range of pesticides. A 30% reduction in runoff losses of a poorly sorbed compound ($K_p = 10$, Fig. 5.10) is possible by reducing sediment concentration from 50-100 g/L (typical for bare fallow at slopes >4%) to 1-5 g/L (achievable with stubble retention). However, it is also apparent that almost all pesticides with $K_p$ values greater than 1000 will present some fraction of their losses in agricultural runoff in dissolved form.

Eqn. 5-5 also illustrates the effect of soil organic carbon (OC) on partitioning of pesticides into runoff sediment and water phase (in so far as $K_p$ is linearly related to OC and sediment has the same OC as the soil it eroded from). The net effect is that a pesticide, which has a particular $K_{OC}$, will present a range of $K_p$ values depending on the OC content of the soil/sediment and will therefore vary in percent transported in the water phase in runoff depending on soil/sediment OC (Fig. 5.11).

A pesticide with $K_{OC}=200$ (e.g. metolachlor) can have 5% in sediment in runoff with 40 g/L sediment for OC of 0.5%, but has 30% in sediment when OC=5%, because $K_p$ varies from 1 to 10. This is consistent with the field runoff results for metolachlor of Buttle (1990), who found sediment was an important vector for transport of metolachlor in runoff, with total losses in the sediment phase of 31-46% from upslope areas (OC=2.7%, slope ~9%) and 20-37% in toe-of-slope areas (OC=4.7%, slope 1.6-3.3%). These results are explained by the high sediment concentrations occurring (e.g. ~100 g/L) and the reasonably high OC status.
Similarly, endosulfan ($K_{OC}=16,400$) can have 40 to 5% in water (20 g/L sediment) for OC from 0.5-5%, because $K_P$ varies from 82-820, and will have a greater proportion in the water phase as the sediment concentration is reduced. One outcome of the general decline in soil organic carbon of agricultural soil under cultivation, and particularly soils used for growing cotton in Australia where OC of 0.5-1.5% is not uncommon, is that a greater proportion of pesticides will be transported in the water phase where they may be more difficult to manage.

![Fig. 5.11. Percent of pesticide loss in the water phase in runoff as a function of sediment concentration in runoff and soil/sediment organic carbon, for $K_{OC}$ of 200 (e.g. metolachlor) and $K_{OC}$ 16,400 (e.g. endosulfan), derived from Eqn. 5-5.](image)

While the equation used here (Eqn. 5-5) is useful, for instance in solving an apparent dilemma in the observed runoff behaviour of endosulfan, it does require reasonable estimates of partition coefficients for pesticides and soils of interest, preferably under field conditions during runoff. The use of the rainfall simulator to derive such data is presented in the following section.
5.6 Part B. Sediment-water partition coefficients $K_P$ and $K_{OC}$

(a) Gatton

Sediment-water partition coefficients ($K_P$ and $K_{OC}$) for bulk runoff samples from plots at Gatton rank in decreasing order, endosulfan, dimethoate, prometryn, with $\beta$- greater than $\alpha$-endosulfan (Table 5.4). These partition coefficients are compared with other sites, and with published values, in a later section. $K_P$ values were similar for bare and covered plots (2 hrs after spraying) for all pesticides, as was found for percent in the water phase (Table 5.1). $K_P$ values for endosulfan compounds were similar for plots two hrs after spraying with EC and ULV formulations.

Table 5.4. Mean sediment-water partition coefficients $K_P$ and $K_{OC}$ for Gatton (OC=1.3%) for runoff from plots two hr after one spray and for plots sprayed twice (6-15 and 1-9 days after spraying).

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Time since first spray -</th>
<th>$K_P$</th>
<th>Times Increase</th>
<th>$K_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 hr</td>
<td>6-15 days</td>
<td>1-9 days</td>
<td>2 hr</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>None</td>
<td>2 hr</td>
<td>6-15 days</td>
<td>1-9 days</td>
</tr>
<tr>
<td>Alpha</td>
<td>28.3</td>
<td>77.6</td>
<td>2.7</td>
<td>2,200</td>
</tr>
<tr>
<td>Beta</td>
<td>81.7</td>
<td>224.2</td>
<td>2.7</td>
<td>6,300</td>
</tr>
<tr>
<td>Sulfate</td>
<td>No data</td>
<td>No data</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Total</td>
<td>43.3</td>
<td>112.1</td>
<td>2.6</td>
<td>3,300</td>
</tr>
<tr>
<td>Prometryn</td>
<td>3.3</td>
<td>14.2</td>
<td>4.3</td>
<td>250</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>4.7</td>
<td>18.3</td>
<td>3.9</td>
<td>360</td>
</tr>
</tbody>
</table>

$K_P$ values increased with time after spraying for all the pesticides (Fig. 5.12), consistent with the decrease in percent in the water phase (Table 5.1). $K_P$ values increase rapidly in the first day and then more slowly from 1-9 days. Two hours after spraying, $K_P$ values were less than one-half those at latter times (1-9 days) for endosulfan and about one-quarter for prometryn and dimethoate (Table 5.4). Thus pesticides, when freshly sprayed, appear to be poorly sorbed into the soil matrix/aggregates and are more readily desorbed during rainfall, but are more tightly sorbed after about one day of contact with the soil. This behaviour soon after spraying (within one day) may also be related to formulation components such as surfactants that solubilize the pesticide; these rapidly breakdown or separate from the active ingredient (RD Wauchope, pers. comm. 2003). $K_P$ values relate well to $\ln$(days since last spraying) with $R^2$ greater than 0.97 for all pesticides except $\beta$-endosulfan ($R^2=0.79$) (Fig. 5.12). Relating the increase in $K_P$ to the square root of days since spraying (Walker and Barnes 1981) under-predicted the initial rapid increase in $K_P$ and did not plateau as rapidly as the data (Fig. 5.12).

Realistically this study by itself had too little data to identify the shape of the relationship. Also some of the plots were sprayed once and some twice, six days apart. While $K_P$ values increase with time since the first or last spray, this confounds deriving a relationship. A proportion of the first spray is in a more ‘aged’ compartment in the soil (more resistant to desorption and higher $K_P$). Data were plotted against days since the last spray, as this should be the most influential. Concentrations of pesticides in soil (Chapter 3) indicate more than half of the first endosulfan and prometryn
applications, and about 90% of the dimethoate, dissipated from the soil by the second application. In either case, the data indicate that in the first few hours after application, the pesticides were less well sorbed, with $K_P$ increasing towards an upper threshold over time, possibly within one day.

![Graph showing partition coefficients ($K_P$) for bulk runoff samples from Gatton plots, plotted against time since last spray, with fitted In equations (solid lines) and time$^{1/2}$ equations (dashed).](image)

**Fig. 5.12.** Partition coefficients ($K_P$) for bulk runoff samples from Gatton plots, plotted against time since last spray, with fitted In equations (solid lines) and time$^{1/2}$ equations (dashed).

(b) Emerald

Percent in water phase, concentrations in sediment (mg/kg) and in water ($\mu$g/L) all exhibited significant differences between cover treatments (Table 5.2 and Chapter 7). However, $K_P$ for $\alpha$-, $\beta$- and total endosulfan, prometryn, trifluralin and DDE were not significantly different between cover treatments, wheel traffic or between Blocks 2 and 5. This indicates that the treatments affected total concentration of each pesticide, while distribution between water and sediment followed partitioning processes that were independent of treatments. However, this did not occur for endosulfan sulfate; $K_P$ was significantly lower for wheat stubble plots (about one-half) and significantly higher for cotton trash retained plots (about double), compared with other treatments ($P<0.001$). Sediment sizes also varied considerably between these cover treatments (Chapter 6). While this is believed to have influenced transport of the more ‘aged’ pesticides including endosulfan sulfate (Chapter 7), it does not explain why endosulfan sulfate alone gave variable $K_P$ values. This would require desorption to vary with sediment size (which may occur), but this did not occur for the other pesticides.

$K_P$ and $K_{OC}$ values rank in decreasing order: DDE, trifluralin, endosulfan, prometryn, with $\beta$-, sulfate, $\alpha$-endosulfan (Table 5.5). Partition coefficients varied by 30-40% of mean values between plots, for all pesticides except DDE. $K_P$ values were more variable for DDE, probably because concentrations of DDE in the water phase were very low, however this variation was small compared to the large difference of DDE to the other pesticides. All plots were sprayed at more or less the same
time before plots were run, so time since spraying did not influence partitioning. Partition coefficients are compared with other sites, and with published values, in a later section.

Table 5.5. Sediment-water partition coefficients (Kp and Koc) in runoff from Emerald rainfall simulator plots, averaged for all treatments (N=14). Kp values were not significantly different for cover or wheel traffic treatments (except endosulfan sulfate – see text), or between Blocks 2 and 5.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Site</th>
<th>Kp Mean</th>
<th>Kp Standard error</th>
<th>Koc (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>&amp; (% of mean)</td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-</td>
<td></td>
<td>137</td>
<td>48 (35%)</td>
<td>10,200</td>
</tr>
<tr>
<td>β-</td>
<td></td>
<td>260</td>
<td>99 (38%)</td>
<td>19,300</td>
</tr>
<tr>
<td>Sulfate</td>
<td></td>
<td>179</td>
<td>51 (28%)</td>
<td>13,200</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>221</td>
<td>77 (35%)</td>
<td>16,400</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Block 2 (B)</td>
<td>719</td>
<td>306 (43%)</td>
<td>53,200</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Block 2 (B)</td>
<td>14.1</td>
<td>6 (42%)</td>
<td>1,040</td>
</tr>
<tr>
<td>DDE</td>
<td>Block 2 (B)</td>
<td>15,050</td>
<td>11,080 (74%)</td>
<td>1.00x10^6</td>
</tr>
<tr>
<td>Block 5</td>
<td></td>
<td>9,190</td>
<td>426 (5%)</td>
<td>0.66x10^6</td>
</tr>
</tbody>
</table>

A. Soil organic carbon (OC) = 1.3 % for Block 2 and 1.4 % for Block 5.
B. DDT is assumed to have different application histories on Block 2 and 5.

(c) Jondaryan

Partition coefficients for runoff from Jondaryan plots increased significantly with time since spraying (2-34 days) for most of the 13 pesticides that had measurable concentrations in both water and sediment. Partition coefficients for most pesticides increased rapidly between two and five days and more slowly at longer times after spraying (Fig. 5.13), similar to data from Gatton. The data related best to ln(days since spraying) (generally with R^2 >0.90), while the Walker and Barnes (1981) equation (Kp v square root of days since spraying) under-predicted the rapid increase in Kp during the first five days and did not plateau as rapidly as the data, for all pesticides (see examples in Fig. 5.13).

Partition coefficients fell into two main groups. Firstly, pesticides with higher Kp values, being 50-100 at two days after spraying, increasing to 150-300 by day 34 (Fig. 5.13a). These included, in increasing order: total and β-endosulfan, α-endosulfan and diuron, pendimethalin. This does not relate to the order of ‘selected’ values of Koc (Table 2.4): diuron (480), pendimethalin (5,000), endosulfan (12,400). Kp values more or less doubled between 2 and 34 days. Endosulfan sulfate had no trend in Kp with time, with an average of 134. Trifluralin had an average Kp of 574. The OP’s, chlorpyrifos, profenofos and parathion-methyl, also appear to fit with this group (discussed below).

The second group had Kp values of 1-10 at two days after spraying, increasing to 20-40 by 34 days. This group included, in increasing order of Kp: fluometuron, metolachlor, dimethoate and prometryn, with fairly similar Kp, and pyrithiobac sodium (Py_Na) somewhat higher (Fig. 5.13b). Kp values for Py_Na in runoff from the simulator plots were similar to values for tailwater runoff from a furrow irrigation study at Jondaryan, at two times after spraying (data from Silburn 1998) (Fig. 5.13b).
Fig. 5.13. Partition coefficients ($K_p$) in runoff from Jondaryan plots against time since spraying, with
equations fitted against $\ln$(days) (solid line) and examples for days$^{1/2}$.
(a) pesticides with higher $K_p$ values, compared with pyrithiobac sodium (Py_Na),
(b) pesticides with lower $K_p$ values,
(c) organophosphates compared with alpha endosulfan.
Organophosphates had a wide range in $K_P$ values and large changes with time (Fig. 5.13c). Data for the OP's are limits as concentrations, particularly in sediment phase, were often below detection limits at longer times after application, due to low application rates and/or rapid dissipation rates (Chapter 3). Dimethoate was in the low $K_P$ group, with chlorpyrifos, profenofos and parathion-methyl more similar to the high $K_P$ group. Parathion-methyl had a $K_P$ similar to $\alpha$-endosulfan at 2 days after spraying. Monocrotophos had a very low $K_P$ (~2) at 2 days after spraying, similar to dimethoate at that time, increasing to 46 at 5 days. This indicates much greater sorption to sediment than suggested by Wauchope et al. (1992), who give an estimated $K_{OC}$ of 1 (a theoretical estimate due to lack of published data), i.e. a $K_P$ of 0.01 for OC=1%.

5.6.2 Comparison between sites

For the pesticides that were studied at more than one site, $K_P$ values appear to vary more with time after spraying than between sites. The data are therefore summarised separately for longer times after spraying (Table 5.6), which are possibly approaching equilibrium values, and for shorter times after spraying (Table 5.7), which relate to a worse case scenario of a storm soon after spraying. Comparison is somewhat confounded by differences in time since spraying between sites and with the two sequential applications used at Gatton and Emerald. Even so, it is clear that variation in partitioning between sites is not explained by soil properties such as OC content (Table 2.1). OC was similar at the three sites (1.1-1.3%) while $K_P$ values varied by a factor of about two (Table 5.6). $K_P$ values were generally higher at Emerald (greatest CEC) and lower at Gatton (lowest clay content and CEC), and were intermediate for endosulfan but mixed for other pesticides at Jondaryan (highest clay). Realistically, data for a much larger number of soils are needed to determine relationships between partitioning and soil properties reliably.

(a) Partitioning of endosulfan

Sorption data are not widely available for endosulfan isomers, and for endosulfan sulfate in particular. The $K_{OC}$ values measured in runoff for total endosulfan were reasonably similar (±30%) to the value selected by Wauchope et al. (1992) (Table 5.6), though they are lower when recently applied (Table 5.7). The $K_{OC}$ values for $\alpha$-endosulfan are higher than those reported by Peterson and Batley (1993a) (measured after 16 hr adsorption) and values for $\beta$-endosulfan were slightly lower. In the first few days after spraying (Table 5.7) and up until about 15 days (Table 5.6), $\beta$-endosulfan was more strongly sorbed than the $\alpha$-endosulfan. At the longest time after spraying (34 d at Jondaryan), $K_{OC}$ values were higher for $\beta$- than for $\alpha$-endosulfan (Table 5.6). This may be because $\alpha$-endosulfan remaining at this time is a component that is both more sorbed and most resistant to dissipation, particularly volatilisation, as much of the less resistant/sorbed component was dissipated previously. However, the data generally show $\beta$-endosulfan to be less easily desorbed than $\alpha$-endosulfan, consistent with the ‘remobilisation’ study of Peterson and Batley (1993a). Both isomers are much less
sediment-sorbed when first applied (Table 5.7), with $K_{OC}$ values at two hr after spraying one third those after five days or more and one-third to one half of the published values.

The behaviour of endosulfan sulfate is of interest as it is a large proportion of the endosulfan found in cotton fields as the season progresses after multiple applications (Simpson et al. 1998, Kennedy et al. 1998). $K_{OC}$ values measured in runoff indicate that endosulfan sulfate was generally associated with sediment to a similar degree as the parent isomers, with decreasing $K_{OC}$ ranking $\alpha-$, sulfate, $\beta-$endosulfan at Emerald (Table 5.6), consistent with Peterson and Batley (1993a). $K_{OC}$ values were almost twice the value determined by Hugo (1999) for laboratory adsorption.

<table>
<thead>
<tr>
<th>Pesticide (common name)</th>
<th>Partition coefficients</th>
<th>Published $K_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gatton (6-15 DSS)</td>
<td>Emerald (8-11 DSS)</td>
</tr>
<tr>
<td>INSECTICIDES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>78</td>
<td>137</td>
</tr>
<tr>
<td>$\beta$</td>
<td>224</td>
<td>260</td>
</tr>
<tr>
<td>Sulfate</td>
<td>--</td>
<td>179</td>
</tr>
<tr>
<td>Total</td>
<td>112</td>
<td>221</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>18.3</td>
<td>--</td>
</tr>
<tr>
<td>DDE</td>
<td>Block 2(F)</td>
<td>15,050</td>
</tr>
<tr>
<td>Block 5</td>
<td>--</td>
<td>9,190</td>
</tr>
<tr>
<td>HERBICIDES</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trifluralin</td>
<td>--</td>
<td>719</td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>--</td>
<td>260</td>
</tr>
<tr>
<td>Diuron</td>
<td>--</td>
<td>186</td>
</tr>
<tr>
<td>Pyridthiobac Sodium</td>
<td>--</td>
<td>33.2</td>
</tr>
<tr>
<td>Prometryn</td>
<td>14.2</td>
<td>14.1</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>--</td>
<td>(17 DSS)</td>
</tr>
<tr>
<td>Fluometuron</td>
<td>--</td>
<td>22.1</td>
</tr>
</tbody>
</table>

A. Soil organic carbon (OC) = 1.3% Gatton, 1.35 % Emerald, 1.1% Jondaryan.
B. Sources: Wauchope et al. (1992), Hornsby et al. (1996), U - USDA-ARS Pesticide Properties Database.
C. Peterson and Batley (1993a), adsorption to natural sediments (OC 1-5%) after 16 hr mixing.
D. Calculated from Hugo (1999) laboratory adsorption $K_D = 42$ and OC = 0.58 %, after 24 hr mixing.
E. Increases with pH and OC, at OC=0.64%, $K_{OC}=9$, 13 at pH6.5, 7.2, i.e. $K_D = 0.06$ and 0.08.
F. DDT is assumed to have different application histories on Block 2 and 5.
HO Howard (1991) estimated from other properties.

Hugo (1999) measured $K_D$ values for (laboratory) adsorption of endosulfan sulfate that were considerably lower than for the parent isomers. The rate of adsorption during kinetic studies was also much slower for the sulfate. Hugo (1999) considered endosulfan sulfate more soluble, more polar and more hydrophilic than the parent isomers. That is, it should be less sorbed to soil/organic matter than
the parent isomers, as indicated by the lower laboratory adsorption $K_D$. However, in the field, endosulfan sulfate is suggested to be formed in soil by aerobic microbial activity upon the parent isomers after they sorb to the clay/organic matter complex (Hugo 1999). Thus in field situations endosulfan sulfate is formed in, and incorporated into, the clay/organic matter complex in soil and appears more tightly sorbed or more slowly desorbed than during adsorption.

Further study of desorption of endosulfan sulfate at longer times after spraying (e.g. week and months) would be useful to clarify its behaviour under relevant field conditions.

Table 5.7. Partition coefficients ($K_P$ and $K_{OC}$) in runoff from rainfall simulator plots soon after spraying at Gatton and Jondaryan, compared with published soil-water $K_{OC}$. All plots sprayed once.

<table>
<thead>
<tr>
<th>Pesticide (common name)</th>
<th>Calculated partition coefficients</th>
<th>Published $K_{OC}$ $(a)$</th>
<th>Published $K_{OC}$ $(b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_P$ Gatton (2 hr) Jondaryan (2 days)</td>
<td>$K_{OC}$ Gatton (2 hr) Jondaryan (2 days)</td>
<td>Mean</td>
</tr>
<tr>
<td><strong>INSECTICIDES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endosulfan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>28 52</td>
<td>2,200 4,700</td>
<td>4,000$^{C}$</td>
</tr>
<tr>
<td>β</td>
<td>82 113</td>
<td>6,300 10,300</td>
<td>20,000$^{C}$</td>
</tr>
<tr>
<td>Sulfate</td>
<td>--- ---</td>
<td>--- ---</td>
<td>7,240$^{C}$</td>
</tr>
<tr>
<td>Total</td>
<td>43 75</td>
<td>3,300 6,800</td>
<td>12,400</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>--- 96</td>
<td>--- 8,700</td>
<td>6,070</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>4.7 2.0</td>
<td>360 180</td>
<td>20</td>
</tr>
<tr>
<td>Profenofos</td>
<td>--- 28</td>
<td>--- 2,600</td>
<td>2,000</td>
</tr>
<tr>
<td>Parathion-methyl</td>
<td>--- 59</td>
<td>--- 5,350</td>
<td>5,100</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>--- 1.9</td>
<td>--- 170</td>
<td>1(est)</td>
</tr>
<tr>
<td><strong>HERBICIDES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>--- 105</td>
<td>--- 9,500</td>
<td>5,000</td>
</tr>
<tr>
<td>Diuron</td>
<td>--- 43</td>
<td>--- 3,900</td>
<td>480</td>
</tr>
<tr>
<td>Pyrithiobac sodium</td>
<td>--- 7.9</td>
<td>--- 720</td>
<td>13$^{EU}$</td>
</tr>
<tr>
<td>Prometryn</td>
<td>3.3 4.4</td>
<td>250 400</td>
<td>400</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>--- 10.6</td>
<td>--- 960</td>
<td>200</td>
</tr>
<tr>
<td>Fluometuron</td>
<td>--- 3.8</td>
<td>--- 340</td>
<td>100</td>
</tr>
</tbody>
</table>

See Table 5.6 for: A - soil OC%, and B-HO - sources of published data.

5.6.3 Comparison with published sorption data

$K_{OC}$ is used for comparison with published values (Table 5.6) rather than $K_D$ or $K_P$, as $K_{OC}$ should be less dependent on site-specific OC content. Laboratory soil-water sorption coefficients are generally measured after 24 hr of mixing (Wauchope et al. 1991). The published $K_{OC}$ values for α- and β-endosulfan were determined for adsorption to natural sediments (OC 1-5.3%) after 16 hr of mixing (Peterson and Batley 1993a). When compared to these data, $K_{OC}$ values for endosulfan compounds in rainfall simulator runoff were considerably lower at two hr after spraying and increase with time after spraying to be equal to or greater than published values at 4-7 days (Fig. 5.14).

Across the range of pesticides studied two days or less after spraying, $K_{OC}$ values in runoff approximately coincided with published values at about $K_{OC}=5000$ (e.g. α-endosulfan, parathion methyl, profenofos), but are considerably larger than soil-water $K_{OC}$ values as $K_{OC}$ decreases Fig. 5.15.
Thus pesticides generally considered poorly sorbed (e.g. soil sorption according to Wauchope et al. 1992) consistently had much higher partition coefficients in runoff and were more associated with sediment than expected. The more extreme examples are (Table 5.7):
- Dimethoate (published $K_{OC}=20$), with $K_{OC}$ of 360 and 180 at Gatton and Jondaryan, respectively.
- Pyrithiobac sodium (published $K_{OC}=9-21$), with $K_{OC}$ of 720 at Jondaryan.
- Monocrotophos (published $K_{OC}$ estimated as 1), with $K_{OC}$ of 170.

In contrast, prometryn had (somewhat coincidently) very similar $K_{OC}$ to published values (Table 5.7), but at longer times after spraying the $K_{OC}$ values in runoff was several times published values. To a lesser extent, the $K_{OC}$ for fluometuron also approached its published value. This variation in similarity to published values presumably relates, in part, to the sorption chemistry of each individual pesticide in relation to soil properties (OC, clay content and type, pH, CEC, etc.).

At longer times after spraying, runoff $K_{OC}$ values were considerably greater than the published soil sorption coefficients (Table 5.6, Fig. 5.16), especially for trifluralin (at 50 days and ~1 yr after spraying), pendimethalin, diuron, dimethoate and pyrithiobac sodium. There was still a considerable bias towards runoff $K_{OC}$ values exceeding published soil sorption coefficients more at lower $K_{OC}$ values (Fig. 5.16), by as much as 2 orders of magnitude. $K_{OC}$ values in runoff approximately coincided with published values at about $K_{OC}=20,000$ (e.g. endosulfan).

At Emerald, $K_{OC}$ values are generally greater than published values, except for $\beta$-endosulfan, which was similar to the published data (Table 5.6, Fig. 5.16). The $K_{OC}$ value was around twice the published values for $\alpha$-endosulfan, endosulfan sulfate and prometryn (17 DSS), and six times that published for trifluralin (50 DSS). $K_{OC}$ values for DDE (>17 yr since spraying) were much larger than the selected value (50,000, Hornsby et al. 1996), but similar to estimates for the parent DDT.

Fig. 5.16. Partition coefficients ($K_{OC}$) in runoff compared with published soil sorption values from Wauchope et al. (1992), at Emerald and Jondaryan (34d) after spraying, compared with 2d at Jondaryan (dashed line).
5.7 Discussion

This analysis has shown that partition coefficients measured in runoff from rainfall simulator plots increased significantly with time after spraying and therefore had a complex relationship with published soil sorption coefficients. Systematic changes in partitioning occur at two time scales: (a) during the time of mixing or within a runoff event (Baker et al. 1978b, Gouy and Belamie 1993, Truman et al. 1998b) and (b) with time after spraying (this chapter and previous literature) or time of contact. Both phenomena appear to result from the multiple (fast-slow) phases of adsorption-desorption, from a chemical viewpoint, and the heterogeneity of soil solids and pore spaces (mobile-immobile or interior-exterior domains), from a physical viewpoint (Brusseau and Rao 1989, Pignatello 1989, Wauchope et al. in press). Adsorption and desorption are not fully instantaneous and are bi-phasic. Considerable adsorption/desorption occurs in, say, the first hour of mixing, followed by a continuing slower phase over days or weeks (Talbert and Fletchall 1965, Hance 1976, Karickhoff 1980, Novak et al. 1994, Hugo 1999, Wauchope et al. in press).

Results presented here and in the literature (Baker and Laflen 1979, Spencer et al. 1985, Gouy and Belamie 1993, Truman et al. 1998b, and others, Section 5.2.2) indicate that partition coefficients in runoff \((K_P)\) are generally larger than laboratory soil sorption \(K_D\) values. Several factors contribute to this observation. The published values were selected from a range of values often varying over an order of magnitude (Wauchope et al. 1992). Importantly, the soil sorption coefficients used for comparison with runoff \(K_{OC}\) values were not measured on the soils studied with the rainfall simulator and were probably measured on soils of markedly different properties, in particular lower clay contents. The published \(K_{OC}\) values were determined from laboratory studies of adsorption on soil-water ‘slurry’, typically after shaking or mixing for 24 hr. In contrast, the runoff partition coefficients result from desorption, after considerable time of contact (days-weeks) and a comparatively short time of mixing (<40 min). These conditions all tend to increase the apparent \(K_P\), as explained below.

In reality, direct comparison of general laboratory measures of sorption with field observations where dynamics have an important influence on sorption is difficult – the laboratory method and the rainfall simulator are measuring different things. For a fair comparison the laboratory studies would need to consider these dynamics. It is arguable that the rainfall simulator gives useful estimates of field partitioning behaviour (Gouy and Belamie 1993), but not necessarily any more so than desorption studies on aged soil. Indeed, further (reasonably simple) studies of desorption of pesticides through time of contact in soil, such as that of Boesten and Van Der Pas (1983) would be informative.

A further factor that can influence partitioning in runoff, as compared to in the soil, is sediment enrichment. If the composition of the sediment was considerably enhanced, in particular in organic carbon, by preferential transport of carbon-rich sediment, partition coefficients in runoff would be greater than for the soil (Leonard et al. 1979). However, comparison of organic carbon in sediment and in the soil during the rainfall simulator studies indicated little enrichment occurred. This is reasonably typical of erosion on clay soils (Rose and Dalal 1988) where sediment is dominantly
composed of aggregates with similar composition to the bulk soil. Concentrations of pesticides in sediment also indicate no enrichment compared to the soil, rather concentrations were depleted (i.e. were less than in the soil) due to desorption (increasingly so with less sorbed pesticides) and (suspected) lower concentrations in the surface few mm of soil than in the sampled depth (Chapter 4).

The partitioning observed in runoff was influenced by two main factors – time after spraying and the sorption tendency of the pesticide (the time of mixing being short in all cases). Thus taking the more extreme states of each factor, there are several main cases, which are considered below.

Case (i) – short time, high K_D. In the first few days after spraying, more sorbed compounds such as endosulfan can exhibit K_P values lower than K_D values (Fig. 5.14), because the time of contact and the time of mixing are short. The short time of contact with the soil means that, firstly, a component of the recently sprayed pesticide is incompletely sorbed into the soil matrix/aggregates, increasing contact between the applied water and the pesticide. There is also the possibility that formulation components such as surfactants solubilize the pesticide for a short time after spraying; these then breakdown rapidly or separate from the active ingredient (RD Wauchope, pers. comm. 2003). Secondly, because the pesticide has not diffused into the interior of soil aggregates, sediment particles are below their potential equilibrium concentration. The first factor increases the water phase concentration while the second factor decreases the sediment phase concentration; both contribute to a decrease in the partition coefficient. A short time of mixing would generally result in a higher K_P value. However when the pesticide is mostly on the exterior of soil particles slow kinetics cannot limit desorption and time of mixing will have little influence.

Case (ii) – longer time, high K_D. For more sorbed pesticides at longer times after spraying, when more of the pesticide is in the interior of soil particles and slow kinetics can limit desorption, a short time of mixing will contribute to higher K_P values. As the fast (exterior) phase has been depleted (by dissipation) and the slow (interior) phase has increased (by diffusion) before the runoff event, water phase concentration is reduced and sediment phase concentration increased, and K_P is higher. The slow phase pesticide buried in organic solids or in micro-pores of soil aggregates is considered inaccessible to microorganisms and degradation (Pigatello 1989). Thus there is a greater proportion of ‘slow’ to ‘fast’ phases with aging and an increase in partition coefficient. The results for endosulfan and other pesticides are consistent with this logic, which is basically saying that pesticide sorption in soils behaves according to a two-compartment, bi-phasic (fast-slow) model (Karickhoff 1980, Pigatello 1989, Truman et al. 1998a).

Case (iii) – low K_D pesticides. For less sorbed compounds (e.g. K_OC <1000 or K_P <10), K_P values were greater than K_D values, increasingly so for less sorbed compounds and with greater time after spraying. Thus compounds that would normally to be considered weakly sorbed, with K_D values of one or less (i.e. dimethoate, fluometuron and pyrithiobac sodium) had partition coefficients in runoff of 20-30, or 20-200 times greater than expected. This is probably caused by preferential leaching of the ‘fast’ phase out of the runoff-mixing layer during the rainfall event, particularly before
runoff begins. Once runoff occurs, only the remaining ‘fast’ phase is available to be extracted into the runoff. Meanwhile the tightly bound ‘slow’ phase is not desorbed in the time of the runoff event. Pignatello (1989) considered that ‘resistant’ fractions (difficult to desorb but not irreversible and maybe a ‘very slow’ fraction) and slow kinetic reactions are possible for compounds normally considered to be weakly sorbed. The result is the “selective extraction” described by Baker et al. (1978b) and higher apparent $K_P$ values. With greater time after spraying, the proportion of ‘fast’ phase decreases and the proportion of ‘slow’ phase increases, further increasing the $K_P$.

Compared with the more sorbed pesticides, weakly sorbed pesticides will exhibit much more transient behaviour during the runoff event. The data considered here were flow-weighted averages for each runoff event, so these transient processes occurring within the event were averaged. Because runoff did not begin immediately, average water phase concentrations were reduced because some of the ‘fast’ phase was removed and sediment phase concentrations were increased by inclusion of the ‘slow’ phase, and the $K_P$ is increased. As runoff progresses, the proportion of ‘fast’ to ‘slow’ phases decreases, resulting in an increasing apparent partition coefficient, as observed by Guoy and Belamie (1993) and Truman et al. (1998a). The ‘slowness’ of desorption of the ‘slow’ phase inhibits repartitioning. The runoff-mixing layer under rain is a continuous dilution system, unlike a batch sorption study, and this study suggest that non-equilibrium desorption conditions exist as found in the more detailed studies of Truman et al. (1998a).

These results have consequences for management of pesticide runoff and for planning and interpreting pesticide runoff studies. Because partitioning, expressed as percent in the water phase or as a partition coefficient, changes with time after spraying, especially during the first few days after spraying, the choice of when after spraying to run experiments such as rainfall simulator plots is important. This is not to say that plots run very soon after spraying give ‘wrong’ answers — in fact, they probably represent the true worst case critical scenario — they just don’t represent behaviour at longer times, which may be more representative of the majority of runoff events. Time after spraying should always be included as an experimental variable in studies of pesticide runoff and partitioning. This also applies to interpreting past pesticide runoff studies, e.g., many rainfall simulator studies have been run soon after spraying (24-48 hr), which may have over-emphasised water phase transport.

### 5.7.1 Models for change in partitioning with time after spraying

The increase in $K_P$ values with time after spraying appeared to relate to ln(days). Relating the increase in $K_P$ to the square root of days, as suggested by Walker and Barnes (1981) for soil sorption, under-predicted the rapid early increase in $K_P$ and did not plateau as rapidly as the data. When the equations are fitted to the (short term) measured data and extrapolated out to 365 days (Fig. 5.17), the days$^{0.5}$ equation predicts a continuously increasing $K_P$ with time for both weakly (dimethoate) and more sorbed (endosulfan) pesticides. This is unlikely and more importantly, leads to a large deviation away from known $K_P$ values with time. The ln(days) equation at least gives a more conservative
extrapolation. However, at short times the ln(days) equation is problematic because the fitted intercept can have negative values, whereas the days$^{0.5}$ equation has a fixed initial value of $K_P$.

Fig. 5.17. Comparison of ln (days) (solid lines) and days$^{0.5}$ (dashed lines) equations for increase in partition coefficient $K_P$ with time after spraying over one year.

In reality, neither equation has any physical basis. A two-compartment kinetic model is probably preferable, so long as it can mimic the observed behaviour (as demonstrated by Truman et al. 1998a). Further study of pesticide desorption and runoff partitioning is required, over longer times after spraying (i.e. over say four or five half-lives of the pesticide in soil), to better define the changes that occur and to develop suitable models.

5.8 Conclusion

Partitioning between the sediment and water phases in runoff from rainfall simulator studies was considered, in terms of the percentage in the water phase and as partition coefficients, for pesticides with a wide range of properties. Particular attention was paid to endosulfan, for which reported values of percentage in the water phase appeared to conflict.

Observations of percentage of endosulfan in the water phase vary widely, from less than 20% to greater than 95% in the literature, and from 15% to 45% in the rainfall simulator studies depending on site, crop residue cover and time after spraying. However, all reported values are explained by differences in sediment concentration and soil/sediment organic carbon, using a simple equation derived from first principles (Eqn. 5-5). Thus for endosulfan, there is a wide range of percentages in water possible, e.g. 10–95%, due to the range in sediment concentration and soil/sediment organic carbon than might occur in cotton fields.
Percentage in the water phase in runoff varied systematically with pesticide solubility. In the first few days after spraying, percent in water for a wide range of pesticides used in the cotton industry agreed with the empirical relationship with solubility derived by Wauchope (1978). However, several pesticides of moderate/intermediate solubility had less in the water phase than predicted with the relationship – percent in the water phase changes rapidly, from about 5% to 90% in this range of solubility. Percent in the water phase decreased with time after spraying for each pesticide, consistent with an increase in partition coefficient. Thus at longer times after spraying (e.g. 5-10 days) more soluble pesticides had lower percentages in the water phase than suggested by the relationship with solubility and would be somewhat more manageable using erosion control practices than is generally thought. Conversely, water phase transport is significantly different when rain occurs in the first 24 hr after spraying. For example, at two hr after spraying, the percentage of endosulfan in water phase was almost twice that observed when rain was applied latter.

The analysis indicated that the relationship with solubility, and a similar relationship with soil sorption coefficients, were useful first approximations for estimating the percentage in water phase in runoff for a range of pesticides used in the Australian cotton industry. However, the empirical relationships only apply where runoff contains a sufficiently large sediment concentration and do not account for the observed increase in partition coefficient with time. Where a partition coefficient and sediment concentration can be estimated, partitioning in water and sediment can be calculated using a simple equation. Where sediment concentration varies widely, particularly to low values, or partition coefficients increase with time after spraying, particularly for more soluble chemicals, it is an over simplification to expect ‘percent in water’ to be a characteristic of a particular pesticide.

Partition coefficients in runoff were similar for bare soil and crop residue cover and for wheel traffic treatments, for pesticides with a wide range in sorption, even though these treatments had large effects on runoff, sediment and pesticide runoff concentrations (Chapter 7). That is, the treatments affected sediment concentrations and concentrations of each pesticide, while distribution between water and sediment followed partitioning processes that were independent of treatments. This makes interpreting effects of management practices on partitioning easier, as the distribution in water and sediment phases can be calculated using Eqn. 5-5 with a constant $K_P$ value for each pesticide.

Partition coefficients in runoff ($K_P$) from the rainfall simulator studies increased with time after spraying and were generally greater than soil sorption $K_D$ values, increasingly so for pesticides of lower sorption. Therefore pesticides that would normally be considered very poorly sorbed had $K_P$ values considerably greater than their soil sorption coefficients, particularly at longer times after spraying. Conversely, endosulfan, which is considered moderately/highly sorbed, had partition coefficients in runoff considerably lower (and water phase transport higher) than its soil sorption coefficient in the first day or so after spraying. $K_P$ values increased rapidly in the first few days after spraying and more slowly over the next few weeks, for all pesticides. Thus partition coefficients in runoff were not a constant for a pesticide-soil combination.
Partitioning appears to be influenced by both time of contact with soil (after spraying) and time of mixing (during rain or in the laboratory). The results are conceptually consistent with a two-compartment, bi-phasic (fast-slow) adsorption-desorption model (Karickhoff 1980, Pignatello 1989, Truman et al. 1998a) with the soil in the runoff-mixing layer under rainfall being a continuous dilution system, unlike a batch sorption study, under non-equilibrium desorption conditions. The ‘slow’ phase sorption, due to diffusion into soil domains that are less accessible to desorption, leads to increasing partition coefficients in runoff with greater time of contact. The continuous dilution leads to an interaction whereby the ‘fast-slow’ system is more influential for more weakly sorbed pesticides, whether this is because the compound is inherently poorly sorbed or due to a short time of contact. That is, when there is a greater ‘fast’ fraction for whatever reason. The short time of mixing under rain means that the water phase is mainly interacting with the ‘fast’ or most accessible fraction. Infiltration before runoff starts removes/relocates some of the ‘fast’ fraction in the runoff-mixing layer. The short time of mixing limits diffusion of the ‘slow’ fraction out of the interior of soil solids or the sediment phase.

The rainfall simulator appears to provide useful estimates of pesticide partition coefficients applicable to runoff and some insights into their dynamic nature. These findings have consequences for managing pesticide runoff and for planning experimental studies.
CHAPTER 6. MANAGEMENT PRACTICES FOR CONTROL OF RUNOFF LOSSES FROM COTTON FURROWS UNDER STORM RAINFALL. I. RUNOFF AND SEDIMENT ON A BLACK VERITOSOL
CHAPTER 6. MANAGEMENT PRACTICES FOR CONTROL OF RUNOFF LOSSES FROM COTTON FURROWS UNDER STORM RAINFALL. I. RUNOFF AND SEDIMENT ON A BLACK VERTOSOL

6.1 Introduction

In 1998-99, cotton (Gossypium hirsutum L.) was grown on some 550,000 ha in inland New South Wales and Queensland (Cotton Yearbook 1999). Some 82% of the area was irrigated, predominantly by furrow irrigation. In the current production system, the potential for soil erosion by water in the summer cropping season is enhanced by summer dominant rainfall, occurrence of high intensity thunderstorms, frequent irrigation leaving the soil wet and causing erosion directly, and management practices that leave the soil bare. Erosion potential is reduced by the low slopes (e.g. <1%) of many irrigated fields. A review of available data (Chapter 1), concluded that runoff from cotton fields of 100–200 mm/year was typical. Annual soil losses (8–12 t/ha) are higher than expected given the low slopes, partly due to direct and indirect effects of irrigation. This soil erosion leads to sedimentation of farm drains and off-farm drainage networks (Connolly et al. 1999). Given the levels of pesticide usage in cotton production, considerable transport of pesticides occurs in runoff and sediment from cotton fields (Kennedy et al. 1998; Simpson et al. 1998), and may contribute to contamination of inland waterways (Muschal and Cooper 1998).

Concerns about pesticides in the cotton industry and impacts on the riverine environment were raised in the LWRRDC/CRDC/MDBC program ‘Minimising the Impact of Pesticides on the Riverine Environment’ initiated in the mid 1990’s (Schofield 1998). Program aims included development of practical and economic methods to minimise transport of pesticides from application sites, and development of best management practices (BMP). To achieve these aims, improved cotton farming systems, which reduce sediment and pesticide transport from cotton fields while maintaining or improving production, are needed. Historically there has been little development of conservation cropping systems for irrigated cotton in Australia, as evidenced by the bare soil on all but a few small areas of irrigated cotton. In developing such farming systems general principles of soil and water conservation developed in dryland cropping (Freebairn et al. 1996) should be applicable.

Retention of crop residues to provide surface cover is one of the most effective and robust management principles developed for dryland conservation cropping (Freebairn et al. 1996). Retention of cover was also effective in managing soil erosion under cotton in the United States. Mutchler et al. (1985) found that (dryland) cotton production creates very erodible field conditions.

---

1This chapter was published with minor changes as:
Soil losses were considerably higher during conventionally tilled cotton than for soybeans and corn under similar tillage. Soil loss and runoff were reduced significantly when cotton was grown in crop residues retained, without tillage, from wheat and soybeans crops. Mutchler and McDowell (1990) found that soil erosion from fields growing cotton could be controlled with no-till and reduced tillage systems when a winter cover crop provided cover during the cotton crop. No-till gave the greatest control as it retained the greatest cover. Soil loss was not controlled to acceptable levels when conventional tillage (disk, chisel, disk) preparation for cotton planting buried the cover crop residues, or with any of the tillage systems (conventional, reduced or no-till) without cover in addition to the cotton canopy. Both studies used residues from crops prior to the cotton crop to provide cover under the cotton, as it is difficult to provide sufficient cover for erosion control in cotton-cotton rotations.

Carroll et al. (1995) determined that the critical period for soil erosion from irrigated cotton in the Emerald Irrigation Area (EIA) was early in the growing season, from pre-plant irrigation to canopy closure. During this period there is a high risk of runoff and soil erosion, due to low cover levels, low soil moisture deficits, unconsolidated soil and occurrence of intense storms.

A management practice that is well established in the Australian cotton industry, and is now being adopted in grain cropping, is controlled traffic. In an 8-row cotton system, tractor wheel traffic is restricted to two of the inter-rows (furrows) while a further two furrows receive traffic from implement wheels. Furrows used frequently for tractor wheel traffic are expected to be more compacted, and give more runoff and soil loss, than non-wheel tracks (Baker and Laflen 1979).

Several features of furrow irrigated cotton are different to dryland grain cropping studied in previous conservation cropping research in Australia, apart from use of irrigation. Furrow irrigated cotton is generally grown on low sloping lands (<1%) whereas erosion research in dryland cropping has been on steeper slopes (>2%). Cotton under furrow irrigation is grown in a hill-furrow system, similar to ridge-till in the United States (Stein et al. 1986); while the coarse scale topography of a field may be virtually flat much of its fine scale surface has steep slopes (e.g. 50%). These differences may alter the dominance of various erosion processes and the effectiveness of control practices.

Adoption of improved farming systems is more likely to occur when both efficacy and practicality have been proven in the specific context, in this case Australian irrigated cotton farms. This chapter describes a study designed to test the efficacy of two management practices, namely retention of surface cover and controlled traffic, in controlling runoff and soil erosion from cotton furrows under simulated storm rainfall. Effects of treatments on runoff amounts and rates, sediment concentrations and soil losses, and on sediment sizes, are presented. The influence of hill-furrow geometry on erosion-deposition and sediment size processes is also considered. The efficacy of these treatments in controlling transport of pesticides in runoff is presented in Chapter 7.
6.2 Methods

6.2.1 Location and soil

The study was carried out on an irrigated cotton farm in the Emerald Irrigation Area (EIA, left bank, portion 137, "Blocks 2 and 5") described in Chapter 2. The soil is a black Vertosol (Isbell 1996) and is strongly self-mulching and strongly cracking. Soil at the Block 5 simulator site had higher clay and CEC, and slightly less silt and fine sand, than at the Block 2 site (Table 6.1).

Table 6.1. Selected properties for Vertosol surface soil (0-25 mm) from sites used for rainfall simulator studies in Blocks 2 and 5, Emerald, Queensland.

<table>
<thead>
<tr>
<th>Site (Block)</th>
<th>Coarse Sand (%)</th>
<th>Fine Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Organic Carbon (%)</th>
<th>CEC (cmol(+) /kg)</th>
<th>pH (H₂O 1:5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>22</td>
<td>18</td>
<td>58</td>
<td>1.3</td>
<td>60</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>16</td>
<td>15</td>
<td>67</td>
<td>1.4</td>
<td>79</td>
<td>8.4</td>
</tr>
</tbody>
</table>

(a) Hill-furrow geometry and plot conditions

Cotton was grown on 1-m row spacing, planted into the top of hills ('permanent' beds) separated by furrows used for irrigation and wheel traffic (see hill-furrow geometry in Fig. 6.6). Each 1 m by 12 m rainfall simulator plot contained a single, central furrow and its adjoining hills, with two plots (a non-wheel track and a wheel track) fitting under the rainfall simulator. At the time of the study the hills were 0.25 m high, with side-slopes of approximately 50%. Mean slope along furrows was 1.0% and 1.3% in Blocks 2 and 5, respectively, although furrow slopes on individual rainfall simulator plots varied. Cotton had only recently emerged, giving <5% cover. Surface soil (e.g. 0-50 mm) was loose and at about air-dry moisture content. Subsoil was moist and firm, with no cracks present, having been irrigated before planting.

6.2.2 Experimental rationale and design

The study was conducted 2-3 weeks after cotton planting during the critical period for soil erosion. This period (pre-plant irrigation to canopy closure) has a high risk of runoff and soil erosion due to low cover levels, low soil moisture deficits, unconsolidated soil, and occurrence of intense storms (Carroll et al. 1991, 1995). Runoff and sediment movement were measured using a rainfall simulator to apply rain to cotton hill-furrow systems with a range of on-ground covers (0-60%), each with and without prior wheel traffic. Sixteen plots were run; half on non-wheel tracks and half on wheel tracks, across four cover treatments (see numbers of plots in Table 6.2). The main treatments, cover and prior wheel traffic, are described below.
(a) **Cover treatments**

Cover treatments studied related to the following management of residues from prior crops.

(i) Cotton ‘trash’ from the previous year’s cotton crop:
- Bare from ‘rake and burn’. After cotton picking the previous year, cotton plants were pulled, raked into windrows and burnt. The soil was then cultivated 3 times, with the hills rebuilt on each occasion (re-hilling). The resulting cover after planting was 1-2%.
- Trash mulched. As above, except that after pulling, plants were mechanically mulched and spread evenly instead of raking and burning. The three cultivation and re-hilling operations buried much of the residue, resulting in 6-10% cover with 2.8 - 3.0 t/ha of cotton trash.
- Trash retained. Cotton trash was added evenly to an area of the mulched treatment to investigate the potential benefits of retaining more cotton trash on the surface. This resulted in 47-56% cover with average of 6.8 t/ha of cotton trash. (Cotton trash is dense and woody, and thus gives a low cover per unit mass).

(ii) Stubble from wheat grown during the previous winter (after a cotton crop). Plots were run on two areas, one with cover of 15-25% (1.8 t/ha of wheat stubble) and one with 30-35% cover (2.8 t/ha of wheat stubble). Initial analysis of variance found runoff and soil loss responses were not significantly different (n.s.d.) between these areas. Thus wheat stubble plots were analysed as one treatment in analysis of variance (see below). Cover was added by hand after planting, as farming operations buried most of the cover from the crop. Cover on wheat plots was concentrated in the furrows, with bare hills, in contrast to cotton trash plots where cover was evenly distributed. Thus a wheat stubble plot with 25% cover had 100% cover (in the furrow) on 25% of the plot area.

(b) **Prior wheel traffic treatments**

Because 2 plots fit under the rainfall simulator, data were collected from pairs of adjoining plots, one a non-wheel track and one a wheel track, on the cover treatments. The furrow in wheel track plots had been used for tractor wheel traffic over the previous several seasons whereas the furrow in non-wheel track plots had received no traffic from either tractor or implement wheels. The soil in wheel track furrows was noticeably firmer and more compacted than in non-wheel track furrows. Tyre marks, which can alter flow and erosion processes, were not visible in the furrows.

(c) **Experimental sites**

Studies were conducted on two cotton irrigation fields (‘Block 2’ and ‘Block 5’). On Block 2, all cover treatments were studied (3 cotton treatments and the 2 levels of wheat cover), each with a wheel and non-wheel track plot. An additional pair of plots (wheel and non-wheel track) was run for the bare treatment to fulfill the requirements of a companion study of pesticide transport. On Block 5, pairs of plots (wheel and non-wheel track) were studied for the bare and mulched cotton trash treatments. Block 5 was nominally steeper than Block 2, and furrow slope was intended to be a treatment. Mean furrow slope on the plots was significantly higher ($P<0.05$) on Block 5 (1.28%) than on Block 2 (1.0%). However in absolute terms the difference is small and there were no statistically
significant effects of slope on runoff, soil loss and sediment concentration (n.s.d.). Thus slope was not considered as a treatment. For treatments common to Blocks 2 and 5, that is bare and mulched cotton trash, there were no significant differences between blocks in any runoff and erosion responses. Thus soils at these sites were considered similar and results from the two blocks were pooled.

6.2.3 Rainfall simulator and runoff and sediment measurements

The rainfall simulator is described in Chapter 2. Rain was applied at 95 mm/h for 40 min or more, simultaneously to 2 neighbouring plots (one wheel track and one non-wheel track). Intense storms were applied as they cause the majority of long-term total soil loss in this type of environment (Wockner and Freebaim 1991) and thus it is important that management practices are effective for such storms. Each plot was 1 m wide and 12 m long, contained by metal plot sides, and consisted of a central furrow and two hillsides. Runoff rate and sediment concentration were measured at the outlet of each furrow every 1-2 min. Towards the end of each run on most treatments (i.e. those that reached steady state runoff), velocity, width and depth of flow were measured in three sections along each furrow. Flow velocity was measured by timing the passage dye over one-metre lengths. Velocities are maximum velocities in the cross section and have not been adjusted to obtain an average velocity.

Results are presented as totals (for runoff and soil loss) and event averages (flow weighted mean sediment concentration) for 65 mm of rain, and as averages for the final ‘steady state’ after 55 mm of rain (runoff rate, flow velocity). Block (2 versus 5), furrow slopes and rainfall intensities for individual plots, and interactions were not significant in determining differences in runoff, sediment concentration and soil loss (ANOVA Chapter 2) in all but one case (for time to runoff, a slope and cover by wheel traffic interaction were significant, Table 6.2). Thus, only the main treatments (wheel traffic and cover) and their interactions were considered in the results. To show effects of cover for storms smaller than 65 mm, total runoff and soil loss from the first 35, 45, 55 and 65 mm of rain were also derived. These storms approximate average annual recurrence intervals (ARI) of one in 5, 10, 20 and 30 years, respectively, for 95 mm/hr rainfall at Emerald (Pilgrim 1987).

6.2.4 Rainfall wet surface and sediment sizes measurements

Duplicate samples of runoff were taken for measurement of undispersed sediment sizes at four times more or less evenly spaced during runoff. One sample was used for wet sieving (sieve apertures of 5, 2, 1, 0.5, 0.25, 0.125 mm) and one for sedimentation/pipette sampling (silt-sized 0.02-0.002 mm and clay-sized <0.002 mm sediment) (Loch and Donnollan 1983). Sediment 0.02-0.125 mm was determined by difference. Sediment size distributions were not significantly different (n.s.d.) through time. These samples were pooled in the analysis. Such consistency of sediment size distribution through time is typical of runoff from larger rainfall simulator plots on cultivated clay soils (Loch and Donnollan 1983, Cleary et al. 1987) where runoff flow driven processes dominate, but would not be the case where rainfall driven processes dominate (Proffitt et al. 1993; Hairsine et al. 1999).
To determine the undispersed size distribution of source eroding material, surface soil (0-5 mm) was sampled with a spatula from the eroding side-slopes of the hills after 30-40 min of rain, as described by Cleary et al. (1987). These samples were placed in bottles of 'rain' water from the simulator and sizes measured as described above. Surface samples were only taken from bare plots. For ease of discussion, surface and sediment undispersed sizes classes are grouped as coarse (>5-0.25 mm), medium (0.25-0.02 mm) and suspended (<0.02 mm), to represent the rolling (or contact) bedload, saltating bedload and suspended load classes, respectively, used by Walker et al. (1978) and Loch and Donnollan (1983). Undispersed silt and clay (i.e. the components of the suspended class) in surface soil and sediment are also reported separately.

6.3 Results and discussion

6.3.1 Effects of cover and wheel traffic on runoff

Runoff commenced at the plot outlet sooner from bare plots than from covered plots (Table 6.2). Time to runoff more than doubled with 50% cover. Thus cover significantly increased the amount of rain required to cause runoff (Table 6.2). However, cover was more effective in delaying commencement of runoff from non-wheel tracks than from wheel tracks (Fig. 6.1). With 50% cover, wheel tracks ran off after 44 mm of rain while non-wheel tracks required 65 mm of rain before runoff. Only 26 mm of rain was needed to cause runoff for bare plots, with no difference due to wheel traffic (n.s.d.). Time to runoff was also negatively correlated with furrow slope (P<0.01), as runoff can more easily overcome storage in irregularities along the furrow on steeper furrows, although this had no significant effects on total runoff and soil loss.

Table 6.2. Runoff and soil loss during 65 mm of rain, averaged for cover and wheel traffic treatments. Runoff rate and flow velocity are means during the last 10 mm of rain. N is the number of plots. Values with the same letter are not significantly different (at P=0.05) within main treatments (using analysis of variance, where other interactions are not significant)

<table>
<thead>
<tr>
<th>N</th>
<th>Mean cover (%)</th>
<th>Time to runoff (min)</th>
<th>Rain to runoff (mm)</th>
<th>Total runoff (mm)</th>
<th>Final runoff (L/s)</th>
<th>Flow velocity (m/s)</th>
<th>Total soil loss (t/ha)</th>
<th>Sediment conc. (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare (rake &amp; burn)</td>
<td>6 1 16.0</td>
<td>25.9 a</td>
<td>17.6 a</td>
<td>0.191 a</td>
<td>0.151 a</td>
<td>3.41 a</td>
<td>19.4 a</td>
</tr>
<tr>
<td></td>
<td>Cotton trash mulched</td>
<td>4 10 19.8</td>
<td>32.0 b</td>
<td>12.9 b</td>
<td>0.166 a</td>
<td>0.143 a</td>
<td>2.17 b</td>
<td>17.0 a</td>
</tr>
<tr>
<td></td>
<td>Wheat stubble</td>
<td>4 27 24.6</td>
<td>41.1 c</td>
<td>9.5 b</td>
<td>0.158 a</td>
<td>0.051 b</td>
<td>0.61 c</td>
<td>6.4 b</td>
</tr>
<tr>
<td></td>
<td>Cotton trash retained</td>
<td>2 52 33.9</td>
<td>55.9 d</td>
<td>1.2 c</td>
<td>0.039 b</td>
<td>n.d.</td>
<td>0.08 c</td>
<td>5.6 b</td>
</tr>
<tr>
<td></td>
<td>(Significance)</td>
<td>t*w^A</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
</tbody>
</table>

|    | Wheel track | 8 15 19.7 | 31.2 a | 14.2 a | 0.175 a | 0.116 a | 2.33 a | 14.6 a |
|    | Non-wheel track | 8 17 23.0 | 36.4 a | 10.5 b | 0.140 b | 0.139 a | 1.64 b | 13.1 a |
|    | (Significance) | t*w^A | * | * | ** | * | * | * |

n.d., not determined, * P<0.05; ** P<0.01; *** P<0.001
^A t*w, cover treatment by wheel traffic interaction significant (P<0.05), furrow slope significant (P<0.01).
(a) Total runoff from 65 mm of rain

Total runoff was significantly lower for treatments with greater cover and with no wheel traffic (Table 6.2). Where cover was >45%, no runoff occurred on non-wheel track plots and only 2.5 mm on wheel track plots. Within each wheel traffic treatment, cover explains much of the variance in runoff ($R^2=0.80$), irrespective of cover type (cotton trash or wheat stubble) and location (in furrow or overall), with runoff decreased linearly with increasing cover (Fig. 6.2).

Wheel track plots gave 4.5 mm more runoff than non-wheel track plots at all covers (Fig. 6.2). On bare plots, this represents 30% greater runoff for wheel tracks than for non-wheel tracks. As amounts of runoff from the hills would be similar for both types of bare plot, the reduced runoff is presumably due to greater infiltration in the furrow on non-wheel track plots. Of the two treatments, retaining >45% cover had the greater effect on runoff, reducing runoff from 15 - 20 mm to 0 - 2.5 mm. Eliminating wheel traffic alone (with no cover) reduced runoff by only 4.5 mm. Surface sealing restricts infiltration on bare plots, overriding much of the improved infiltration potential of the subsoil in non-wheel track plots. Combining cover and no wheel traffic gave least runoff, as it reduces restrictions to infiltration at both the surface (seal) and subsoil.

(b) Steady state runoff rates, infiltration rates and flow velocities

Runoff rates during the last 10 mm of applied rain declined with increasing cover, but were not significantly different for bare, cotton trash mulched and wheat stubble treatments (Table 6.2). For these plots, runoff rates had reached steady state. On cotton trash retained plots, runoff rates had not reached steady state and were significantly lower, but would continue to increase with further rainfall. Wheel tracks gave 25% higher runoff rates (averaged across all covers) than non-wheel tracks. For plots that attained steady state runoff, final infiltration rates were 31 - 46 mm/h for wheel track plots and 44 - 54 mm/h for non-wheel track plots, irrespective of cover. Final infiltration rates were, on average, 11 mm/h lower on wheel track plots. These final infiltration rates probably reflect ponding on the compacted or firmer soil a few cm below the surface in the furrows, whereas at earlier times infiltration is probably determined by the degree of surface sealing (Silburn and Connolly 1995). Thus final infiltration rates relate to traffic treatment, while early time behaviour (e.g. time to runoff) is related to cover (which affects surface sealing), but the influence of traffic treatments more evident at higher covers. These final infiltration rates are in the high end of the range of final infiltration rates measured on a wide variety of bare clay soils (Loch and Foley 1994).

Flow velocity in the furrow during steady state runoff also decreased with increasing cover (Table 6.2). In particular, velocities on wheat stubble plots (where cover was concentrated in the bottom of furrows) were about one third of those in bare and cotton trash mulched plots. Average flow width was 160 mm for bare and cotton mulch treatments, while average flow depths were about 12 mm. That is, flow in furrows was shallow and broad, with 16% of the plot area covered in water.
Fig. 6.1. Cumulative rainfall at the commencement of runoff from cotton furrows for a range of cover, with and without wheel traffic. Linear regression lines ($R^2 = 0.89$, $P<0.001$) have significantly different slopes ($P<0.003$) and a common intercept (n.s.d.).

Wheel tracks (solid line): - Rain before runoff (mm) = 25.25 + (0.7877 - 0.402) Cover (%)
Non-wheel tracks (dashed line): - Rain before runoff (mm) = 25.25 + (0.7877) Cover (%).

Values with cover 15–35% are wheat stubble, cover 45–60% are cotton trash retained.

Fig. 6.2. Runoff from 65 mm of rain on cotton furrows for a range of cover, with and without wheel traffic. Linear regression lines ($R^2 = 0.80$, $P<0.001$). Wheel tracks had 4.47 mm greater runoff ($P=0.007$) for all covers; slopes were not significantly different.

Wheel tracks (solid line): - Runoff (mm) = (14.92+4.47) - 0.2966 Cover (%);
Non-wheel tracks (dashed line): - Runoff (mm) = 14.92 - 0.2966 Cover (%).
6.3.2 Effects of cover and wheel traffic on soil loss

Soil losses were strongly affected by cover, reducing by more than an order of magnitude when cover was >50% (Table 6.2). Mean soil losses were significantly different for treatments, with bare > cotton mulch > wheat stubble = cotton trash retained, and wheel tracks > non-wheel tracks (Table 6.2). Within wheel traffic treatments, soil losses were strongly related to cover, irrespective of the type of cover and its location (Fig. 6.3). Regression analysis indicated that soil loss declined exponentially with cover, with significantly different, parallel curves for wheel and non-wheel tracks ($R^2 = 0.92$, $P<0.001$). Soil losses from wheel track plots were 0.74 t/ha greater than from non-wheel track plots across the range of cover. That is, there was 22% greater soil loss from wheel tracks on bare plots. The combination of retaining cover and no wheel traffic gave the least soil loss, though cover had by far the greater effect.

![Graph showing soil loss vs. cover for wheel tracks and non-wheel tracks.](image)

6.3.3 Effects of cover and wheel traffic on sediment concentration

Effects of cover and wheel traffic on soil loss are related to the runoff response to these treatments (Fig. 6.2). However, cover had a larger effect on soil loss than due to the runoff responses alone, as illustrated by flow weighted mean sediment concentration (Table 6.2). Sediment concentration decreased with increasing cover, indicating that, with more cover, there was not only less runoff, but also less sediment in that runoff. Regression analysis indicated that sediment concentration decreased exponentially with cover (sediment concentration (g/L) = $2.02 + 18.82 \exp(-0.0409 \text{ Cover}%)$), with no significant difference between wheel and non-wheel track plots ($R^2=0.75$, $P=0.004$).
The bare and mulched cotton trash treatments, with low cover, had significantly greater sediment concentrations (3-4 times greater) than wheat stubble and retained cotton trash treatments (Table 6.2). This indicates cover would still reduce soil loss by about two thirds if the same runoff occurred from all treatments, as might occur for very wet soil conditions.

6.3.4 Effects of cover for a range of storm sizes

Cover was effective in reducing runoff and soil loss for a range of storm sizes <65 mm (Fig. 6.4). For smaller storms, no runoff and soil loss occurred for many of the higher cover treatments, reflecting the greater amount of rain required to cause runoff for higher cover (Fig. 6.1). Thus the treatments can potentially eliminate runoff from smaller rainfall events, of greater frequency, than the full event applied with the simulator. For the soil moisture conditions and rainfall intensity of 95 mm/h studied, runoff would not occur for rainfall events of average annual recurrence intervals (ARI) and duration less than:

On bare furrows, 1 in 3 year ARI (16 min duration, 26 mm)
50% cover on non-wheel tracks, 1 in 30 year ARI (41 min duration, 65 mm)

This also illustrates why large storms are often applied in rainfall simulator studies. For small storms, there may be no measurable response for some treatments.

![Fig. 6.4. Effects of cover on (a) runoff, and (b) soil loss, for storms approximating four average annual recurrence intervals (ARI) for 95 mm/h rainfall at Emerald. Lines were fitted by regression to runoff and soil loss from the first 35, 45, 55 and 65 mm of rain, with traffic treatments pooled.](image)

6.3.5 Sediment sizes in soil surface and in runoff

(a) Surface soil after rainfall wetting

After rainfall wetting, the soil surface had a low proportion of silt and very low proportion of clay-sized particles, 5.7 and 1.3%, respectively (Table 6.3). Given that the soils have 15–18% silt and 58–67% clay when dispersed (Table 6.1), a high proportion of silt and clay was bound into aggregates.
and little clay dispersion occurred during rainfall wetting. Approximately 91% of particles were in the sand size range (0.02-2.0 mm) (Table 6.3). Based on previous studies on Vertosols, these aggregates are expected to have a low wet density (e.g. 1.42 g/cm³, Loch and Donnollan 1983, Silbum and Loch 1989) and to be considerably more erodible/transportable than similar sized primary particles (Loch and Donnollan 1983).

Table 6.3. Percent by weight of aggregate sizes in rainfall wet soil surface and undispersed sediment sizes in runoff. In the coarse size class, only 1-2% were >2 mm, for both surface and sediment. Values (means) followed by the same letter are not significantly different (within size classes). For sediments, coarse sizes equate to rolling bedload, medium to saltating bedload and suspended sediment to sum of silt and clay (Walker et al. 1978; Loch and Donnollan 1983).

<table>
<thead>
<tr>
<th>Source of sample</th>
<th>Coarse &gt;5 - 0.25 mm</th>
<th>Medium 0.25 - 0.02 mm</th>
<th>Suspended &lt; 0.02 mm</th>
<th>Silt 0.02 - 0.002 mm</th>
<th>Clay &lt; 0.002 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain wet soil surface</td>
<td>52.6 a</td>
<td>40.4 a</td>
<td>7.0 a</td>
<td>5.7 a</td>
<td>1.3 a</td>
</tr>
<tr>
<td>Runoff - bare plots (Significance)</td>
<td>43.6 b</td>
<td>23.1 b</td>
<td>33.4 b</td>
<td>29.5 b</td>
<td>4.0 b</td>
</tr>
<tr>
<td>Enrichment ratio</td>
<td>0.83</td>
<td>0.57</td>
<td>4.80</td>
<td>5.17</td>
<td>3.09</td>
</tr>
</tbody>
</table>

* P<0.05; ** P<0.01; *** P<0.001

(b) Runoff (bare plots)

Sediment was eroded mostly as aggregates rather than as primary particles, consistent with the aggregated nature of the rainfall wet soil surface. While the soil had 58–67% clay (Table 1), only 4% of sediment was clay sized (Table 6.3). This is a feature of Vertosols (Loch and Donnollan 1983; Freebairn et al. 1996) whereas sediment from soils with lower clay content, or less aggregation, often contains fewer aggregates and more primary particles (Meyer et al. 1980). Sediment from bare plots had less medium and coarse particles, and a greater proportion of suspended sizes (silt and clay), than the rainfall wet soil surface (Table 6.3). Silt and clay-sized particles were significantly enriched in sediment, with enrichment ratios of 5.17 and 3.09, respectively. These sediment sizes fit the definition of suspended load of Walker et al. (1978) and Loch and Donnollan (1983); a large proportion of particles of these sizes that are eroded from the hills are likely to be transported out of the furrows.

Enrichment ratios <1 for medium and coarse sediment suggest these sizes were major contributors to the considerable deposition observed in the furrows (it could also indicate aggregate breakdown during transport). However, a reasonably high proportion of coarse sized sediment was transported. Indeed, coarse sediment had a higher enrichment ratio than medium sized sediment, whereas a smaller enrichment ratio is expected based on size. Enrichment ratios for individual size classes in the coarse (rolling) size range were 0.80–1.04 while those in the medium (saltating) size range were 0.52–0.67. While the coarse sediment should settle rapidly to the bed of the furrow, its transport along the furrow is enhanced by rolling, associated with rapid transport, whereas medium sized sediment is subject to saltation and slower transport (Walker et al. 1978). Transport of coarse sediment may be further enhanced as coarse particles on the bed may limit supply of finer particles into the flow (Hairsine et al. 1999) and medium sized sediment may have higher wet densities then coarse sediment (Silbum and Loch 1989). Thus net deposition is not simply proportional to sediment...
size nor is sediment transport simply inversely proportional to sediment size, due to the different efficiencies of the rolling and saltating transport mechanisms.

### 6.3.6 Effects of treatments on sediment sizes

Sediment size distributions and concentrations were similar for bare and low cover cotton trash mulched plots (Table 6.4). Cover was not sufficient to significantly alter the sizes generated or change the selectivity of deposition in the furrows, consistent with the small differences in runoff and soil loss. Wheat stubble and retained cotton mulch treatments had significantly different proportions and concentrations of sediment in most size classes, compared with low cover plots. However, these two covered treatments gave opposite results (Table 6.4), due to the amounts and location of cover for each treatment, as discussed below.

#### Table 6.4. Mean sediment sizes in runoff, comparing cover treatments and wheel traffic, as percent in size class and as concentration in runoff. Values (means) followed by the same letter are not significantly different (within size classes). Coarse sediment sizes equate to rolling bedload, medium to saltating bedload and suspended sediment is the sum of silt and clay (Walker et al. 1978; Loch and Donnollan 1983).

<table>
<thead>
<tr>
<th>Cover Treatment</th>
<th>Coarse mm</th>
<th>Medium mm</th>
<th>Suspended mm</th>
<th>Silt mm</th>
<th>Clay mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare (rake &amp; burn)</td>
<td>43.6 a</td>
<td>23.1 a</td>
<td>33.4 ab</td>
<td>29.5 a</td>
<td>4.0 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>41.5 a</td>
<td>21.3 a</td>
<td>37.6 b</td>
<td>31.7 a</td>
<td>5.9 ab</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>25.8 b</td>
<td>18.4 a</td>
<td>56.0 c</td>
<td>44.0 b</td>
<td>12.0 c</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>63.9 c</td>
<td>14.7 a</td>
<td>22.2 a</td>
<td>13.4 c</td>
<td>8.8 bc</td>
</tr>
</tbody>
</table>

### Cover Coarse Medium Suspended Silt Clay

#### Comparing sediment sizes across cover treatments – percent in size class

<table>
<thead>
<tr>
<th>Cover Treatment</th>
<th>Coarse</th>
<th>Medium</th>
<th>Suspended</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare (rake &amp; burn)</td>
<td>43.6 a</td>
<td>23.1 a</td>
<td>33.4 ab</td>
<td>29.5 a</td>
<td>4.0 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>41.5 a</td>
<td>21.3 a</td>
<td>37.6 b</td>
<td>31.7 a</td>
<td>5.9 ab</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>25.8 b</td>
<td>18.4 a</td>
<td>56.0 c</td>
<td>44.0 b</td>
<td>12.0 c</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>63.9 c</td>
<td>14.7 a</td>
<td>22.2 a</td>
<td>13.4 c</td>
<td>8.8 bc</td>
</tr>
</tbody>
</table>

#### Effects of wheel traffic – percent in size class

<table>
<thead>
<tr>
<th>Cover Treatment</th>
<th>Coarse</th>
<th>Medium</th>
<th>Suspended</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheel track</td>
<td>42.6 a</td>
<td>16.0 a</td>
<td>41.5 a</td>
<td>34.5 a</td>
<td>7.5 a</td>
</tr>
<tr>
<td>Non-wheel track</td>
<td>39.8 a</td>
<td>24.8 b</td>
<td>35.5 a</td>
<td>28.8 a</td>
<td>6.6 a</td>
</tr>
</tbody>
</table>

#### Comparing sediment sizes across cover treatments - g/L in size class

<table>
<thead>
<tr>
<th>Cover Treatment</th>
<th>Coarse</th>
<th>Medium</th>
<th>Suspended</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare (rake &amp; burn)</td>
<td>8.46 a</td>
<td>4.38 a</td>
<td>6.62 a</td>
<td>5.76 a</td>
<td>0.86 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>7.16 a</td>
<td>3.72 a</td>
<td>6.19 a</td>
<td>5.16 a</td>
<td>1.03 a</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>1.70 b</td>
<td>1.29 b</td>
<td>3.41 b</td>
<td>2.70 b</td>
<td>0.72 a</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>3.60 c</td>
<td>0.82 b</td>
<td>1.18 c</td>
<td>0.72 c</td>
<td>0.46 a</td>
</tr>
</tbody>
</table>

#### Significance

- P<0.05; ** P<0.01; *** P<0.001

#### (a) Wheat stubble treatment

For the wheat stubble treatment, where cover was concentrated in the furrows, the proportion of suspended sediment (and silt and clay individually) was significantly greater than for bare plots, the proportion of coarse sediments was significantly reduced and medium sized sediment was similar (Table 6.4). When individual plots are considered, there is a trend for increasing proportion of suspended sediment and a decreasing proportion of coarse sediment with more cover (Fig. 6.5a).
Since soil loss rates and sediment sizes delivered from the hills would have been similar to those on bare plots, the stubble in the furrows evidently increased trapping of larger sediment (enhancing net deposition, with less re-entrainment due to lower flow velocities, Table 6.2) while suspended sediment was more able to pass through the stubble. Thus concentrations of coarse and medium sediment were greatly reduced, while concentration of silt-sized sediment was only halved and clay was unaffected (g/L in Table 6.4). However, in terms of total quantities, much less sediment was transported from the wheat stubble plots (about 1/5–1/6) and from non-wheel tracks, and total quantities of sediment in all size classes were reduced (Fig. 6.5b), albeit with changed proportions (Fig. 6.5a).

![Fig. 6.5. Suspended (<0.02 mm) sediment (thin lines) and coarse (>0.25 mm) sediment (thick lines) in runoff from bare and wheat stubble plots (cover in furrow) showing effects of cover and wheel traffic treatments (where significantly different), a) data as percent in size class. Wheel traffic had no significant effect on proportions of suspended sediment, b) data as sediment loss in t/ha.](image_url)

(b) Cotton trash retained

On retained cotton trash plots, cover was distributed over both hills and furrows, and the response of sediment sizes to cover was opposite to that for wheat stubble plots. Runoff contained a significantly higher proportion of coarse sediment and a lower proportion of medium and suspended sediment, particularly silt (about half), compared with bare plots (Table 6.4). Concentrations were reduced strongly for medium and silt-sized sediments, but not for coarse sediment (g/L Table 6.4). Sediment size distributions from the hills are expected to be similar for bare and covered hills (Meyer et al. 1980, Meyer and Harmon 1992) and thus do not explain the different responses to cover placement. However, erosion processes on cotton mulch retained plots were very different to the bare and wheat covered plots (characterised by large soil losses from hills and large deposits in furrows).
Less sediment would have been generated off the hills due to the cover, with few micro-rills observed. Large deposits of sediment were not observed in the furrow.

The distribution of sizes appears to reflect limited supply of suspended sediments, particularly silt sizes, and losses of the slower moving, more depositable saltating (medium) sizes by deposition in the furrow. Supply of suspended sediments was limited from the hills by low availability in the rainfall wet surface (Table 6.3) and lower erosion rate, and from the furrow bed by protection from raindrop impact by cover and the depth of flowing water. Coarse sediment was the largest contributor to sediment concentration (g/L Table 6.4) and was apparently still transported reasonably efficiently through the incomplete cover in the furrow, as rolling bedload. Supply of coarse sediment was probably not limiting, as it was relatively abundant on the hills and could also be obtained from the furrow bed. This coarser size distribution from covered plots is more amenable to further reductions in sediment load by deposition further on in the runoff pathway.

(c) Effects of wheel traffic on sediment sizes

Sediment size distributions from wheel track and non-wheel track plots were similar (Table 6.4). Wheel track plots had enhanced transport of more easily transportable coarse (rolling bedload) and suspended sizes, at the expense of medium sized saltating bedload. The effect on coarse sediment is clearer when only bare and wheat stubble plots are considered (Fig. 6.5a), without the confounding and opposing effects of cover types/placement on sediment sizes. Differences in sediment sizes between wheel traffic treatments are related to significantly higher runoff rates from wheel track plots. Even so, wheel traffic treatments had comparatively less effect on sediment size distributions than did cover and its placement. In terms of total quantities, soil losses in each size class were significantly greater for wheel track plots (Fig. 6.5b).

6.4 General discussion

6.4.1 Observed processes of sediment generation and deposition in hill-furrow systems

The hill-furrow geometry had a large effect on erosion processes. The sides of the hills were short but steep and subject to net erosion (Fig. 6.6). The hills provide a lateral source of sediment to the (low sloping) furrow where considerable sediment deposition occurred, with no erosion of the original furrow. An estimate of soil loss from the hills can be made using a mass balance of suspended sediment. If no suspended sediments were lost through deposition or gained through breakdown from larger sizes, the inferred soil loss from the hills is 16.3 t/ha based on the plot area. This is the soil loss from the hills (with 7.0% fines, Table 6.3) required to provide the 1.14 t/ha of suspended sediment measured in runoff from bare plots (33.4% of 3.41 t/ha). For the area of the hills (about 80% of plot area) this is a soil loss of 20.3 t/ha. This is comparable with soil losses of 22.6 (+/- 1.3) t/ha measured directly from bare, short steep slopes (0.45 m long, 50% slope) in a laboratory study, for a 65 mm storm on Emerald Block 2 soil. If 10% of coarse and medium aggregates (containing 76% suspended sized particles) on the surface had dispersed during transport, the supply
of suspended sized sediment would be about doubled and the inferred soil loss from the hills would be only 10 t/ha. Alternatively, if half the suspended sediment eroded from the hill had been deposited, the inferred soil loss would be 40 t/ha. These soil losses are outside the expected range (around 20 t/ha). Thus it is likely that neither aggregate breakdown in transport and deposition of suspended sized sediment were of the scales hypothesised (or both were roughly of the same order and counteracted each other). The mass balance shown in Fig. 6.6 appears a reasonable approximation.

![Fig. 6.6. Mass balance of soil loss and deposition in a bare hill-furrow system for a 65 mm storm, with an indicative mass balance for suspended sediment (fines). All soil losses are on a whole area basis.](image)

On bare plots, much of the furrow bottom was covered in deposited sediment by the end of the rainfall event. Of the 16.3 t/ha of sediment estimated to be eroded from the hills, only 2–4 t/ha left the furrow, thus 12–14 t/ha was deposited in the furrow (Fig. 6.6). The hills were the source of all sediment, with this sediment subjected to size selective deposition in the furrows to determine soil loss from the furrows. Supply of coarse and medium sizes to the furrow was well in excess of the capacity of the flow to transport these sizes (rate of deposition exceeded the rate of re-entrainment). As these larger sizes constituted 93% of the source sediment (Table 6.3), total soil loss from plots was to a large extent limited by transport capacity in the furrow rather than sediment supply, as observed by Stein et al. (1986) for a similar (ridge-till) geometry. However, the mass balance obtained for suspended sediments suggests that supply from hills, rather than transport capacity in furrows, may have been limiting for these sizes (i.e. all fines eroded from the hills appear to have been transported from the furrows). Loch and Donnollan (1983) also found that bedload sediments were transport limited while suspended sediments were supply limited during rill erosion on Vertosols.

When there was cover in the furrows, with bare hills (wheat stubble plots), concentrations of bedload sizes were reduced significantly, as the limiting transport capacity in the furrows was reduced.
Silt-sized sediment concentration was also reduced significantly (Table 6.4), indicating that with lower flow velocity, opportunities for deposition were enhanced while those for re-entrainment were reduced and transport capacity (rather than supply from the hills) became limiting. Concentrations of clay-sized sediment were not significantly different but were a small component of sediment load. Thus management practices that reduce transport capacity in the furrow were effective in reducing soil loss. The retained cotton trash treatment, with partial cover (about 50%) on both hills and furrows, gave some benefits of cover in the furrow (reduced concentration of the less transportable saltating bedload, but was less effective for rolling bedload) and also gave some benefits due to reduced sediment supply from the hills (reduced concentrations of silt and clay sizes). The net result was that sediment concentrations were similar for plots with bare hills and cover in the furrows (wheat stubble treatment, average 27% cover) and plots with higher cover (cotton trash retained, 52% cover). If runoff was similar, say with wetter antecedent conditions, the two systems of cover placement would give about equal soil losses. Because runoff was strongly related to overall cover percent, total soil loss was least for plots with greatest cover. Optimal cover placement is discussed further in a later section.

6.4.2 Large storms and small plots in context

The relevance of small plots and simulated rainfall studies to larger catchments is discussed by Wauchope (1978), who observed that catastrophic losses of pesticides from small plots were the result of unusually large runoff volumes, not of unusually high concentrations. In our study, even though large storms were applied (65 mm at 95 mm/h, 1 in 30 year ARI), the runoff events produced (up to 20 mm or 32% of rainfall) were not particularly large. For example, runoff of 50-75% and >80% of event rain can occur from wet and very wet catchment conditions, respectively, on Vertosols (Freebairn et al. 1996). The lower runoff from the simulated events is consistent with drier surface antecedent soil moisture conditions (an air-dry layer over moist subsoil) and the large moisture holding capacity of Vertosols. However, runoff events do not have the same probability as the rainfall event that produced them. Connolly et al. (1999) simulated 50 years of daily water balance and soil losses for the Emerald study site, with many combinations of storm sizes occurring on a wide range of antecedent catchment conditions. Based on their annual series for daily runoff for bare (rake and burn) irrigated cotton, runoff of 20 mm in a day has a probability of about 0.5–0.7, or a 1 in 1.4 - 2.0 year ARI.

The rainfall simulator study allowed direct comparison of several treatments, providing a relative comparison of treatment responses, and detailed sampling which is difficult during natural rainfall experiments. These responses are for a particular set of conditions. For instance, a limited range of flow energy in the furrows was considered (i.e. low slope, low discharge), with low rates of re-entrainment of deposited sediment. Under rain, longer furrows would generate larger runoff discharges and flow energies, with greater capacity to re-entrain deposited sediment and ultimately to erode the furrow (Meyer et al. 1983, Meyer and Harmon 1985, Gilley et al. 1992). Thus having demonstrated the potential of cover with the rainfall simulator, the study was followed up with field scale research and on-farm development trials of practical systems for retaining cover under cotton
Simpson et al. 1998, Waters et al. 1999), and modelling studies comparing treatments over longer times and taking into account the physical changes that occur through various scales, e.g. longer furrows (Connolly et al. 1999, 2001). The rainfall simulator study provided key parameters for the modelling, in particular, data on sediment sizes and effects of cover, which were not studied in detail in the initial field plot and catchment studies.

6.4.3 Implications of sediment sizes for off-site management options

Sediment in runoff can be managed after it leaves furrows by enhancing sediment deposition in tail-drains, vegetative filters, and 'silt' traps (Carroll et al. 1991). These methods reduce the flow velocity by reducing slope, or increasing roughness or cross-section area. Slower velocity allows more time for sediment to deposit and, more importantly, reduces bedload transport capacity. Sediment settling velocity and transport capacity are both influenced by sediment size and density. Larger, denser sediment particles settle more rapidly and are less easily transported at lower velocities (Meyer et al. 1983), and therefore are more easily trapped, than smaller, less dense sediment. The high proportion of larger sized sediment transported from furrows in this study should create opportunities to manage sediment delivery off-site. With 44% of sediment >0.25 mm and 68% >0.02 mm, there should be potential to deposit 44-68% of the sediment. This was confirmed by Simpson et al. (1998), who found 62% of total soil movement from furrows collected in bedload traps.

However, soil loss and flow velocity data from the EIA suggest that tail-drains of ≥0.1% slope are capable of transporting most sediment sizes transported from furrows and are not efficient in retaining sediment. Carroll et al. (1991, 1995) found that soil losses from tail-drains in the EIA were similar to, or sometimes greater than, from the furrows. This is consistent with the large amount of sediment deposited in EIA main drains (Connolly et al. 1999). Carroll et al. (1991) determined flow velocities of 0.17–0.35 m/s in a tail-drain of 0.1% slope, greater than the velocities measured in bare furrows under the rainfall simulator (0.14–0.15 m/s) at 1% slope. Larger particles may well be settling to the tail-drain bed but are apparently still being transported. There appears to be considerable scope for reducing these sediment loads using improved management within the field (e.g. cover) and in tail-drains by reducing tail-drain slope or increasing roughness (Carroll et al. 1991, Connolly et al. 1999).

6.4.4 Optimal cover placement

This study included treatments with cover in furrows or spread on hills and furrows, but did not include cover on hills alone. In a similar study of a hill-furrow system (ridge-till) with <1% furrow slope, Stein et al. (1986) found that crop residues placed only on hill sideslopes, with bare furrows, did not reduce soil movement. Transport capacity in the furrows was apparently unchanged, and could be met by eroding the furrow (Meyer and Harmon 1985). Stein et al. (1986) found that residues in the furrow bottom or spread on hills and furrows were equally effective in reducing net soil loss, as they reduced transport capacity in the furrows. In our case, cover in the furrow appeared to reduce transport capacity for bedload and silt-sized sediment, i.e. >98% of the sediment supplied. Sediment
concentration was reduced as much with 25% cover (100% in furrows) as with 50% cover spread overall. However, total runoff was inversely related to the overall cover, so soil loss was least with greatest overall cover. Having some cover on the hills also gave the lowest concentrations and losses of silt and clay-sized sediment, by reducing their supply. This may be particularly important on less aggregated soils, which produce a greater proportion of clay-sized sediment, than in this study. These sizes of sediment settle slowly, are less likely to be deposited on-farm, and are more likely to contribute to off-site water quality problems than coarser sediments. The best of both systems would be provided if the partial overall cover system also had 100% cover in the furrow (only 20% of the overall area), i.e. 10% increase in total cover (e.g. from 50% to 60%). If the quantity of crop residues is limited, placement in the furrow bottom provides the greatest benefit. However, if sufficient crop residues are available, cover should be placed on both hill and furrow, maximising total cover, while maintaining high cover in the furrow.

6.4.5 Practical requirements of effective cover retention in cotton

Implementing stubble retention in furrow-irrigated cotton requires considerable adaptation of technology and solving new problems in irrigation, weed and insect management (Anthony 1999). To reduce erosion and transport of chemicals, crop residues are required on the surface (not buried), providing cover from planting or pre-plant irrigation, through to canopy closure, and preferably until the last irrigation. To be effective the cover should be in the furrow (at least) and anchored to the soil to avoid removal by irrigation and storm runoff. There is considerable doubt about whether an effective cover can be provided using cotton trash from a previous crop, especially when tilled (Silburn et al. 1998; Simpson et al. 1998). Thus other crops need to be grown in rotation with cotton, either as a winter double-crop (Waters et al. 1999) or cover crop (not harvested) or in a longer season rotation (Anthony 1999). Double cropping from wheat into cotton has been successful in commercial trials in the EIA, giving good erosion control, reasonable yields and unforeseen benefits of reduced insect pressure and less insecticide application (Waters et al. 1999, Whyte 2000, Waters 2001).

Some current farming practices are potentially in conflict with retention of cover in irrigated cotton. For instance, tillage has disadvantages as it reduces the amount of cover and creates unanchored cover. Tillage is used in irrigated cotton to maintain hill-furrow shape, create a seedbed, and control weeds. It is also used to break the pupae cycle of the insect pest Helicoverpa armigera (Murray 1999) and this requires reasonably complete tillage, preferably soon after picking. Other operations involving soil disturbance include application of herbicides and fertilisers that need to be incorporated or injected into the soil.

Perceived conflicts between competing requirements may be overcome by:

- Considering operations according to their different timing in the growing sequence. For example, pupae control is required after picking, whereas the critical time for erosion control is early in the crop and during irrigation, some 5-7 months later. Pupae control, reforming hills and planting a winter cereal crop soon after picking may be a feasible option for a redesigned system.
• Zonal tillage/farming or strip tillage (Marshall et al. 1996) where different zones of the hill/furrow system are managed for different purposes, e.g. seedbed/herbicide and fertiliser incorporation zone (top of hill), wheel traffic and irrigation/runoff zone (furrow) requiring anchored stubble, and hill side-slope (stubble cover preferred). Marshall et al. (1996) trailed a strip tillage approach to pre-planting preparation for dryland cotton into standing wheat stubble, successfully preparing a seed bed and incorporating fertiliser and trifluralin herbicide in 300 mm tilled strips. Thus only 15% of the area was disturbed on ‘double-skip’ planting, or 30% of the area on one-metre rows. Further flexibility may be offered in ‘wide-bed’ systems where furrows are used every second metre with two cotton rows per bed.

Stubble in furrows slows the advance of irrigation water, requiring redesign of irrigation practices (inflow rate, furrow cross section etc.). Slower irrigation advance may have drawbacks on some soils, but would be beneficial on soil with low infiltration rates and poor ‘subbing’ (lateral wetting of beds). At both Emerald and Narrabri, trials also indicated that timing of early irrigations might need to be reassessed (delayed) for stubble retention systems (Anthony 1999, D. Waters pers. comm.), which may be due to reduced evaporation from the soil.

6.5 Conclusion

This study illustrates that retaining crop residues on the soil surface to provide cover is effective in reducing runoff and sediment movement from cotton furrows, especially when wheel traffic is avoided. Avoiding wheel traffic, without retaining cover, was less effective. The soil, a black Vertosol, was found to have a reasonably high infiltration capacity and a surface (after rainfall wetting) dominated by coarse and medium sized aggregates, with only 7% silt and clay sized particles. Erosion processes were strongly affected by hill-furrow geometry, with large soil losses from the hills and considerable deposition in the furrows, resulting in five-fold enrichment of suspended (<0.02mm) sediment. Coarse sediment (>0.25mm) was transported more efficiently than medium (0.25-0.02mm) sediment. Interpretation of surface soil and sediment size data, and an approximate erosion-deposition mass balance, indicates that soil loss from a hill-furrow system on a low slope was likely to be controlled by the limiting transport capacity of flow in the furrows. Cover in the furrows reduced the flow velocity and further limited sediment transport. Thus sediment concentrations were similar for plots with bare hills and cover in the furrows (wheat stubble treatment, average 27% cover) and plots with higher cover (cotton trash retained, 52% cover). However, because runoff was strongly related to overall cover percent, total soil loss was least for plots with greatest cover. The associated benefits of cover in reducing runoff transport of pesticides are described in Chapter 7. The challenge for the cotton industry is to develop practical farming systems that can provide this cover.
Pesticides in Runoff

Runoff Losses From Cotton Furrows Under Storm Rainfall. II. Transport of

Chapter 7: Management Practices for Control of
7.1 Introduction

Given high levels of pesticide usage in cotton production, considerable transport of pesticides can occur in runoff and sediment from cotton fields (Kennedy et al. 1998, Simpson et al. 1998), and may contribute to contamination of inland waterways (Muschal and Cooper 1998). Concerns about management of pesticides in the cotton industry and possible impacts on the riverine environment were addressed in the LWRRDC/CRDC/MDBC program ‘Minimising the Impact of Pesticides on the Riverine Environment’ (Schofield 1998), of which this study was a part. Program aims included development of practical and economic methods to minimise transport of pesticides from application sites, and of best management practices (BMP), in our case, for reducing transport in runoff.

Management options for reducing pesticide transport in runoff include (i) pesticide use and choice, (ii) soil and water management within the field, or (iii) managing runoff after it leaves the field. In developing within-field best management practices for control of pesticide runoff, many general principles of soil and water conservation developed in dryland cropping (Freebairn et al. 1996) should be applicable. One of the most effective and robust of these management principles is retention of crop residues to provide surface cover. Retention of surface cover is generally not practiced in irrigated cotton production in Australia. The benefits of cover in reducing soil erosion have been clearly demonstrated in a variety of farming systems including dryland cropping (Freebairn et al. 1996), dryland cotton (Mutchler and McDowell 1990) and irrigated cotton (Chapter 6). However, few studies have measured effects of surface cover on pesticide and nutrient transport in runoff in Australia, even in dryland cropping where most erosion research has occurred. Two Australian studies, Rose and Dalai (1988) and Palis et al. (1990), found reductions in runoff losses of total N with cover. As total N is mainly organic N, which is strongly sorbed to soil (Walter et al. 1979), both results reflect the strong effect of cover on erosion.

The effectiveness of soil and water conservation practices, including retaining cover, in controlling potential pollutants other than sediment depends on two factors:

- Properties (e.g. sorption coefficient) of the particular chemical (Wauchope 1978; Walter et al. 1979), which vary widely for pesticides (Wauchope et al. 1992). These chemical properties, combined with soil properties that affect sorption, determine whether the dominant transport agent for a chemical is water or sediment (Wauchope 1978).

---

2 This chapter was published with minor changes as: Silburn DM, Simpson BW, Hargreaves PA (2002). Management practices for control of runoff losses from cotton furrows under storm rainfall. II. Transport of pesticides in runoff. *Australian Journal of Soil Research* 40, 21-44.
How well the conservation practice (e.g., cover) reduces the dominant transport agent (sediment or water). For chemicals adsorbed to sediment, erosion control practices generally reduce runoff losses, but not necessarily in proportion because control practices sometimes reduce transport of coarse particles more than fine particles (Leonard 1990). For chemicals transported in water (in solution phase), a practice will reduce transport only to the extent that it reduces runoff, with the proviso that the cover is not a direct source or sink for the chemical. However, few chemicals are fully non-sorbed (nitrate is one) or fully adsorbed (DDT is close) in soil (Walter et al. 1979). Many are moderately sorbed and will be partially transported on sediment. Also sorption tends to increase with time after application and is partly non-reversible (Wauchope 1978).

Cover can also have a direct effect, by intercepting and dissipating pesticide sprays, and can be a source or sink of pesticides in runoff (Wauchope 1987). This aspect is under-researched, but will depend on pesticide chemistry (such as volatility, persistence and sorption) and the nature of the cover (age, microbial activity etc.). Persistence data mainly relate to insecticides on plant foliage, with some data for herbicides, mainly on grasses (Willis and McDowell 1987). Half-lives, particularly for the component dislodgable by rainfall, are generally shorter than for pesticides on soil (Willis and McDowell 1987), indicating potential for cover to provide a direct effect on runoff of pesticides.

In a review of studies in the United States (Fawcett et al. 1994), conservation tillage, defined as retaining a minimum of 30% crop residue cover after planting, usually reduced runoff losses of pesticides (mostly herbicides) from cropped lands compared with conventional (bare, tilled) but some data are conflicting. For herbicides, average reductions across all natural rainfall studies were 70, 69 and 42% for no-till, chisel plow and ridge-till, respectively. This was in spite of the fact that many of the herbicides ran off more in the solution phase rather than adsorbed to sediment and thus depend on the degree to which the treatment reduces runoff. However, for individual studies, herbicide runoff from no-till varied from none to twice that from conventional. For example, Isensee and Sadeghi (1993) found no-till corn gave higher losses and concentrations of several herbicides than conventional tillage, with runoff similar or greater from no-till. This illustrates that the case for cover being effective in reducing agrochemical transport in runoff, for all chemicals in all circumstances, is by no means clear-cut. Given the chemical-specific (and soil related) nature of responses to erosion control practices, some local evaluation is warranted for key chemicals in industries such as the Australian cotton industry.

7.1.1 Requirements for managing runoff of pesticides from irrigated cotton

Simpson et al. (1998) determined that the early part of the growing season was the period of major potential risk for pesticide transport in runoff, because of the greater occurrence of runoff and erosion (Carroll et al. 1995), and because soil concentrations of herbicides and insecticides, particularly endosulfan, were elevated due to recent applications. The highest risk period for the more water-soluble herbicides (e.g. prometryn, fluometuron and diuron) was the first 4-6 weeks after application. The risk period for endosulfan was extended by repeated applications resulting in a short-
term build-up in the soil and partial conversion to endosulfan sulfate which is slightly more persistent (Kennedy et al. 1998). This period may typically extend for some 8-12 weeks after planting, with six applications of endosulfan not atypical. Thus it is highly likely that, when storm rainfall occurs during this period, an endosulfan application was made some time in the previous two weeks.

Early in the cotton season, the plants are small and the major potential source of pesticides in runoff is the soil. Latter in the season washoff of pesticides applied to plants also contributes. Thus it is important to have management practices capable of controlling pesticide transport from the soil (i) when crop canopy cover is small, early in the cotton season, (ii) during storm rainfall events, which compared with irrigations, are less easily managed in terms of timing of pesticide applications and the amounts and rates of runoff generated.

In this study, a rainfall simulator was used to evaluate effects of two management options available to cotton growers, namely retention of on-ground cover and controlling wheel traffic, on runoff of several pesticides from a hill-furrow system used in cotton production. Effects of these treatments on runoff, sediment losses and sizes, and erosion processes, were described in Chapter 6.

7.2 Methods

7.2.1 Location and soils

The study was carried out on an irrigated cotton farm in the Emerald Irrigation Area (left bank, portion 137, “Blocks 2 and 5”), using the rainfall simulator plots described in Chapter 6 and the general methods in Chapter 2. The soil is a black Vertosol (Isbell 1996). Soil properties are given in Chapter 6 (Table 6.1). The soil surface (after rainfall wetting), and sediments produced by erosion, mainly consist of aggregates >0.02 mm rather than primary particles, with a low proportion of silt-sized particles and little dispersed clay (Chapter 6).

7.2.2 Hill-furrow geometry, rainfall simulator and plot conditions

A rainfall simulator (Chapter 2) was used to apply rain (at 95 mm/hr for >40 min) simultaneously to two neighbouring plots (a non-wheel track and a wheel track). Each plot was 1 m wide and 12 m long and contained a single, central furrow and its adjoining hills, as described in Chapter 6. Average furrow slope was about 1.0% (see hill-furrow geometry in Fig. 6.6). Runoff rate and sediment concentration was measured every 1-2 min from the outlet of each plot (Chapter 6). Surface soil (e.g. 0-50mm) was loose and at about air-dry moisture content. Subsoil was moist and firm, with no cracks, having been irrigated before planting. Cotton had only recently emerged, giving <5% cover. Surface cover provided by crop residues varied according to treatments described below.

7.2.3 Experimental design

Pesticide transport in runoff and sediment was measured during simulated storms on plots with a range of on-ground covers (0 to 60%), each with and without prior wheel traffic. The study was conducted 2-3 weeks after cotton planting during the major risk period for soil erosion (Carroll et al.
1995) and pesticide transport in runoff (Simpson et al. 1998). Reasonably large, intense storms were applied (1:30 average annual recurrence interval (ARI)) as they cause the majority of long-term total soil loss in the region (Wockner and Freebairn 1991) and can contribute a disproportionately large amount of the total pesticide load in runoff (Leonard et al. 1979). However, the resulting runoff events were of a size that is expected reasonably frequently, e.g. 1:1.4–2.0 ARI for runoff from bare plots (Chapter 6). Herbicides were applied at or before planting and endosulfan was applied twice before the rainfall simulator study. The main treatments studied, cover and prior wheel traffic, are described in Chapter 6, and are summarised below.

(a) Cover and wheel traffic treatments

Cover treatments studied related to the following management of residues from prior crops.

a) Cotton ‘trash’ from the previous years cotton crop:
   - Bare from ‘rake and burn’, with cover of 1-2%.
   - Cotton trash mulched with cover of 6-10%.
   - Cotton trash retained with cover of 47-56% of mainly added cotton trash.

b) Wheat stubble on two areas, one with cover of 15-25% and one with 30-35% cover. Initial analysis of variance found pesticide runoff responses were not significantly different (n.s.d.) between these areas, they were analysed as one treatment in analysis of variance (see below).

For cotton trash retained and wheat stubble treatments, cover mainly consisted of cover added by hand after planting, as farming operations buried most of the cover from the crops. Cover on wheat stubble plots was concentrated in furrows, with bare hills, in contrast to the cotton trash plots where cover was evenly distributed. These differences in cover placement affected the size distribution of sediment in runoff, although total runoff and soil loss were related to percent cover alone (Chapter 6).

Data were collected from pairs of adjoining plots for each cover treatment, one a wheel track (used for tractor wheel traffic over the previous several seasons) and one a non-wheel track. Non-wheel track furrows were also used for pre-plant irrigation a month before the rainfall simulator study, after applications of trifluralin and before application of prometryn and endosulfan. Furrows used for tractor wheel traffic are more compacted, and give more runoff and soil loss, than non-wheel tracks (Baker and Laflen 1979, Chapter 6), and therefore may affect pesticide runoff.

(b) Experimental sites

Sixteen plots were run; half on non-wheel tracks and half on wheel tracks, across the four cover treatments (see numbers of plots in Table 7.2), on two cotton fields (Blocks 2 and 5). On Block 2, all cover treatments were studied (3 cotton mulch treatments and the 2 levels of wheat cover), each on a pair of plots (wheel and non-wheel track), with an additional pair of plots for the bare treatment. On Block 5, bare and cotton trash mulched were studied, each with a pair of plots (wheel and non-wheel track). Soils and pesticide applications at these sites were similar. No significant differences were found between blocks in runoff and erosion (Chapter 6) or in pesticide runoff responses and results from the two blocks were pooled, unless otherwise indicated. One exception is DDE (see below).
7.2.4 Pesticides

The study involved the scenario of a storm occurring several weeks after cotton planting, with pre-plant and plant herbicide applications and two endosulfan applications between planting and the rainfall event. Thus time between application and the rainfall event varied between pesticides (Table 7.1). Endosulfan (applied as α and β isomers in the ratio of approximately 70:30), endosulfan sulfate (a toxic breakdown product), trifluralin, DDE and prometryn were studied, to provide a contrast between pesticides of different properties (Table 7.1) and to show how these properties affect responses to management. Endosulfan and trifluralin have lower solubility in water and higher soil sorption \( (K_{OC}) \) than prometryn, while DDE has very low solubility and very high \( K_{OC} \). Because crop residues were added to covered plots by hand after planting, trifluralin, prometryn, DDE and the majority of endosulfan sulfate were in the soil under the cover, whereas endosulfan was applied after the cover was placed and would have been partially intercepted where there was cover. This created two pesticide application 'sub-treatments', which are considered in the results.

Table 7.1. Selected properties (solubility, \( K_{OC} \) and field half-life from Wauchope et al. 1992) and amount, method and time of application for pesticides studied.

<table>
<thead>
<tr>
<th>Pesticide Type and Name</th>
<th>Type and group</th>
<th>Solubility in water (mg/L)</th>
<th>Soil sorption ( K_{OC} ) (L/kg)</th>
<th>Field dissipation half-life (days)</th>
<th>Amount applied (whole area basis, gai/ha)</th>
<th>Time between application and rainfall (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endosulfan</td>
<td>Insecticide Cyclodiene Organochlorine</td>
<td>0.32</td>
<td>12,400</td>
<td>50</td>
<td>1900 (2 ULV sprays after planting)</td>
<td>4 – 7 from last application</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>Herbicide Substituted Aniline</td>
<td>0.32</td>
<td>8000</td>
<td>60</td>
<td>1120 (incorporated before planting)</td>
<td>48 – 52</td>
</tr>
<tr>
<td>Prometryn</td>
<td>Herbicide s-triazine</td>
<td>33.0</td>
<td>400</td>
<td>60</td>
<td>625 (50% band on hills at planting)</td>
<td>15 – 18</td>
</tr>
<tr>
<td>p,p' DDE</td>
<td>Breakdown product of DDT Organochlorine</td>
<td>0.065</td>
<td>380,000 – 880,000</td>
<td>2 – 16 years</td>
<td>Unknown</td>
<td>unknown (~ 17+ years)</td>
</tr>
</tbody>
</table>

(a) Pesticide applications

Endosulfan was applied as an experimental treatment as ultra low volume formulation (ULV) at 4 L/ha (240 g.a.i./L, 960 g.a.i./ha) twice in the week before the rainfall simulator study. Rainfall simulator plots were run 4-7 days after the second application, to mimic a high risk but not atypical scenario. By this time concentration of total endosulfan in the surface soil (0-25 mm) was about 4 mg/kg or 900 g/ha, 47% of the applied amount (Table 7.1). This concentration is similar to maximum concentrations measured in soils several times in each season during multiple commercial applications in the EIA (Simpson et al. 1998) and Warren NSW (Kennedy et al. 1998). Concentrations of α, β and sulfate endosulfan in soil, in wheat stubble and in runoff did not change appreciably over the four days.
of the simulator study (n.s.d. in multi-variate regression analysis). That is, differences between plots can be attributed to treatments rather than differences in time since application. Endosulfan sulfate in soil included a considerable proportion of ‘aged’ endosulfan sulfate carried over from the previous cotton season (Chapter 3).

Trifluralin was applied as a farm operation, as Treflan®, incorporated into the soil at 2.8 L/ha (400 g.a.i./L, 1120 g.a.i./ha) before pre-irrigation and planting, 7 weeks before rain was applied. Prometryn was applied by the farmer during cotton planting, as Cotogard® at 5 L/ha on a 50% band on the hills (250 g.a.i./L, 625 g.a.i./ha on a whole area basis), 15-18 days before rain was applied. Multi-variate regression analysis indicated that differences in time after spraying (between plots) were not significant in determining runoff transport of these herbicides. DDE (p,p’) was present in the soil as a residual breakdown product of the insecticide DDT, probably last used in the 1977-78 cotton crop in the EIA (Geoff Waite, QDPI personal communication), some 17 years before the study, although there are no records of specific applications. Concentrations of DDE in 0-25 mm soil in Block 5 were 66-77% of those on Block 2, based on the sampling program of Simpson et al. (1998), presumably due to differences in applications in the past.

(b) Pesticide sampling and analysis

Samples of rainfall and runoff water were taken as described in Chapter 2, with samples taken through the hydrograph analysed for total concentrations of each pesticide (i.e. total in water and sediment) and a bulked sample analysed for concentrations of pesticides in the water and sediment phases (separately). Before rain commenced, samples of crop residues (wheat stubble or cotton trash) and soil (0-25 mm) were taken from eight locations and composited, with separate samples from the top of the hill and the bottom of the furrow. At each sampling location, crop residues (if any) were collected from a known area, and the soil sample taken from this area. Thus the soil samples did not include pesticides intercepted by crop residues. Samples for pesticide analysis were placed in glass jars with Teflon sealed lids to prevent contamination, placed in insulated boxes with ice immediately after collection and transferred to the laboratory by air courier (at ~4°C). Water samples were normally extracted within 24 hrs of sampling. Soil and crop residue samples were stored at -15°C until analysis was commenced.

Runoff, rainwater, crop residue and soil samples were analysed for endosulfan (α, β isomers and endosulfan sulfate), prometryn, trifluralin and p,p’-DDE, using the DNRM methods described in Chapter 2. The rainwater used had no detectable residues of α, β and sulfate endosulfan, and trace concentrations of trifluralin, prometryn and DDE, all 150-200 times lower than the lowest concentrations found in runoff.

(c) Pesticide data presentation

Results for pesticide transport in runoff are presented as flow weighted average concentrations (µg/L), total losses (grams active ingredient per ha, g/ha) and percent of applied amount, in runoff during 65 mm (about 40 min) of applied rain. Total endosulfan is used to describe the sum of α, β
isomers and endosulfan sulfate. Concentration in runoff refers to concentration in water and sediment combined (μg/L of runoff). Concentrations of pesticides transported on sediment are presented as μg/L (i.e. per L runoff) so they are directly comparable with concentrations in runoff and in the water phase. However, concentrations in sediment as mg/kg (i.e. per kg of sediment) are also presented (as is often the case in the literature) where appropriate. Rainfall intensities, furrow slope and time since application for individual plots, Block (2 versus 5) and interactions were not significant in determining differences in means for pesticide runoff (ANOVA Chapter 2) and are therefore not considered.

7.3 Results and discussion

7.3.1 Effects of cover and wheel traffic on pesticide transport

(a) Endosulfan concentration in runoff

Average concentrations in runoff of total endosulfan, and its α, β and sulfate components, were significantly lower (all \( P<0.001 \)) for higher cover treatments (wheat stubble and cotton trash retained) than for low cover treatments (bare and cotton trash mulched), and declined with increasing cover (Fig. 7.1). For α, β and total endosulfan, cover explains >82% of the variance in concentrations in runoff, irrespective of cover type (wheat stubble or cotton trash) or placement (in furrow or overall), once wheel traffic was accounted for (Fig. 7.1). With 45-60% cover, concentrations of total, α and β endosulfan were one fifth of those from bare plots, similar to the reduction in sediment concentration in runoff (Chapter 6). Concentrations of α, β, sulfate and total endosulfan in runoff were highly correlated with concentrations of sediment in runoff (all \( R^2>0.85, \ P<0.001 \)), which were also significantly affected by cover (Chapter 6). Wheel track plots had higher concentrations of α, β and total endosulfan in runoff than non-wheel track plots (all \( P<0.05 \)), by similar amounts across the range of cover (Fig. 7.1). For example, total endosulfan concentrations were 27 μg/L greater for wheel tracks at all covers, a 17% greater concentration for bare plots.

Concentrations of total endosulfan in runoff consisted of about equal α (50–55%) and β (41-45%) isomers, and a low proportion of endosulfan sulfate (3–4%), comparable with concentrations in the soil (0-25 mm) in the proportions 56% α, 41% β and 3% sulfate. Thus concentrations of endosulfan sulfate in runoff were more than an order of magnitude lower than the α and β isomers (Fig. 7.1). Endosulfan sulfate concentrations decreased with increasing cover (Fig. 7.1d), but to a lesser extent than the parent endosulfan isomers. With 45-60% cover, concentrations of endosulfan sulfate were one third to half of those for bare plots (Fig. 7.1d). Endosulfan sulfate concentrations were related to cover treatment rather than decreasing continuously with increasing cover (Table 7.2), with a greater reduction with wheat stubble (0.30 of concentrations from bare plots) than cotton trash retained (0.46 of concentrations from bare plots), even though cotton trash retained had more cover and similar sediment concentrations in runoff (Chapter 6) (see later discussion). Regression analysis against cover (Fig. 7.1d) indicates no significant difference in endosulfan sulfate concentrations due to
Concentration in runoff (\(\mu g/L\)) may be influenced by wheel traffic. However, ANOVA on treatments (Table 7.2) indicates a significant difference (\(P=0.024\)) of 0.8 \(\mu g/L\) greater for wheel tracks, or 21% for bare plots, similar to the effect of wheel traffic on concentration of total endosulfan.

**Fig. 7.1.** Mean concentrations (flow weighted) of endosulfan in runoff (water and sediment) during 65 mm of rain, from plots with a range of cover, with and without wheel traffic (solid and dashed lines respectively), for

- **(a) total endosulfan** (\(\alpha, \beta\) and sulfate),
  \[ y (\mu g/L) = (3.919+A) + 181.8 \exp(-0.0312.\text{cover%}) \]
  \[ R^2 = 0.83, P<0.001, \]
  \(A = 0.0\) for wheel tracks, \(A = -26.98\) non-wheel tracks, \((P = 0.025)\).

- **(b) \(\alpha\) endosulfan,**
  \[ y (\mu g/L) = (-1.296+A) + 101.9 \exp(-0.0309.\text{cover%}) \]
  \[ R^2 = 0.83, P<0.001, \]
  \(A = 0.0\) for wheel tracks, \(A = -14.50\) for non-wheel tracks, \((P = 0.025)\).

- **(c) \(\beta\) endosulfan,**
  \[ y (\mu g/L) = (0.3028+A) + 77.27 \exp(-0.0289.\text{cover%}) \]
  \[ R^2 = 0.82, P<0.001, \]
  \(A = 0.0\) for wheel tracks, \(A = -11.66\) for non-wheel tracks, \((P = 0.025)\).

- **(d) endosulfan sulfate,**
  \[ y (\mu g/L) = (1.779) + 4.544 \exp(-0.0633.\text{cover%}) \]
  \[ R^2 = 0.65, P<0.001, \]
  wheel tracks and non-wheel tracks were not significantly different,

A is the difference due to wheel traffic (where significant). \(N=16\) in all cases.

Values with cover 15–35% are wheat stubble, cover 45–60% are cotton trash retained.
Table 7.2. Mean concentrations (µg/L) in runoff of endosulfan sulfate, trifluralin, prometryn and DDE (block 2 only) from cotton furrows during 65 mm of rain, comparing cover treatments and with or without wheel traffic. Concentrations are flow-weighted averages. Within columns, means followed by the same letter are not significantly different within cover or traffic treatments (at \( P=0.05 \)). * \( P<0.05 \); ** \( P<0.01 \); *** \( P<0.001 \)

| Cover or traffic Treatment | Number of plots | Mean cover (%) | Endosulfan sulfate | Trifluralin | Prometryn | DDE
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare (rake and burn)</td>
<td>6</td>
<td>1</td>
<td>5.7 a</td>
<td>10.2 a</td>
<td>46.9 a</td>
<td>18.8 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>4</td>
<td>10</td>
<td>5.3 a</td>
<td>11.2 a</td>
<td>42.2 a</td>
<td>19.9 a</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>4</td>
<td>27</td>
<td>1.7 b</td>
<td>4.3 b</td>
<td>40.2 a</td>
<td>7.0 b</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>2</td>
<td>52</td>
<td>2.7 b</td>
<td>6.6 ab</td>
<td>48.9 a</td>
<td>10.2 b</td>
</tr>
<tr>
<td>(Significance)</td>
<td></td>
<td></td>
<td>***</td>
<td>*</td>
<td>n.s.d.</td>
<td>***</td>
</tr>
<tr>
<td>Wheel tracks</td>
<td>8</td>
<td></td>
<td>4.6 a</td>
<td>10.2 a</td>
<td>49.9 a</td>
<td>13.3 a</td>
</tr>
<tr>
<td>Non wheel tracks</td>
<td>8</td>
<td></td>
<td>3.8 b</td>
<td>6.9 b</td>
<td>38.7 b</td>
<td>14.0 a</td>
</tr>
<tr>
<td>Wheel traffic</td>
<td></td>
<td></td>
<td>+21 %</td>
<td>+48 %</td>
<td>+29 %</td>
<td>-</td>
</tr>
<tr>
<td>(Significance)</td>
<td></td>
<td></td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>n.s.d.</td>
</tr>
</tbody>
</table>

(b) Endosulfan total loss in runoff

Total loss of endosulfan (g/ha) in runoff (during 65 mm of rain) declined markedly with increased cover (Fig. 7.2a), from 20-40 g/ha for bare plots to 0.0-0.8 g/ha with 45-60% cover. The response was similar for α, β and sulfate (Fig. 7.2bcd). Cover explained >92% of the variance in runoff losses for all forms of endosulfan, irrespective of cover type (cotton trash or wheat stubble) or placement (in furrow or overall), once wheel traffic was accounted for (Fig. 7.2). Cover had a stronger effect on g/ha losses than on average concentrations, as duration and amount of runoff and soil loss were less for plots with more cover. For instance, compared with bare furrows, runoff was halved with 25% cover and almost eliminated with 50% cover (Chapter 6). Thus while concentrations for α, β and total endosulfan were reduced 5 fold at the highest cover, total losses were reduced by more than 70 fold. Similarly, losses of endosulfan sulfate were reduced more than 30 fold (Fig. 7.2d) even though concentrations were only halved for cotton mulch retained plots.

Total losses were lower for non-wheel tracks than for wheel tracks, across all covers, for all forms of endosulfan, e.g. 39% lower for total endosulfan. This resulted from lower concentrations in runoff (Fig. 7.1) and smaller runoff amounts (Chapter 6) from non-wheel tracks. Of the two practices, retaining cover had the greater effect. Controlled traffic alone (without cover) was of less benefit for reducing endosulfan transport from storms on this soil. The combination of retaining cover and no wheel traffic gave the least endosulfan transport in runoff.

As similar amounts of endosulfan were applied to all plots (except one pair of plots that received 11% more by mistake, Fig. 7.2), losses in g/ha directly relate to percentage of the amount applied, as indicated by the second Y-axis in Fig. 7.2. Losses of total endosulfan, even for bare furrows (20-40 g/ha), represent a small proportion (1.1-2.1%) of the total amount applied (~1900 g/ha). However, this small proportion resulted in high concentrations (100-200 µg/L) in runoff.
Fig. 7.2. Total losses of endosulfan (g.a.i./ha) in runoff (water and sediment) during 65 mm of rain, from plots with a range of cover, with and without prior wheel traffic (N=16 in all cases), for

(a) total endosulfan ($\alpha$, $\beta$ and sulfate),
$$y \text{ (g/ha)} = 0.183 + 37.83 \exp(-0.0639 \text{ cover})$$
for wheel tracks,
$$y \text{ (g/ha)} = -1.331 + 25.33 \exp(-0.0639 \text{ cover})$$
for non-wheel tracks,
which are significantly different and non-parallel, $R^2 = 0.93$, $P<0.001$.

(b) $\alpha$ endosulfan,
$$y \text{ (g/ha)} = 0.0337 + 20.73 \exp(-0.0645 \text{ cover})$$
for wheel tracks,
$$y \text{ (g/ha)} = -0.7388 + 13.86 \exp(-0.0645 \text{ cover})$$
for non-wheel tracks,
which are significantly different and non-parallel, $R^2 = 0.93$, $P<0.001$.

(c) $\beta$ endosulfan,
$$y \text{ (g/ha)} = 0.1221 + 15.80 \exp(-0.0632 \text{ cover})$$
for wheel tracks,
$$y \text{ (g/ha)} = -0.5132 + 10.47 \exp(-0.0632 \text{ cover})$$
for non-wheel tracks,
which are significantly different and non-parallel, $R^2 = 0.93$, $P<0.001$.

(d) endosulfan sulfate,
$$y \text{ (g/ha)} = 0.0872 + 1.164 \exp(-0.0614 \text{ cover})$$
for wheel tracks,
$$y \text{ (g/ha)} = -0.1798 + 1.164 \exp(-0.0614 \text{ cover})$$
for non-wheel tracks,
significantly different by 0.267 g/ha and parallel ($P<0.001$), $R^2 = 0.92$, $P<0.001$. 
Losses of α endosulfan were 1.3 times more than β from bare plots, reflecting their concentrations in the soil. As the applied endosulfan contained 70:30 α and β isomers, losses of β endosulfan represent a greater percent of the applied amount (up to 3% Fig. 7.2c) than for the α isomer (up to 1.8%, Fig. 7.2b). This is consistent with slower dissipation of the β isomer from soil after application (Kennedy et al. 1998). Losses of endosulfan sulfate represent a small proportion of the applied endosulfan, < 0.1% (Fig. 7.2d), consistent with low levels in the soil.

(c) Trifluralin concentrations and losses in runoff

Average concentrations of trifluralin in runoff were lower (about one half) for higher cover plots (wheat stubble and cotton trash retained) than for lower cover plots (Table 7.2). Concentrations related to cover treatment more so than decreasing with increasing cover, similar to endosulfan sulfate (and DDE, see discussion). Cover was less effective in reducing concentrations for trifluralin than for endosulfan. Concentrations were higher for wheel tracks than for non-wheel tracks, by 48% on average, a larger effect than for other pesticides. This is probably due to removal of trifluralin by the pre-planting irrigation, applied only to non-wheel track furrows and when only trifluralin was present.

\[
\text{Wheel tracks (solid line): Loss (g/ha)} = (-0.0919) + 2.26 \exp(-0.0346 \text{Cover}%),
\]
\[
\text{Non-wheel tracks (dashed line): Loss (g/ha)} = (-0.0919-0.609) + 2.26 \exp(-0.0346 \text{Cover}%).
\]

Fig. 7.3. Total losses of trifluralin in runoff during 65 mm of rain, from cotton furrows with a range of cover, with and without prior wheel traffic. Regression lines are parallel and significantly different by 0.61 g/ha (P=0.05). \( R^2 = 0.49, P=0.011, N=16. \)

Total losses of trifluralin in runoff were strongly related to cover and wheel traffic (Fig. 7.3), as total losses are more related to amounts of runoff and soil loss than to concentrations in that runoff. Thus losses were small with cover > 50% as there was little runoff and soil loss (Chapter 6). Losses were 0.61 g/ha less for non-wheel track plots across the range of cover (Fig. 7.3), i.e. about one third lower for bare plots. Data were more variable for trifluralin than for other pesticides, consistent with other observations of the behaviour of trifluralin (Wauchope 1978, Leonard et al. 1979). Total losses
were a small proportion of the applied amount (0.1-0.25% for bare plots), consistent with both incorporation during application and loss by volatilisation reducing concentrations in the soil surface layer that interacts with runoff (Leonard et al. 1979).

(d) Prometryn concentrations and losses in runoff

Average concentrations of prometryn in runoff were similar (n.s.d.) for all cover treatments (Table 7.2). Concentrations were 29% higher from wheel tracks than from non-wheel tracks. Concentrations of prometryn in runoff were not correlated with concentrations of sediment in runoff ($R^2=0.027$, n.s.). The lack of response of prometryn concentrations to cover is different to the other pesticides studied, because it is less strongly sorbed to soil (Table 7.1). Similar results have been obtained for other poorly sorbed herbicides (Baker et al. 1978). However, total prometryn losses in runoff were still related to cover and wheel traffic (Fig. 7.4), being reduced by more than an order of magnitude with >50% cover and by 3 g/ha in the absence of wheel traffic (Fig. 7.4). These responses strongly reflect effects of treatments on amounts of runoff (Chapter 6). This is further illustrated by results from one wheat stubble - wheel track plot (labelled 'high runoff amount' in Fig. 7.4), which gave similar runoff to bare plots and accordingly produced a prometryn loss similar to bare plots.

(e) DDE concentrations and losses in runoff

Average concentrations of DDE in runoff from bare plots on Block 5 (9.4 µg/L) were half those from Block 2 (18.8 µg/L) ($P<0.001$), due to lower concentration of DDE in soil on Block 5. For Block 2, where cover treatments were compared, DDE concentrations in runoff from the low cover
cotton trash mulched treatment were similar to bare plots, and those for wheat stubble and cotton mulch retained plots were 37% and 54% of those from bare furrows, respectively (Table 7.2). Thus DDE concentrations relate more to cover treatment, similar to trifluralin and endosulfan sulfate, than to the amount of cover as was found for α and β endosulfan. Concentrations of DDE in runoff were highly correlated with concentrations of sediment in runoff ($R^2 = 0.85, P<0.001$). Concentrations of DDE in runoff were similar for wheel and non-wheel tracks (Table 7.2), reflecting the similar sediment concentrations in runoff for wheel and non-wheel tracks (Chapter 6). Concentrations in runoff of DDE, not applied for almost 20 years, were greater than those of trifluralin, applied about 50 days previously, a telling reminder of the ‘unique persistence’ of DDT (Wauchope and Leonard 1980).

![Graph](image)

**Fig. 7.5.** Total loss of DDE in runoff during 65 mm of rain, from cotton furrows with a range of cover with and without wheel traffic. One non-wheel track plot had elevated DDE losses due to steeper slope and elevated soil loss. Block 5 is shown separately as it had lower levels of DDE in soil and runoff than Block 2. Amounts of DDE applied are unknown. Regression lines for Block 2 are parallel and significantly different by $0.53 \text{ g/ha} (P<0.05)$. $R^2=0.93, P=0.001, N=12$. Wheel tracks (solid line): $\text{Loss (g/ha)} = (-0.135) + 3.757 \exp (-0.0453 \text{ Cover}%)$
Non-wheel tracks (dashed line): $\text{Loss (g/ha)} = (-0.135-0.534) + 3.757 \exp (-0.0453 \text{ Cover}%)$

Total DDE losses in runoff from plots on Block 2 decreased exponentially with increasing cover (Fig. 7.5), with higher losses for wheel tracks (by 0.53 g/ha), strongly reflecting effects of treatments on soil losses (Chapter 6). Data from Block 5 show a similar trend in DDE losses with cover and wheel traffic (Fig. 7.5) though at overall lower levels. The effect of soil loss is further illustrated by one non-wheel track plot which had higher than average furrow slope and gave higher than expected soil loss (based on its cover) and gave a corresponding higher DDE loss in runoff than other non-wheel track plots (point labelled ‘steeper slope’ in Fig. 7.5).
Cover was more effective in reducing concentrations of α, β and total endosulfan in runoff (reduced 5 fold with 45-60% cover) than for endosulfan sulfate, trifluralin and DDE (reduced by about one half) and prometryn (no reduction). This occurred because concentrations of α, β and total endosulfan in soil surface (0-25 mm) were significantly lower with increasing cover, whereas concentrations of other pesticides were not significantly different between cover treatments (Fig. 7.6). Lower soil concentrations are expected to give lower runoff concentrations in almost direct proportion (Leonard et al. 1979). The α and β endosulfan were applied over the cover whereas trifluralin and prometryn were applied before the cover was placed, and DDE and endosulfan sulfate existed in the soil under the cover. (Little new sulfate formed from recent applications, as the soil surface was dry.)
and 21% in soil under the stubble 12 hours after application. At 2.4 days after application these levels declined to 5% on stubble and 19% under stubble, while bare soil still retained 50%. Similar results were obtained for wheat stubble and cotton trash at another site with generally cooler conditions (Chapter 3), but with a greater contrast with bare soil because dissipation from soil was slower. The extent to which endosulfan remaining on stubble would washoff and contribute to runoff is unknown, but it would be a much smaller amount than was available from the soil. Thus the greater the cover, the less endosulfan there was on the plots (i.e. on the soil and cover), and subsequently, in runoff. This is an additional mechanism whereby cover reduced endosulfan concentration in runoff, over and above effects of cover in reducing runoff amounts and sediment loads.

7.3.3 Effects of treatments on transport in sediment or water phase

(a) Pesticide concentrations transported in sediment

Concentrations transported on sediment (per L of runoff water, µg/L) decreased with increased cover for all pesticides (Table 7.3). This is expected given that concentration of sediment in runoff (g/L) decreased with cover. Sediment concentrations from covered plots (wheat and cotton trash retained) were one third of those from plots with low cover (Chapter 6). However, cover had a stronger effect on concentrations of α, β and total endosulfan transported on sediment than on sediment concentrations, indicating that some additional process was operating. Sediment from plots with more cover also contained less α, β and total endosulfan, that is, the concentration per unit mass of sediment was significantly lower (mg/kg, Table 7.3). For example, mg/kg concentrations from cotton mulch retained plots were one third to one half those from bare plots. This is consistent with the lower concentrations of α and β endosulfan measured in the soil surface on covered plots (Fig. 7.6) and implies that some sediment (with low endosulfan concentrations) was sourced from soil under the cover or otherwise protected by the cover. Because spray droplets do not all fall vertically, the vertical projection of cover reduces pesticide inputs to areas of soil that are accessible to raindrops and flow.

Prometryn transported on sediment (µg/L) was significantly lower (about one third) for wheat and cotton trash retained than for bare plots (Table 7.3). This had little effect on total prometryn concentration, which were not affected by cover (Table 7.2), as prometryn was mainly transported in the water phase. Endosulfan sulfate, trifluralin and DDE concentrations transported on sediment were reduced with higher cover, but related to cover treatment rather than decreasing with increasing cover. This is because sediment from wheat stubble plots had concentrations per unit mass of sediment (mg/kg, Table 7.3) similar to or less than bare plots, whereas sediment from cotton trash retained plots had significantly greater concentrations. These cover treatments also had contrasting sediment size distributions (Chapter 6), which we believe led to interactions between pesticides, sediment sizes and cover placement (see discussion). Where covered plots gave concentrations per unit mass of sediment greater than for bare plots (i.e. endosulfan sulfate, trifluralin and DDE from cotton trash retained), cover was less effective in reducing concentrations transported in sediment (µg/L).
Wheel traffic treatments had no significant effects on pesticide concentrations transported on sediment, consistent with similar sediment concentrations in runoff for traffic treatments (Chapter 6).

Table 7.3. Mean pesticide concentrations in runoff from cover treatments, in sediment per L of runoff and per kg of sediment, and in the water phase, and ratios of concentrations for higher cover (25-60%, wheat stubble and cotton trash retained) over those for lower cover (<10%, bare and cotton trash mulched). Within columns, means followed by the same letter are not significantly different (at $P=0.05$). Wheel traffic had no significant effects on concentrations in sediment per L of runoff and per kg of sediment. * $P<0.05$; ** $P<0.01$; *** $P<0.001$

<table>
<thead>
<tr>
<th></th>
<th>Endosulfan</th>
<th>Trifluralin</th>
<th>Prometryn</th>
<th>DDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>sulfate</td>
<td>total</td>
</tr>
<tr>
<td>Concentration transported on sediment (µg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare (rake and burn)</td>
<td>63.1 a</td>
<td>54.7 a</td>
<td>4.0 a</td>
<td>126.7 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>52.9 a</td>
<td>47.6 a</td>
<td>4.7 a</td>
<td>109.3 a</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>15.8 b</td>
<td>17.1 b</td>
<td>0.6 b</td>
<td>36.6 b</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>6.2 b</td>
<td>8.1 b</td>
<td>1.8 c</td>
<td>18.6 b</td>
</tr>
<tr>
<td>(Significance)</td>
<td>***</td>
<td>***</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Concentration in sediment (mg/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare (rake and burn)</td>
<td>3.28 a</td>
<td>2.84 a</td>
<td>0.23 a</td>
<td>6.58 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>3.15 ab</td>
<td>2.83 a</td>
<td>0.23 a</td>
<td>6.51 a</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>1.93 bc</td>
<td>2.09 ab</td>
<td>0.12 b</td>
<td>4.47 ab</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>1.15 c</td>
<td>1.46 b</td>
<td>0.36 c</td>
<td>3.35 b</td>
</tr>
<tr>
<td>(Significance)</td>
<td>*</td>
<td>*</td>
<td>***</td>
<td>*</td>
</tr>
<tr>
<td>Concentration transported in water (µg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare (rake and burn)</td>
<td>23.9 a</td>
<td>11.8 a</td>
<td>1.4 a</td>
<td>32.6 a</td>
</tr>
<tr>
<td>Cotton trash mulched</td>
<td>22.6 a</td>
<td>11.0 a</td>
<td>1.2 b</td>
<td>30.2 ab</td>
</tr>
<tr>
<td>Wheat stubble</td>
<td>16.2 b</td>
<td>9.2 ab</td>
<td>0.9 bc</td>
<td>23.3 bc</td>
</tr>
<tr>
<td>Cotton trash retained</td>
<td>11.8 b</td>
<td>6.7 b</td>
<td>0.8 c</td>
<td>16.9 c</td>
</tr>
<tr>
<td>(Significance)</td>
<td>***</td>
<td>**</td>
<td>***</td>
<td>***</td>
</tr>
</tbody>
</table>

(b) Pesticide concentrations transported in the water phase

For endosulfan and its components, concentrations in the water phase decreased significantly with increasing cover, with concentrations halved with >50% cover (Table 7.3). This contrasts with a much stronger reduction in concentrations transported on sediment, which decrease 7 fold with >50% cover. Concentrations in the water phase were similar (n.s.d.) with increased cover for trifluralin, prometryn and DDE (Table 7.3). Concentrations in the water phase were greater for wheel tracks than for non-wheel tracks for all pesticides (though only significant for endosulfan its components and prometryn). A similar response was observed for nitrate in runoff (Chapter 4). This may relate to the greater compaction and lower infiltration in wheel tracks (Chapter 6) with less leaching of desorbed components and more efficient extraction into runoff due to perching of water in the few cm of

228
pesticide rich soil above the compacted layer in the furrow. The greater total concentrations from wheel tracks (Fig. 7.1, Table 7.2) are solely due to these greater concentrations in the water phase.

For all pesticides, cover was more effective in reducing concentrations transported in sediment than concentrations in water (see ratios of concentrations Table 7.3). For trifluralin, prometryn and DDE, the reduction in transport on sediment was the sole effect of cover on concentrations.

(c) Total pesticide losses in water and sediment phases

As a percentage of total losses, pesticide transported in the water phase was 0.5% for DDE, trifluralin 7-11%, endosulfan 18-27% (α and sulfate about 1.5 times β), and prometryn 80%, for lower cover treatments (bare and cotton trash mulched). Effects of cover on losses in runoff, in total and in the water phase, are shown in Fig. 7.7 for endosulfan and prometryn, as curves fitted for all plots.

Endosulfan was mainly transported on sediment, while prometryn was transported mainly in water. Behaviour of trifluralin and DDE was similar to that of endosulfan, but with even less transport in the water phase for trifluralin and almost none for DDE. Total losses in the water phase deceased with greater cover for all pesticides, even though concentrations in the water phase did not decrease with cover for trifluralin, prometryn and DDE (Table 7.3). For the less sorbed, more soluble prometryn (Fig. 7.7b), control was only due to reduced runoff with cover, because the majority was transported in the water phase and cover did not affect concentration in the water phase. Cover provided more control of more highly sorbed pesticides (endosulfan, trifluralin and DDE) due to a large reduction in soil loss with cover (Chapter 6).
7.3.4 Interactions between cover, sediment sizes and pesticide transport

Aside from the obvious effects of cover in reduced pesticide transport by reducing runoff and sediment movement, two additional responses to higher cover treatments were observed:

(a) **Interception and dissipation of endosulfan on cover**

The strongest response of pesticide concentrations in runoff to cover was observed for pesticides applied on top of the cover (i.e. α, β and total endosulfan). There were several features of the data for these pesticides that did not occur for the other pesticides: (i) concentrations in the soil decreased with increasing cover, (ii) concentrations in runoff were lower for cotton trash retained than for wheat stubble, that is, concentrations decreased continuously with increased cover, (iii) concentrations in sediment (per kg of sediment) also decreased significantly with increased cover rather than relating to cover treatments, largely masking the response to sediment sizes (see below). These features are all in response to cover intercepting and dissipating endosulfan applied on top of the cover. Washoff from the cover was probably not a major source of endosulfan in runoff because endosulfan dissipated rapidly on the cover resulting in much lower levels on cover than on soil. The net result is that cover reduced endosulfan concentrations in runoff over and above effects of cover in reducing runoff amounts and sediment loads.

It is more difficult to determine how rapidly or consistently crop residue cover will dissipate, and thereby reduce runoff losses of, other pesticides, as there is little data available on pesticide sorption, persistence and washoff from crop residues. Pesticides that persist on crop residues and are readily washed off by rain would presumably be a source of pesticides in runoff, though not necessarily at a greater rate than from soil. Available dissipation data (Willis and McDowell 1987) mainly relate to insecticides applied to plant foliage and indicate fairly rapid dissipation. Mean half-lives for dislodgable residues for insecticide groups were 2.5-4.9 days. Half-lives for (dislodgable) endosulfan on cotton foliage at 30°C were about 1 day, in reasonable agreement with data for dissipation of endosulfan from crop residues (Chapter 3). The limited data for herbicides, mainly on grasses, indicates that, on average, half-lives for herbicides were 8 ±4 days, though none of the more water soluble, persistent herbicides of interest in cotton and grain cropping (e.g. atrazine, prometryn, diuron, metolachlor) were represented. Baker et al. (1982) found little or no effect of application above or below crop residues on concentrations in runoff water and sediment for three herbicides (atrazine, alachlor and propachlor). Martin et al. (1978) found these herbicides (and cyanazine) were rapidly washed off corn residue by rainfall, with most (60–90%) of the applied amounts recovered in the washoff water. In both studies rain was applied within 24 hours of pesticide application (about 20 hr and 12 hr, respectively) when differences due to dissipation from crop residues would have had little time to become apparent. The dissipation data, albeit not for crop residue cover, does appear to indicate more rapid dissipation on plants than on soil and that further study of the use of crop residues to reduce pesticide runoff via this dissipation mechanism may be fruitful.
For pesticides applied before or under crop residues (trifluralin, DDE, endosulfan sulfate and prometryn) concentrations in runoff were lower for wheat stubble than for cotton trash retained, though the latter had considerably more cover. For example, endosulfan sulfate concentrations were reduced by 70% with wheat stubble (mean 27% cover), but by only 53% with cotton trash retained (mean 52% cover), even though these treatments gave similar sediment concentrations (Chapter 6). This is because sediment from cotton trash retained plots contained significantly greater concentrations of these pesticides (i.e. mg/kg) than those from wheat stubble plots; about double for trifluralin, prometryn and DDE, and 3 times for endosulfan sulfate (Table 7.3). Sediments from these cover treatments also had contrasting undispersed size distributions due to different placement of cover – wheat stubble in the furrows, cotton trash evenly spread over hills and furrows (Chapter 6). Runoff from wheat stubble plots had a considerably higher proportion of suspended sediment (<0.02 mm) and less coarse sediment (2-0.25 mm) than cotton trash retained plots. Thus cover treatments that produced a greater proportion of coarse sediment also give higher concentrations (mg/kg) of trifluralin, prometryn, DDE and endosulfan sulfate in sediment, and treatments with more suspended sediment had lower concentrations. The most obvious case was for endosulfan sulfate (Fig. 7.8).

![Graph](image)

**Fig. 7.8.** Concentration of endosulfan sulfate in sediment (mg/kg) was (a) significantly greater where sediment contained a greater proportion of coarse (>0.25mm) sediment, and (b) lower where runoff contained more medium (0.25-0.2mm, diamonds) and suspended (<0.02mm, open squares) sized sediment.
Regression analysis revealed a consistent (though not always significant) trend for increasing concentrations of pesticides in sediment (mg/kg) with increasing percent coarse sediment and decreasing concentration with increasing percent suspended and medium (0.02-0.25mm) sizes. When data were adjusted for differences in pesticide concentrations in the soil, these trends were also evident for endosulfan, with suspended sediment explaining 56% of variation in mg/kg concentrations in sediment, while percent coarse sediment explained 37%. Endosulfan sulfate concentrations in sediment (adjusted for soil concentrations) were negatively correlated with suspended sediment ($R^2=0.86$) and positively correlated with coarse sediment ($R^2=0.63$). DDE concentrations in sediment were positively correlated with coarse sediment ($R^2=0.66$) and negatively correlated with suspended ($R^2=0.52$) and medium sediment ($R^2=0.54$). Variations in concentrations of trifluralin and prometryn in sediment were not as strongly related to sediment sizes (e.g. $R^2<0.3$).

These data imply that coarse sediments contained higher concentrations of these pesticides than suspended sediments. The opposite is often expected for soils where larger particles are primary mineral particles (Karickhoff and Brown 1978, Walter et al. 1979, Rose and Dalai 1988). However, for aggregated clay soils, pesticide concentrations in coarse particles up to twice those in fine particles have been measured in aggregates (Ghadiri and Rose 1993a) and eroded sediments (Ghadiri and Rose 1993b). Richardson and Epstein (1971) found higher concentrations of endosulfan on 'sand sized' particles (of high organic matter content) than on fines for one of the two silt loam soils they studied, although other pesticides were dominantly sorbed to clay sized sediment.

Higher pesticide concentrations in larger aggregates and sediments may be related to higher organic matter contents (Ghadiri and Rose 1993b) and preferential preservation of pesticides entrapped within larger aggregates, for example, by greater protection from volatilisation, leaching or microbiological degradation. Also breakdown products such as endosulfan sulfate may be more likely to form from sorbed parent isomers within aggregates where the parent isomers are less exposed to volatilisation. These processes would presumably be reinforced with aging. In our study, evidence for this is confounded due to the direct effect of cover on the most recently applied pesticide (endosulfan). However, Silburn and Spann (unpublished data from the Jondaryan study) found greater concentrations in larger sediments for endosulfan and several other insecticides, and the relative difference in concentration across sediment sizes increased with time after application. The inference made from the present study, and other more direct data, is that the assumption of greater concentrations of chemicals on finer sediments should be applied with caution for aggregated clay soils. Also, if finer sediments have lower concentrations than the bulk soil and are selectively transported, enrichment ratios less than one are possible.
7.3.5 Comparison between pesticides

The study is for the scenario of a storm occurring several weeks after cotton planting, with associated herbicide applications, followed by two endosulfan applications, with each pesticide applied at recommended rates and dissipated to differing degrees by the time rain was applied. Transport in runoff for each pesticide is to a large extent determined by its concentration in the soil at the time of the applied rain, which depends on application amount and method, time since application and dissipation rate. Concentrations and losses in runoff both rank in decreasing order: total endosulfan, α-endosulfan, β-endosulfan, prometryn, DDE Block 2, trifluralin = DDE Block 5, endosulfan sulfate, the same order as concentrations in the soil (Fig. 7.6) with the exception of trifluralin. These results reflect the recent and comparatively large amount of endosulfan applied, with more α applied than β. Prometryn was applied less recently and as a band spray (i.e. a lower rate), but is more persistent than endosulfan. Prometryn is the most prone to leaching of the pesticides studied. Leaching prior to runoff starting may have reduced runoff losses, but did not prevent runoff transport. Potential for DDE losses in runoff would be similar throughout the year and for years to come. Trifluralin concentrations and total losses in runoff were an order of magnitude less than those for endosulfan and a quarter those of prometryn. Lower losses of trifluralin compared with other pesticides has also been observed in catchment runoff studies (Leonard et al. 1979), and reflect effects of (i) incorporation during application, and volatilisation, reducing the concentration in the soil surface layer which interacts with runoff and erosion (Leonard et al. 1979), and (ii) the longer time since applications of trifluralin than the other pesticides. Runoff transport of endosulfan sulfate was low because little sulfate was present at this time of the year, but would increase somewhat as the season progressed (Simpson et al. 1998).

7.3.6 Management of pesticide runoff from cotton fields

Retention of crop residues on the soil surface to provide cover gave considerably lower concentrations and total losses of pesticides in runoff during rain. The benefits of cover in reducing pesticide transport in runoff were further enhanced when wheel traffic was avoided (to reduce soil compaction and runoff) and where pesticides sprayed onto the cover dissipated rapidly and prevented levels building up in the soil. Cover was particularly effective for more sediment sorbed pesticides (endosulfan, trifluralin and DDE), and gave considerably lower total losses for prometryn, a less sorbed pesticide, albeit with no reduction in concentrations.

Practical considerations in implementing retention of cover in cotton are discussed in the companion paper (Chapter 6). Given reassurance from this and other work (e.g. Simpson et al. 1998) that cover can be effective in reducing pesticide runoff, retention of cover was trailed in commercial scale cotton crops. Double cropping from wheat into cotton, with wheat stubble retained, performed well in the Emerald Irrigation Area (Waters et al. 1999, Waters 2000) and at Bourke NSW (Whyte 2000), giving good erosion control, acceptable yields and reduced runoff of pesticides. Also at both locations, an additional benefit was significantly lower insect pressures in early to mid-season,
requiring fewer insecticide applications and further reducing risks of pesticide runoff. At Bourke, the number of insecticide applications was halved in wheat stubble-cotton compared with bare fallow-cotton, in each of two seasons (Whyte 2000). Beneficial insect populations were also higher in wheat stubble-cotton, for instance, with three times the number of spiders. This is consistent with results from China, where some 2.5 million ha of cotton is grown in a wheat-cotton intercropping system, with insect population structures more diverse and more stable, and less prone to pest insect outbreaks, than in single cotton cropping (Xia 1994). Growing cotton in wheat stubble appears one step closer to an ecologically balanced system than growing cotton on bare soil.
CHAPTER 8.
CONCLUSION
8.1 Introduction

This study considered runoff of pesticides from cotton fields using a rainfall simulator. The Australian cotton industry is dominantly based on clay soils on low sloping land and uses a hill-furrow surface geometry. These conditions are different to those in many pesticide runoff studies. When this study commenced there has been little research into hydrology, erosion and pesticide runoff in the industry. Furthermore most studies of pesticide dissipation, sorption and runoff have been on more coarsely textured soils, more typical of North America. This was a poor basis for assessing the risk of runoff of pesticides used in the industry, in particular the insecticide endosulfan, with confidence.

Based on the literature, the factors that determine pesticide runoff from soil during a rainfall are:

- Application rate and dissipation, resulting in the concentration of the pesticide in a shallow surface layer (e.g. 0-25mm) at the start of the runoff producing rainfall,
- Leaching of the pesticide out of the surface soil during the event,
- Extraction of the pesticide from the soil into runoff, in water and by entrainment of sediment,
- Distribution of pesticides in runoff between water and sediment phases, which affect the mode of transport, options for management off-site and environmental fate.
- Management practices that affect these factors, by changing hydrology, erosion or pesticide load.

Properties of the pesticide may affect each of these processes. There are many pesticides, and other chemicals, that may contaminate soils and they can vary widely in volatility, degradation, mobility and partitioning. Most pesticide runoff studies involve only a few pesticides. The runoff concentrations observed are the result of the conditions of the study, and the timing of runoff after spraying, as much as they are due to the properties of the pesticide. Rather the data must be interpreted within a framework that separates the inherent behaviour of different pesticides, the causal factors and conditions of the study. Wauchope and Leonard (1980) investigated such a framework but there seems to have been little progress since. In this thesis, the factors listed above were investigated and a simple framework is used to interpret runoff of pesticides used in the Australian cotton industry, using data from simulated rainfall studies.

8.2 Dissipation before the rainfall event

Dissipation of pesticides from the surface soil 0-25 mm layer was studied in typical cotton growing conditions at four sites (Chapter 3). Data was obtained on soil concentrations, initial losses and dissipation for the period immediately after spraying (generally covering 1-3 half-lives), relating to the period of potentially high runoff concentrations rather than to long term persistence. While the major emphasis was on dissipation of endosulfan from soil and crop residues, several organophosphate
(OP) insecticides (chlorpyrifos, dimethoate and profenofos) and a range of herbicides (fluometuron, metolachlor, prometryn, diuron, pendimethalin, pyrithiobac sodium) were also studied.

8.2.1 Dissipation from bare soil

Concentrations in the surface 0-25 mm layer followed first-order dissipation in most cases. Half-lives were 6-20 days for endosulfan (total of α-, β- and some sulfate), 8-13 days for OP’s, and 13-32 days for herbicides. However, larger initial losses (within day 1) and more rapid dissipation extending out to 2.5-5 days (i.e. two-phase dissipation) were observed for endosulfan when sprayed at higher temperatures and for several OP’s. The response to temperature, the properties of endosulfan (low solubility, high vapour pressure, high K_H) and direct measurements of vapour by Kennedy et al. (1998, 2001) indicate these initial losses are more likely related to volatilisation. Initial losses of 30-60% occurred for dimethoate except when sprayed in the evening. Large initial losses occurred for dimethoate, profenofos and chlorpyrifos at a site where no initial loss was observed for endosulfan, even though these pesticides are expected to be less volatile than endosulfan. Dissipation for the OP’s was typically rapid and multi-phasic. These OP’s are susceptible to hydrolysis, and for chlorpyrifos at least, the rapid dissipation may be due to clay-catalysed hydrolysis (Racke 1993).

In terms of being able to predict pesticide concentrations in surface soil, as a precursor to predicting pesticide runoff, the greatest uncertainty is probably related to the occurrence or otherwise of these large initial losses and early rapid dissipation. Large errors in the effective application rate represent a large difference in the starting soil concentration used for calculating dissipation (Walker 1976). Models that missed this early rapid dissipation would over-predict pesticide runoff. Most current models lump such losses in an ‘application efficiency’ with few physical processes (e.g. effects of temperature) considered due to lack of data. The initial losses appear to relate to environmental conditions in the first few hours after spraying. Contact with the soil for a few hours at moderate temperatures (e.g. 20°C) appears to prevent initial losses although results were more consistent for endosulfan that for the OP’s. Modelling of runoff of volatile pesticides such as endosulfan could be improved by including a temperature effect on application efficiency. Further study is required, for instance, simultaneous measurements of vapour losses, soil concentrations and climatic conditions in the first few days after spraying, and also to determine the loss mechanism in the case of the OP’s.

At a site exposed to rainfall, dissipation in the surface 0-25 mm soil was more rapid than in the 0-50 mm soil layer, but this varied from no effect for the most rapidly dissipated OP’s to 1.6 times faster for endosulfan, and varied according to K_OC for the herbicides. Herbicides with lower K_OC values dissipated faster in the surface layer than those with higher K_OC, due to greater downward movement of the less sorbed herbicides. For example, the most mobile herbicide, pyrithiobac sodium, dissipated 1.7 times faster in the 0-25 mm layer. Downward movement increases concentrations in 25-50 mm soil over time, which increases the apparent half-life in 0-50 mm soil. That is, degradation is not necessarily any different. Movement below 50 mm in the soil was minimal.
Half-lives in 0-25mm soil were generally considerably lower than published 'selected' values (Wauchope et al. 1992, Hornsby et al. 1996). Only for dimethoate and profenofos were selected values similar to values observed here, but only when rapid early losses were ignored. Chlorpyrifos dissipated much more rapidly than generally observed elsewhere, though still within the range of published data. The herbicides studied dissipated at 2-3 times the rate of selected values ($t_{1/2}$ 60-90d), although pyrithiobac sodium's dissipation was consistent with data for soil of similar pH. These results are consistent with observations that "runoff available residues" dissipate more rapidly than generally expected for bulk soil (Wauchope and Leonard 1980). The shallow depth of soil studied (which enhanced downward movement) and surface application, without incorporation into the soil, contributed to more rapid dissipation due to exposure to climatic extremes.

Half-lives for endosulfan were generally lower than those found in North American studies (Stewart and Cairns 1974, Spencer et al. 1985) and than the 'selected' value (50 days, Wauchope et al. 1992). This simply reflects the limited data available when the selected values were compiled. Half-lives were 5-11 days for $\alpha$-endosulfan and 9-27 days for $\beta$-endosulfan, but dissipation of the two isomers was affected differently by site and/or environmental factors. Half-lives were closer to values determined in India (Rao and Murty 1980, Agnihotri et al. 1996, Kathpal et al. 1997) and recent studies in cotton fields in Australia (Kennedy et al. 2001) (i.e. in warmer climates). A half-life of ten days presents a considerably different environmental risk than a half-life of 50 days. However, even with a half-life of 6-20 days, the high application rate of endosulfan and repeated applications early in the growing season mean that it is present in reasonably high concentrations in the surface soil for a considerable portion of the cotton growing season (Kennedy et al. 1998, 2001, Simpson et al. 1998). It is thus not surprising that endosulfan is predicted to occur commonly in runoff from cotton fields under this pattern of use (Connolly et al. 2001).

Effects of a number of factors on dissipation of endosulfan were investigated. Dissipation of $\alpha$- and $\beta$-endosulfan was only slightly more rapid where soil was temporally wetter after rain, but formation of the sulfate metabolite was much greater, reducing the overall dissipation rate of total endosulfan. Little endosulfan sulfate formed in dry soils. Considerable endosulfan was physically relocated from the cotton hills into the furrows by local soil erosion under rain. Half-lives were slightly longer after two applications than after a single application, which is thought to relate to adverse effects on endosulfan-degrading soil microbes (El Beit et al. 1981) or simply the inclusion of more aged and stable residues from the first spray in the soil after the second spray. Endosulfan formulation (ULV or EC) and band spraying appeared to have no systematic effects on dissipation. Band spraying simply reduced the soil concentration averaged over the area.

Even though dissipation half-lives for the various pesticides cover a limited range, the combination of different application rates and dissipation rates lead to large differences in soil concentrations. Data for dissipation under local conditions and for the surface soil that contributes to pesticide runoff should allow an improved risk assessment.
8.2.2 Dissipation of endosulfan from crop residues

Retaining crop residue cover on the soil surface was effective in reducing runoff of pesticides, but was more effective for endosulfan sprayed over the cover than for pesticides present in the soil under the cover (Chapter 7). Thus dissipation of endosulfan after spraying on wheat and cotton crop residues was investigated under field conditions at two of the study sites. Endosulfan dissipated rapidly from crop residue cover due to large losses (e.g. 75-90%) within the first day after spraying, presumably due to volatilisation. This is consistent with the known volatility of endosulfan on plant foliage (Wilson et al. 1983, Silburn et al. 1996, Kennedy et al. 2001). Half-lives for endosulfan on crop residues after the initial loss were similar to those in soil, except that sometimes β-endosulfan dissipated as rapidly as α-endosulfan, which has also been observed in foliage (Kennedy et al. 2001). Half-lives for endosulfan in soil under cover were also similar to those in bare soil.

Reduction in pesticide runoff by retaining cover has generally been attributed to less runoff (containing soluble pesticides) and sediment (containing sorbed pesticides) (Walter et al. 1979). The data for endosulfan indicate that an additional benefit of retaining crop residues on the soil surface is that it intercepts and dissipates the pesticide more rapidly than when sprayed onto soil. However, it is not known if this will occur for other pesticides, particularly those that are less volatile and more stable. Washoff of herbicides directly from crop residues is often suggested where greater runoff concentrations are found for conservation tillage (Baker et al. 1978, Blevins et al. 1990, Gaynor et al. 1995). However, considerably more needs to be known about the behaviour of pesticides on crop residues (discussed in Chapter 3), especially as retaining cover is one of the main practices for managing soil erosion and water quality (Freebain et al. 1996). This should include studies of dissipation and washoff of pesticides, with a range of properties, on crop residues.

8.3 Pesticide extraction from soil to runoff

Wauchope and Leonard (1980) showed that a large amount of the variation in pesticide runoff is related to application rate, formulation and placement, and dissipation. Here the analysis was simplified by only considering placement on the soil surface (i.e. not on plant foliage etc) of liquid/emulsified formulations, although some soil-incorporated sprays were included. By comparing pesticide runoff to the concentration in the soil surface at the start of rain, one set of factors (i.e. those that occur before the rainfall event – application and dissipation, considered above) were separated from those that occur during the rainfall event. Pesticide concentration in runoff should then be a function of (a) the concentration in the soil, (b) the distribution with depth in the soil, (c) desorption and leaching out of the soil surface, and extraction into runoff in the water phase, and (d) extraction of the sorbed pesticide into runoff with sediment.

The runoff extraction process was investigated in Chapter 4, in a simple empirical analysis, by comparing concentrations in the soil and the event average concentration in runoff, using data from rainfall simulator studies in cotton fields and data from the literature. The ratio of runoff concentration to soil concentration, or the slope of the relationship between concentrations in soil and
runoff (linear regression fitted through the origin), was termed the runoff extraction ratio or \( E_{RO} \), with similar ratios for runoff in the water phase (\( E_{WAT} \)) and sediment phase (\( E_{SED} \)), and the ratio of concentration in sediment and soil per kg was termed the sediment enrichment ratio (\( E'_{SED} \)).

8.3.1 Rainfall simulator studies in cotton fields

Rainfall simulator studies with a variety of spray and cultural treatments were conducted at three sites, providing data for concentrations in soil (0-25mm) before rain and in runoff (event average concentration) in total, and in the sediment and water phases. Data were available for 14 pesticides, with endosulfan (\( \alpha- \) and \( \beta- \)isomers and the sulfate) and prometryn included at all sites. These pesticides varied widely in solubility (0.003-700,000 mg/L) and ranged from tightly sorbed (DDE, \( K_D \sim 15,000 \)) to weakly sorbed (fluometuron, dimethoate and pyrithiobac sodium, \( K_D < 30 \)).

(a) Runoff extraction on bare soil

Total concentrations in runoff (in water and sediment) of each pesticide were closely related to concentrations in the soil (0-25mm) before rain, generally with a similar relationship for all pesticides and sites. Thus runoff extraction ratios were similar for pesticides with a wide range in sorption properties and for the three soils, over four orders of magnitude range in concentrations. As a first approximation, concentration in runoff (\( \mu g/L \)) = 28 times concentration in soil (mg/kg), (or \( E_{RO} = 28 \)). Runoff extraction was also approximately similar for dissolved N and P, and organic N.

\( E_{RO} \) values were not related to partition coefficients (\( K_P \)) measured in runoff from the plots. However, runoff extraction did decrease with time after spraying and was lower for aged DDE and trifluralin at one site. This is considered to relate to a reduction in the concentration in the surface few mm of soil (compared to the average for 0-25mm soil) over time, due to dissipation and downward movement. Runoff extraction is equivalent to complete extraction of pesticide from a soil depth of less than 2mm (assuming complete extraction into 50mm of rainfall). \( E_{RO} \) values were similar within the range of slopes studied 0.2-4%, for long and short plots, and for banded and blanket spray plots. Band spraying is accounted for when average soil concentrations are calculated on a whole area basis. Where cover reduces sediment concentration in runoff, the runoff extraction in the sediment phase was reduced. Runoff extraction was significantly lower for a weakly sorbed pesticide (dimethoate) in only one instance and this did not occur for a range of other weakly sorbed pesticides at the other sites.

Concentrations in the water and sediment phases in runoff, and in sediment (mg/kg), were linearly related to soil concentrations, within groups of pesticides with similar partition coefficients, but varied widely between these groups. This variation between groups is accounted for by normal partitioning (partitioning total runoff extraction using \( K_P \) and sediment concentration, Eqn 5-5). Thus \( E_{WAT} \) decreased and \( E_{SED} \) increased as the \( K_P \) increased, associated with the pesticide or the observed increase in \( K_P \) with time after spraying. The sediment concentration in runoff, which ranged from 10-60 g/L, had a secondary effect on \( E_{RO} \), so long as sediment concentration was not too low. This occurred because higher sediment concentrations were associated with lower concentrations of
pesticide in the sediment (mg/kg), due to greater desorption (based on normal partitioning) and less physical enrichment.

Physical enrichment due to size-selective sediment sorting was limited compared with that observed on coarser textures soil (e.g. enrichment ratio up to 8). Enrichment ratios were mostly less than 1.0 (due to desorption) and no greater than 2.0. Thus for all pesticides, the concentration in sediment (mg/kg) was within about a factor of two of the soil concentration adjusted for desorption using the normal partitioning equation. OC and clay were also only slightly enriched in sediment. This occurred despite considerable deposition in the furrows and 3-5 fold enrichment of fine-sized sediment (Chapter 6). This is because the soils eroded as aggregates (due to low sand and high clay content), and because coarser sediment had greater concentrations of sorbed pesticides than finer (suspended) sediment, the opposite of what is normally expected (e.g. where coarser sediment is sand).

The notable similarity of runoff extraction ratio for all pesticides in the rainfall simulator studies was probably because (a) the main factor that limits runoff of weakly sorbed chemicals, i.e. leaching from the runoff mixing zone, was ineffective due to low infiltration and ponding of infiltrated water in the shallow tilled layer in the bottom of furrows, resulting in more complete mixing (discussed below), and (b) sediment concentrations were high enough to ensure transport of more strongly sorbed pesticides. Logically if there was little sediment in runoff there would be little transport of sorbed pesticide, but this only occurred on covered plots where sediment concentration was reduced. Also all pesticides generally had at least some transport in both the water and sediment phases (Chapter 5), which dilutes the response to sediment load. The concentration of pesticide extracted from soil into runoff appears to be determined by the soil concentration and the mixing and erosion processes, with, in the absence of significant leaching and the presence of sufficient sediment transport, little differentiation between pesticides of different partition properties. This is partly because, on any plot, the same mass of soil and the same volume of water are involved in mixing, independent of the chemical being considered, and because factors that increase extraction of solutes also tend to increase detachment of sediment.

The similarity of runoff extraction ratios between sites was probably due to somewhat similar soils, hydrology and erosion. However, the conditions studied would apply during early season storm events on much of the land used for irrigated cotton production in Australia and large areas of dryland cropping on clay soils after some period of fallow. Where hydrologic and erosion differed markedly from the conditions studied here, due to cultural practices and/or markedly different soil properties, runoff extraction would also differ and differentiation between pesticides according to sorption may occur. In particular, runoff extraction of weakly sorbed pesticides will decrease with considerably greater infiltration and runoff extraction of tightly sorbed pesticides will decrease when sediment concentrations are considerably lower.
8.3.2 Comparison with published data

Analysis of published natural and simulated rainfall data of Leonard et al. (1979), Baker (1980), Spencer et al. (1985) and five other studies in US croplands (Section 4.8) indicate the results from the rainfall simulator studies are not atypical. Higher runoff extraction was found for much more erosive conditions (e.g. steep US croplands) and lower runoff extraction occurred under low erosion conditions (e.g. furrow irrigation on low sloping fields in California). Apart from these cases, runoff extraction was similar on average for the rainfall simulator studies in Australian cotton fields and the dominantly water-transported herbicides studied by Leonard et al. (1979) on catchments and by Baker (1980) on simulator plots, catchment data for glyphosate (Edwards et al. 1980), low concentrations of 2,4-D (White et al. 1976) and high concentrations of acidic herbicides (Trichell et al. 1968). That is, the runoff concentration (C_{RO})-soil concentration (C'_{SOIL}) data for all of these studies plot near each other, around both the relationship C_{RO} (\mu g/L) = 28.C'_{SOIL} (mg/kg) from the simulator studies and C_{RO} (\mu g/L) = 50.C'_{SOIL}^{1.2} from Leonard et al. (1979). The furrow irrigation data of Spencer et al. (1985) for five pesticides was also similar (E_{RO} \approx 30) once adjusted to a higher sediment concentration. Extraction ratios were between 15 and 80 for the majority of cropland pesticide data, that is less than a factor of 2-3 around the average, but were as high as 200 for the most erosive conditions. Runoff of 2,4-D was also consistent for the rainfall simulator plots and catchment of White et al. (1976).

The analysis of the rainfall simulator and published data presents a conceptual framework where the major drivers of observed pesticide runoff were separated between (a) application rate and dissipation, described by the soil concentration at the start of rain, which may account for five orders of magnitude differences in runoff concentration, and (b) runoff extraction during the rainfall event, which appears to vary over a limited range.

8.3.3 Effects of leaching on chemical runoff

Importantly, runoff does not usually begin immediately during rain. Infiltration and leaching, by reducing the concentration in the runoff-mixing layer before runoff begins, can significantly reduce runoff of chemicals that are weakly sorbed. Because leaching is dependent on the sorption properties of the chemical, this process should lead to differences in runoff of pesticides with different sorption properties. However, the similarity of runoff behaviour of pesticides observed on the simulator plots and a simple modelling approach indicates that leaching was ineffective. This appears to be because the depth of water infiltrated during the applied storms was small (10-30 mm before runoff) and sorption was sufficiently high, even for the most weakly sorbed pesticides studied. Infiltration would need to be considerably greater, and/or sorption very weak (e.g. K_d < 1), for leaching to significantly reduce concentrations in the 0-25 mm layer. Behaviour of soluble NO_3-N indicated that, where infiltration was increased (by retaining cover) but flow into the subsoil was restricted due to compaction, leaching was also restricted. The hydrologic conditions encountered in the rainfall simulator studies are not atypical of storm rainfall on bare cultivated soil used for grain and cotton cropping in Eastern Australia (i.e. north of Dubbo) after fallowing or irrigation.
This result is consistent with previous studies where, for pesticides considered relatively mobile, most of the surface-applied compound did not move far into the soil with 100-250 mm of infiltration (Briggs 1981, Marley 1980, Walker and Blacklow 1995, Kookana et al. 1985, see Section 1.3.1(f)). This does not mean that some component of a poorly sorbed pesticide will not move deeper into the soil, as evidenced by the downward movement in soil noted in the dissipation studies. Only that the proportion lost from the surface soil in a single, reasonably intense rainfall event was small. This is a rather important outcome, which should be studied more directly, since it is sometimes argued that some pesticides ‘wont runoff because they wash into the soil’.

8.4 Sediment-water partitioning

Pesticide concentrations in the sediment and water phases in runoff from the rainfall simulator plots, for some 15 pesticides used in the cotton industry, were used to determine the percentage of the total loss in runoff in the water phase and the partition coefficient in runoff ($K_P$) (Chapter 5). Percentages in the water phase roughly followed the relationship with pesticide solubility for a range of other pesticides from Wauchope (1978) and a similar empirical relationship with soil sorption $K_{OC}$ values, but only for erosive conditions. These relationships do not reflect the range in responses that occur due to the likely range of concentrations and organic carbon content of sediment, or due to the increase in $K_P$ with time. Because of lower $K_P$ values soon after spraying, less soluble pesticides had 20-45% in water. Conversely, a few days/weeks after spraying, more soluble pesticides had only 60-80% in water. Thus all pesticides tended to have a ‘foot in each camp’ and some potential for management using erosion control practices.

Where sediment concentration varies widely or $K_P$ increases with time, it is an over simplification to expect ‘percent in water’ to be a characteristic of a pesticide. So long as sediment concentration and $K_P$ can be estimated, the percentage in the water phase can be calculated simply from first principles using Eqn 5-5, and behaviour for relevant field conditions can be assessed. This equation was used to show that reported values of percentage in the water phase for endosulfan that appeared to conflict (20-95%) and the values from the rainfall simulator plots (15-45%) are mostly explained by differences in sediment concentration and organic carbon in the studies. A wide range of percentages in water (e.g. 10-95%) will occur for pesticides with $K_P$ values of 5-500 (or solubilities ~1-100), such as endosulfan, for the range of sediment concentrations and organic carbon that might occur in the agricultural environment.

Partition coefficients in runoff ($K_P$) were not affected by cover and wheel traffic treatments, even though these treatments had large effects on runoff, sediment and pesticide runoff concentrations, and caused a large change in the percentage in the water phase. This makes interpreting effects of management practices on partitioning easier, as the distribution in water and sediment can be calculated using Eqn 5-5 with a constant $K_P$ value for each pesticide.

Partition coefficients in runoff ($K_P$) from the rainfall simulator studies increased with time after spraying, rapidly in the first few days and more slowly over the next few weeks, for all pesticides. $K_P$
values were generally greater than soil sorption $K_D$ values, increasingly so for pesticides of lower sorption and at longer times after spraying. Thus pesticides normally considered weakly sorbed had $K_P$ values considerably greater than their $K_D$ values, particularly at longer times. Conversely, moderately/strongly sorbed pesticides, such as endosulfan, had $K_P$ values considerably lower than their $K_D$ values in the first day or so.

Partitioning appeared to be influenced by both time of contact with soil and time of mixing (during rain). The results are conceptually consistent with a two-compartment, bi-phasic (fast-slow) adsorption-desorption model (Karickhoff 1980, Pignatello 1989, Truman et al. 1998a) with the soil in the runoff-mixing layer under rainfall being a continuous dilution system, under non-equilibrium desorption conditions, unlike a batch sorption study. The 'slow' phase, due to diffusion into soil domains that are less accessible to desorption, leads to increasing partition coefficients with greater time of contact. The short time of mixing during rain means that the water phase is mainly interacting with the 'fast' or most accessible fraction and limits diffusion of the 'slow' fraction out of the interior of the soil/sediment phase.

### 8.5 Managing pesticide runoff

Improved practices are needed to minimise soil erosion, and related agrochemical transport, from cotton fields during rain. Two options available to cotton growers, namely retention of surface cover (0-60%) and controlling wheel traffic, were evaluated using simulated rain on a hill-furrow system on a well-aggregated black Vertosol at Emerald (Chapter 6). Increasing cover resulted in an increase in the rain required to initiate runoff, and decreases in runoff, soil loss and sediment concentration. Runoff and soil loss were reduced by an order of magnitude with about 50% cover. No-traffic gave less runoff and soil loss than trafficked plots, but was less effective than cover. Cover and no traffic combined gave least runoff and soil loss. The erosion processes operating on the hill-furrow system and the sizes of undispersed sediments transported from the various treatments, which have consequences for erosion and pesticide transport, were investigated.

Pesticide transport in runoff from the cover and traffic treatments was also studied (Chapter 7). The scenario was a 65 mm storm 3 weeks after planting cotton, with associated herbicide applications and two endosulfan applications after planting. Concentrations of $\alpha$-, $\beta$- and total endosulfan in runoff decreased significantly with increasing cover, irrespective of cover type (wheat stubble or cotton trash) or placement (in furrow or overall). Concentrations of endosulfan sulfate, trifluralin and DDE decreased with cover, but were affected by cover placement. With 45-60% cover, concentrations were reduced 5-fold for $\alpha$-, $\beta$- and total endosulfan, halved for endosulfan sulfate, trifluralin and DDE, and unchanged for prometryn. Cover had more effect on endosulfan because cover intercepted and dissipated the sprayed endosulfan, reducing concentrations in surface soil (Chapter 3) and therefore in runoff. This is a mechanism for reducing pesticide runoff additional to effects of cover on runoff and sediment. Cover placement affected pesticide concentrations because cover in the furrows was more
effective in trapping larger sediment than evenly spread cover. Pesticide concentrations (mg/kg) were apparently greater in larger, aggregated sediment than in fines, possible because larger sediment allows contains more pesticide in the 'slow' desorption phase domain.

Cover had more effect on total pesticide losses (g/ha) than on concentrations, because cover reduced runoff and soil loss considerably. With 45-60% cover, total losses of α-, β- and total endosulfan were 1.4% of losses from bare plots, endosulfan sulfate and DDE 3%, trifluralin 5% and prometryn 8%. Avoiding wheel traffic gave 20-30% lower concentrations and 40% lower losses, due to lower transport in the water phase, and enhanced the effect of cover, but did not prevent large pesticide losses from bare plots. Prometryn was transported mostly in the water phase while other pesticides were transported mostly with sediment. Cover provided more control of more soil-sorbed pesticides (endosulfan, trifluralin and DDE) due to a large reduction in soil loss with cover. Control of the less sorbed prometryn was largely due to cover reducing runoff.

Trials on commercial sized cotton fields have now shown that these results translate into successful farming systems, where cotton is grown in rotation with wheat, with lower soil and pesticide losses (Silburn et al. 1998, Waters et al. 1999, Waters 2001, Whyte 2000).

When endosulfan was sprayed over the cover in the Emerald study (Chapters 6 and 7) interception and dissipation of the pesticide on the cover before rain significantly reduced the soil concentration available for runoff extraction (Chapter 3). In contrast, runoff extraction was significantly higher where pesticides were washed from the cover. This occurred for dimethoate and prometryn (soluble, weakly sorbed pesticides), two hr after spraying (Chapter 4). Behaviour over longer times is uncertain. Further study of pesticide dissipation and washoff from crop residue cover is warranted as retaining cover is a key element in conservation farming systems.

8.6 General comments

The dominant effect of chemical concentration in the soil surface, and therefore application rate and dissipation, on pesticide runoff has several implications. Firstly, uncertainties in dissipation rates, particularly the extent or lack of large initial losses, are probably the greatest source of errors in estimating pesticide runoff. Secondly, it should be possible to learn a lot about runoff potential of different pesticides and field conditions by studying pesticide behaviour on the soil surface under field conditions. Dissipation from the soil surface can be markedly different to dissipation after mixing/sorbing into soil. This logic would also apply to pesticides applied to plant foliage. This does open up the possibility of large variability due to the prevailing field conditions, however it is not an intractable problem as most pesticides have well defined use patterns in each industry and region. In pesticide and nutrient runoff studies it is essential to characterise the load and concentration within the catchment or plot through time, so that an estimate can be made for the start of each runoff event. Otherwise it will be difficult to compare between sites and pesticides.
The rainfall simulator proved to be very useful in studying pesticide runoff. In particular, it allows screening of a range of pesticide, spray and cultural treatments, collection of good quality samples and control over when it rains. This is probably why pesticide scientists were early adopters of rainfall simulators (Chapter 1). It is easier to study cause-and-effect processes with a rainfall simulator than under natural rain because most of the variables can be controlled.

Results from rainfall simulator plots appear reasonably consistent with larger plots and catchments. Time after spraying has a large effect on soil and runoff concentrations, and partitioning, and some effect on runoff extraction. Rainfall simulator studies have probably tended to give larger pesticide losses than from catchment (Wauchope 1978) because the simulator studies were often run very soon after spraying and, for sediment-bound chemicals, sediment loads were measured before gross deposition occurs. Neither of these conditions are intrinsic features of a rainfall simulator. Clearly, a rainfall simulator is an appropriate tool only where overland flow is the dominant hydrologic process and should not be used in isolation, particularly when spatial scale is one of the issues. The best approach is probably the use of a combination process data from rainfall simulator studies, dissipation data etc, and natural rainfall/catchment studies (the ‘reality check’) and a reasonably sophisticated model.

Study of several pesticides together during dissipation and runoff studies was very useful, providing more information but also contrast. This has become much easier with the continued development of multi-residue analysis. I would go so far as to suggest that chemical ‘standards’ should be used in pesticide runoff studies, possibly a very weakly sorbed chemical (bromide or chloride) and something strongly sorbed. Otherwise we will go on confusing pesticide behaviour with site-specific responses. Interpretation of pesticide distribution in runoff using a partition coefficient, in addition to a simple percentage was also valuable.

One outcome of this thesis is that runoff of different pesticides appears to be remarkably consistent (if a little approximate), under a range of conditions, when compared with the concentration in the soil surface. The empirical relationship derived here could be used as a model, that is, predictively. However, I consider that a somewhat more process based approach is preferable, as it will be less likely to fail under a wider range of hydrologic and erosion conditions. An example is the equations for leaching, and runoff extraction in the water and sediment phases, from Leonard et al. (1987). These equations are reasonably simple and model the pesticide runoff behaviour observed in this study very well (the chapter I didn’t write), which is not surprising given the consistency of the data. Indeed, it is worth noting that all of the processes discussed here are considered in pesticide runoff simulation models such as GLEAMS (Leonard et al. 1987), which has been used with some success and provides a longer term view (Leonard et al. 1995, Truman et al. 1998a, Connolly et al. 2001). Unfortunately such models lack transparency. The simple framework used here gives a transparent interpretation of pesticide runoff data, and a guide to planning of future experiments.
CHAPTER 9.
REFERENCES
CHAPTER 9. REFERENCES


Ahuja LR (1986). Characterisation and modeling of chemical transfer to runoff. *Advances in Soil Science* 4, 149-188.


Bruce RC and GE Rayment (1982). Analytical methods and interpretations used by the Agricultural Chemistry Branch for soil and land use surveys. Queensland Department of Primary Industries, Bulletin QB82004.


Burkhard N and Guth JA (1981). Rate of volatilisation of pesticides from soil surfaces; comparison of calculated results with those determined in a laboratory model system. Pesticide Science 12, 37-44.


Finlayson B and Silburn DM (1996). Soil, nutrient and pesticide movements from different land use practices and subsequent transport by rivers and streams. In ‘Downstream Effects of Land Use’ (Eds HM Hunter, AG Eyles, GE Rayment). pp. 129-140. (Department of Natural Resources: Brisbane)


251


252


Knisel WG (ed) (1993). GLEAMS: Groundwater loading effects of agricultural management systems – Version 2.10. University of Georgia (Atlanta), Coastal Plains Experimental Station, Biological and Agricultural Engineering Department, Publication No. 5.


APPENDIX A. PROPERTIES AND BEHAVIOUR OF ENDSULFAN

Endosulfan is an organochlorine (cyclodiene) insecticide, and is the major pesticide in this group used in the cotton industry. It is applied both aerially and by ground applicators for control of insect pests. It is particularly important as it is less expensive than many other pesticides, and is important in the Insecticide Resistance Management strategy (IRM), being used in Stage I and II. It is also considered moderately soft on beneficial insects and useful in integrated pesticide management (IPM) (Murray 1998). However, registration and conditions for use of endosulfan in the cotton industry has been the subject of review during the late 1990's and early 2000's. Endosulfan is also the primary cyclodiene insecticide still used in large quantities worldwide (Parkpian et al. 1998). Most cyclodiene insecticides have been banned due to their persistence, bioaccumulation and toxicity.

Endosulfan has been the subject of considerable study and some regulatory activity in recent years (Schofield 1998), as it is extremely toxic to fish, is frequently detected in inland rivers in cotton growing areas (DLWC 1996, CBWC 1999) and because it was the insecticide used in the largest quantities in the cotton industry during the 1990's. Toxicity appears to be reduced in natural waters, due to sediment and vegetation (Barrett et al. 1991). Peterson and Batley (1992) assessed environmental risk of pesticides commonly used in the cotton industry, using simple risk factor models (using mass applied, toxicity to fish, dissipation rate and sediment-water partitioning). Endosulfan had the highest risk ranking, due to a combination of high usage and high toxicity.

Properties of endosulfan are summarised by Wauchope et al. (1992), USDA-ARS (1994), Weber (1994), Hornsby et al. (1996), and environmental fate and transport are reviewed by Goebel et al. (1982), Gorbach (1982), Howard (1991) and Tomlin (1994). Some of the statements made by Howard (1991) about the behaviour of endosulfan would now be disputed based on new information (e.g. that minimal volatilisation is expected from soil).

A.1 Summary of properties

Endosulfan consists of a mixture of 2 stereoisomers, α- and β- in the ratio 7:3, which have somewhat different chemical and physical properties but similar toxicities. Metabolites in natural systems include endosulfan sulfate, which is significant because it is commonly detected, is as toxic as the parent compounds and may be more persistent (see below), and endosulfan diol, a non-toxic form. Endosulfan is non-ionic, neutral molecule and reasonably hydrophobic.

Wauchope et al. (1992) give selected properties, based on literature review, for endosulfan of: solubility 0.32 mg/L, initial field half-life 50 days, soil sorption $K_{oc}$ 12,400. These properties rank as ‘very low’, ‘moderate’ and ‘high’, according to Weber (1995). Field half-lives vary considerably (5-800 days), and are particularly rapid on plant foliage and in water, and in soil at higher temperatures (see Chapter 3). Solubility in water of α- and β- isomers are 0.53 and 0.28 ppm, respectively (Cotham and Bidleman 1989), 0.51 and 0.45 (Bowman and Sans 1983, Howard 1991), and for endosulfan sulfate, 0.48 (Bowman and Sans 1983), 0.17 (Chapra 1989) and 0.27±0.19 (Hugo 1999).

Endosulfan is quite volatile, particularly the α-isomer (Peterson and Batley 1993), consistent with a Henry’s constant almost an order of magnitude greater than β-endsulfan (Cotham and Bidleman 1989). Cotham and Bidleman (1989) give vapour pressure (mPa) as 6.08 and 3.04, compared with 1.53, 0.023 and 0.83 for ‘endsulfan’ (Barrett et al. 1991, Wauchope et al. 1992,
Tomlin 1994, respectively) and 0.023 for sulfate (Hugo 1999). Evidently this basic property varies considerably between sources. However, high volatility was confirmed under field conditions on soil and cotton foliage (Wilson et al. 1983, Kennedy et al. 1997b, 1998, 2001). Endosulfan is considered stable in sunlight (Tomlin 1994). Field trials have shown that photodegradation of endosulfan in soil and on foliage are probably insignificant (Southan 1996 cited by Kennedy et al. 1997).

A.2 Soil-water sorption

Wauchope et al. (1992) give a selected soil sorption $K_{OC}$ for endosulfan of 12,400, while the Pesticide Properties Database (USDA-ARS 1995) list only two (divergent) values, 2040 and 200,000. Howard (1991) gives estimates of $K_{OC}$, based on other properties, of 2900 and 6800 for $\alpha$- and $\beta$-endosulfan, respectively. Peterson and Batley (1993) measured partition coefficients for adsorption of $\alpha$- and $\beta$-endosulfan in six natural sediments (1-5% OC), which were related to OC content and were lower for $\alpha$- ($K_{OC} = 4,000$) than $\beta$-endosulfan ($K_{OC} = 20,000$). Greve and Wit (1971) measured adsorption on two samples of ‘silt’ (sandy clay, OC 2.4% and sandy peat OC 13.6%), giving $K_D$ values of about 18 and 10 ($K_{OC}$ of 740 and 74), and $K_D$ of about 2.5 on ferric hydroxide gel and 12.5 on activated carbon, with no difference between isomers (linear $K_D$ estimated from their Fig. 9-12).

Hugo (1999) measured adsorption of $\alpha$-, $\beta$- and sulfate endosulfan in batch and kinetics studies on a soil from Warren NSW (Vertosol, 0.57% OC) and other absorbents. Adsorption was about 30% lower for $\alpha$-endosulfan than for $\beta$-endosulfan; $K_D$ was 486, 670 and 42 for $\alpha$-, $\beta$- or sulfate endosulfan, respectively, or $K_{OC}$ of 85,300, 117,500 and 7,400. For the $\alpha$- and $\beta$-isomers, these values appear reasonably high; Hugo (1999) considered that the rapid agitation used during the batch adsorption method created more available adsorption sites by breaking down the soil aggregates. Adsorption was significantly affected by soil OC; $K_D$ values were reduced by two-thirds for both $\alpha$- and $\beta$-endosulfan, and by 44% for the sulfate, when soil OC was halved (to 0.285%) using $H_2O_2$. Hugo (1999) found no adsorption of $\alpha$-, $\beta$- or sulfate endosulfan (or metolachlor) on kaolinite, cellulose, alumina ($Al_2O_3$) or florisil (magnesium silicate), all polar absorbents, but strong adsorption to charcoal, in batch studies.

Endosulfan sulfate added as pure compound had much lower (e.g. > order of magnitude) sorption than the parent isomers during batch adsorption studies but not during desorption from field soils where it had formed in-situ (Hugo 1999, see Chapter 5). Endosulfan sulfate was also less sorbed to coal than the parent isomers. Hugo (1999) hypothesized that the sulfate should have greater water solubility based on the molecular structure.

In adsorption kinetics studies on a Vertosol, Hugo (1999) found sorption was bi-phasic. Approximately 90% of $\alpha$- and $\beta$- endosulfan was adsorbed in 1 hr, respectively, with equilibrium reached in 24 hr, while only 5% of sulfate was adsorbed after 1 hour and adsorption continued to increase at 168 hr (1wk). That is, adsorption of the sulfate was much slower than the parent isomers.

Parkpian et al. (1998) studied adsorption and desorption of $\alpha$-endosulfan in topsoil and subsoil from two soils (a clay and a clay loam) from Thailand. $K_D$ during adsorption (actually Freundlich K with 1/n near 1.0) was approximately linear functions of concentration and ranged 20-200 L/kg (reported values were multiplied by 1000, as per Hugo 1999), or $K_{OC}$ of 3,460-10,990. Equilibrium was approached within about 120 min with much adsorption out to 24 hr. Desorption $K_D$ values were several time greater than those for adsorption and varied with concentration (Freundlich 1/n <1.0). As with any batch desorption study, there were concerns about the artefacts introduced by the method.
used. Radiolabelled α-endosulfan was used so it would not have been possible to distinguish degradation products from the original compound.

A.3 Endosulfan in water and sediment phases in runoff

Reported values for the proportion of endosulfan in the water phase appear to conflict. For example, during studies of endosulfan in the Australian cotton industry (Schofield and Edge 1998), 80-90% was transported in the water phase from irrigated fields at the NSW field study near Warren (Kennedy et al. 1998, 2001), 60-70% in a rainfall simulator study near Warren (Hugo 1999), 20-30% in major erosion events at the Queensland field study (Bruce Simpson 1996, pers. comm.), 27% based on fugacity (Batley and Peterson 1992), compared with 90-98% in irrigation tailwater in California (Spencer et al. 1985) and about 20% based on the empirical relationship with solubility (Wauchope 1978). However, as shown Chapter 5, this variation in percent in water phase in runoff is explained by the concentration and OC content of sediment in runoff, with the ‘default’ $K_{OC}$ of 12,400 applying in most cases, resulting in a wide range in responses and apparent inconsistencies of reported values.

Peterson and Batley (1993a) found percentages of endosulfan desorbed from sediment (remobilised after exposure prior to field sampling) into water of 18 %, 12 % and 14 % for α-, β- and endosulfan sulfate, respectively. They considered these proportions greater than would be expected for such an apparently hydrophobic compound. They suggest this was due to high concentrations of colloidal particles in the water phase produced by shaking the sediment and water in their method. In analysis of water samples from lagoons, Peterson and Batley (1993a) separate the ‘colloidal’ fraction (0.025-0.45 μm, i.e. finer than the normal >0.45μm sediment or ‘particulate’ fraction) and found α-endosulfan was not associated at all, β- endosulfan was bound to a small degree, but endosulfan sulfate appeared to a significant degree. In artificial suspensions, 50% of β- and 90% of sulfate “may have been bound to marcomolecules”, i.e. was not removed by filtering to 0.45 and 0.025 μm. However, such enhanced solubilization of otherwise sediment-sorbed pesticides will commonly occur in experiments where soil/sediment are mixed in water, and in nature (Means and Wijayaratne 1982).

A.4 Degradation and dissipation

Wauchope et al. (1992) give a selected initial half-life of 50 days, while the Pesticide Properties Database (USDA-ARS 1995) lists six field dissipation values/studies ranging from 4-200 days and one aerobic half-life in soil (silt loam pH 6.4) of 27 days. Tomlin (1994) gives a half-lives in soil of 30-70 days for α- and β- endosulfan, and 5-8 months for α-, β- and sulfate endosulfan in the field, as the sulfate is degraded more slowly.

The structure and conversion pathways of endosulfan isomers and metabolites are described by Martens (1976), Miles and Moy (1979) and Peterson and Batley (1993a). Some interconversion of α- and β-isomers occurs. Degradation of endosulfan occurs mainly via biological oxidation to endosulfan sulfate in soil, sediment and plant surfaces, and chemical and biological hydrolysis to endosulfan diol (a non-toxic form) in water and saturated soil (Martens 1976, 1977, Miles and Moy 1979, Gorbach 1982). However, degradation processes are not exclusive because soils and natural waters are complex bio-chemical systems. Martens (1976) found the majority of soil fungi studied in aqueous solutions formed the sulfate while the majority of bacteria formed the diol. Hydrolysis, considered the dominant degradation process in water, is strongly increased with greater pH for both isomers.
(Martens 1976, Peterson and Batley 1991a, 1993a). Thus, at lower pH (6.5), presence of microorganisms greatly enhanced degradation (Miles and Moy 1979) while at higher pH degradation was no slower in sterilised waters (Martens 1976, Cotham and Bidleman 1989). \( \beta \)-endosulfan hydrolyses faster than \( \alpha \)- at each pH (Cotham and Bidleman 1989, Peterson and Batley 1991a).

A.4.1 Dissipation in soil

In soils under aerobic conditions (Martens 1977), the sulfate is the major metabolite (30-60% conversion), with other metabolites detected only in minor quantities (<3% of applied endosulfan). In flooded soils, less metabolites were detected, with 3-8% endosulfate and more diol (2-18%). Rates of dissipation of endosulfan in field soil, which includes degradation, volatilisation and other losses, in soils are discussed further in Chapter 3.

A.4.2 Dissipation in water

Dissipation in water for both \( \alpha \)- and \( \beta \)-endosulfan is reasonably rapid, but is strongly reduced at lower pH and lower temperatures. Hydrolysis appears the most likely degradation process, as degradation was no slower in sterilised seawater (Cotham and Bidleman 1989) and due to the strong pH response. Half-lives at 20°C for \( \alpha \)- and \( \beta \)-endosulfan were 4 and 2 days, respectively, in both sterile and non-sterile seawater (pH 8.0) (Cotham and Bidleman 1989), 5-10 days in distilled water with no difference between isomers (Kaur et al. 1998), and 3.6 and 1.7 days, respectively, in river waters at pH 8.0-8.5 (Peterson and Batley 1993a). Dissipation in water increases strongly with greater pH (Peterson and Batley 1991, 1993a), with half-lives for \( \alpha \)-endosulfan of 30-40 days at pH 7.0-7.5 decreasing to \( \sim \)1 day at pH 9.0, and for \( \beta \) endosulfan of 14-22 days at pH 7.0-7.5 decreasing to <1 day at pH 9.0. Greve and Wit (1971) found half-lives in water (at 20°C) for \( \alpha \)- and \( \beta \)-endosulfan of 150 and 187 days at pH5.5 and 35 and 38 days at pH7.0 under anaerobic conditions (hydrolysis), and 22 and 53 days (at pH5.5 and 7.0) under aerobic conditions (hydrolysis and oxidation) with little difference between isomers. However, half-lives were about 7 days in the presence of dissolved oxygen and a microorganism (at pH 7). Ghadiri et al. (1994a) found degradation of \( \alpha \)- and \( \beta \)-endosulfan in water was rapid, but declined with lower temperatures – half-lives of 15 and 24 hr at 25°C, 55 and 62 hr at 15°C, respectively, and almost infinity at 10°C. Temperature appears to have less effect than pH, except for low temperatures.

In natural waters of high pH, as are found in northern NSW, the hydrolysis rate of endosulfan was rapid, with half-lives of 3.6 days for \( \alpha \)-endosulfan and 1.7 days for \( \beta \)-endosulfan (Peterson and Batley 1993a), similar to half-lives in seawater (Cotham and Bidleman 1989). However, for water in the presence of soil or sediment (Cotham and Bidleman 1989, Peterson and Batley 1993a) or when organic/particulate matter is present in the water (e.g. humic acids Kaur et al. 1998), dissipation \( \alpha \)- and \( \beta \)-endosulfan in water was slower, as rapid hydrolysis is reduced due to sorption (e.g. half-lives 22 and 8.3 days, respectively, in the study of Cotham and Bidleman 1989).

A.4.3 Dissipation from surface/plant canopies

Observed volatility and rate of loss from surfaces are (Beard and Ware 1969, Gorbach 1982): glass plates - \( \alpha \)- > \( \beta \), sugar beet leaves: \( \alpha \)- > \( \beta \) \( \rightarrow \) sulfate. Half-life of endosulfan on cotton plants were 1 day at \( \sim \)28°C in Australia (Wilson et al. 1983) and 0.9 and 1.3 day for \( \alpha \)- and \( \beta \)-endosulfan from cotton in Arizona (30°C) (Willis and McDowell 1987 after Estesen et al. 1979). Coleman (1994) found that over 80% of endosulfan applied to cotton leaves (in a glasshouse)
disappeared within two weeks with initial half-lives of <1d and 3d for α- and β-endosulfan and some conversion to the sulfate (cited by Kennedy et al. 1997b, 1998, 2001). Dissipation rates would be different (more rapid) for the component that is dislodgable by rainfall washoff.

A.4.4 Other studies of endosulfan.


Endosulfan in soil experienced a pesticide-soil microbial interaction wherein the compound is broken down by microorganisms, but in doing so the microbes themselves are inhibited. α- and β-endosulfan are degradable by soil microorganisms when applied at low concentrations, but at high concentrations they inhibit microbial population in soil. When applied at 'low' concentration (280 ppm i.e. very high compared with the 0-10 mg/kg typically found in cotton soils), α- endosulfan was broken down by both bacteria and fungi, whereas β-endosulfan was mostly degraded by bacteria.


APPENDIX B. METHODS FOR NUTRIENT (N AND P) IN RUNOFF

The following is extracted from:

Nitrogen and phosphorus in soil before rain, and in runoff and sediment was measured during simulated storms on a sub-set of the Emerald hill-furrow plots (Block 2). Runoff and sediment results are presented in Chapter 6 and pesticide runoff in Chapter 7. Plots had a range of covers (0 to 60 %), each with and without prior wheel traffic. The study was conducted two to three weeks after cotton planting when N and P concentrations in the soil are elevated due to pre-plant fertiliser application.

B.1 Soil properties

Soil properties at the Emerald rainfall simulator site in Block 2 are given in Table B-1. Total N is very high, total P is medium-high and available (bi-carb) P is medium, according to the ratings of Bruce and Rayment (1982). The surface soil contained high concentrations of NO3-N (Table 1) due to capillary rise and evaporation after the pre-plant irrigation, as observed by Foale et al. (1986).

Table B-1. Selected soil properties for Vertosol surface soil (0-25 mm), used for the rainfall simulator study, Emerald, Queensland. Soil from the hill and furrow were sampled separately as soil on the hill is more likely to contribute sediment and nutrients by erosion during rainfall.

<table>
<thead>
<tr>
<th>Site</th>
<th>Coarse Sand (%)</th>
<th>Fine Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Organic Carbon (%)</th>
<th>CEC (cmol(+)/(H2O 1:5) kg⁻¹)</th>
<th>pH (H2O 1:5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hill</td>
<td>2.4</td>
<td>20.7</td>
<td>19.7</td>
<td>57.2</td>
<td>1.3</td>
<td>62</td>
<td>7.9</td>
</tr>
<tr>
<td>Furrow</td>
<td>1.9</td>
<td>20.8</td>
<td>16.5</td>
<td>59.7</td>
<td>1.2</td>
<td>60</td>
<td>8.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Total N Kjeldahl (mg/kg)</th>
<th>NO3-N (KC1) (mg/kg)</th>
<th>NH4-N (KC1) (mg/kg)</th>
<th>Total P (mg/kg)</th>
<th>P bicarb* (Colwell mg/kg)</th>
<th>Cl⁻ (mg/kg)</th>
<th>EC (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hill</td>
<td>1000</td>
<td>325</td>
<td>5</td>
<td>500</td>
<td>37</td>
<td>194</td>
<td>0.898</td>
</tr>
<tr>
<td>Furrow</td>
<td>900</td>
<td>225</td>
<td>6</td>
<td>500</td>
<td>34</td>
<td>276</td>
<td>0.817</td>
</tr>
</tbody>
</table>

* P bicarb is approx. bio-available P, but is not immediately soluble i.e. will not leach (P Moody, pers. comm.).

B.2 Nutrient sampling and analysis

Before rain commenced, soil samples (0-25 mm) were taken on each plot, from eight locations on the top of the hills and eight locations in the bottom of the furrows. These samples were composited separately for all hill samples and all furrow samples, for all plots. These (2) soil samples were air-dried and analysed for a range of soil physical and chemical properties (Table B-1), including dispersed particles size distribution, organic carbon (OC), total N (TKN) and total P (XRF) (Bruce and Rayment 1982, Rayment and Higginson 1992), and NO3-N and NH4-N by KC1 method.
Three types of runoff samples were taken for nutrient analysis:

(a) Runoff (water and sediment) for nitrogen and phosphorus forms (≈250 ml) were taken from each plot at five times evenly spaced during the runoff hydrograph.

(b) A composite (bulked) sample of runoff during the hydrograph; when each individual runoff samples was taken, an additional portion of runoff was added to a 20L bucket. The duration of sampling for each portion added to the bulked runoff sample was kept constant, providing a flow weighted sample of the runoff hydrograph. After the run, these bulked runoff samples were stirred vigorously and a 250 ml sub-sample taken.

(c) Bulk sediment remaining in the buckets was flocculated using K2SO4, decanted and air-dried.

The runoff samples and sub-samples of bulked runoff were analysed for nutrients. Nutrients in the sub-sample of bulked runoff were compared with the flow weighted mean concentrations measured through the hydrograph. The bulked sediment samples were analysed for dispersed particle size distribution, and where sufficient sample remained, for organic carbon, total N and total P, using the same methods as for soil samples (Bruce and Rayment 1982, Rayment and Higginson 1992). Less sediment was collected for less erosive treatments (i.e. covered and non-wheel traffic). Thus dispersed particle size distribution was missed for one plot (cotton mulch retained non-wheel track). Organic carbon, total N and total P were missed for most higher cover plots; results for these properties are only presented for low cover treatment and no comparison of treatments is attempted.

All runoff samples and sub-samples of bulked runoff were placed in insulated boxes with ice immediately after collection and transferred to the laboratory at about 4°C. Samples were stored at –15°C until analysis was commenced. Sub-samples of runoff and bulked runoff were filtered through Whatman GFF filters (0.7 μm nominal pore size) and constituents in filtered samples were considered to be dissolved in solution, although some may possibly have been present in fine colloidal forms.

filtered sub-samples of runoff and bulked runoff were analysed for Kjeldahl N (TKN) concentrations of particulate N and P calculated by difference between non-filtered and filtered sub-samples were ammonium-N, nitrate-N and P (FRP). Note that: a) total N comprised TKN plus nitrate-N in non-filtered sub-samples; b) TKN comprised organic N plus ammonium-N; c) TKN in filtered sub-samples was measured by automated colorimetric finishes (990). Analytical methods for ammonium-N, nitrate-N and FRP broadly followed colorimetric methods described in Eaton et al. (1995); the method for ammonium n-dophenol reaction (Searle 1984); for nitrate-N on the Griess-Ilosvay reaction reduction; and for FRP on the ascorbic acid acid/phosphomolybdic blue reaction (962). Concentrations of sediment were measured gravimetrically by filtration.

Concentration transport in runoff are presented as flow weighted average concentrations (kg/ha) in runoff during 65 mm (about 40 min) of applied rain. Total N is the sum of dissolved N (i.e. TKN plus NO3-N). Total P is the sum of sediment P and total P (i.e. P04-P). Concentrations of nutrients in sediment are generally presented as mg/L (i.e. per litre of runoff) so they are directly comparable with concentrations in runoff, unless
otherwise indicated. The rainwater used had 0.5 mg/L of total N and 0.04 mg/L total P, 15 and 50
times lower than the lowest concentrations of N and P in runoff, respectively.

Additional references specific to this Appendix.

Bran and Luebbe (1990). Individual/simultaneous determination of nitrogen and/or phosphorus in BD
Norderstedt, West Germany, 9 pp.


Murphy J and Riley JP (1962). A modified single solution method for the determination of phosphate

Searle PJ (1984). The Berthelot or indophenol reaction and its use in the analytical chemistry of
nitrogen - a review. Analyst 109, 549-568.
APPENDIX C. EVALUATION OF ‘BULK’ SAMPLING OF PESTICIDES IN RUNOFF.

One of the constraints in studying runoff of pesticides is the cost of analysis. This is particularly limiting when a number of samples need to be taken during a runoff hydrograph to obtain a reasonable estimate of the event average concentration. The runoff rate, sediment load and pesticide concentration in runoff are all potentially changing through time. However, the most useful data is the event average pesticide concentration – for determining the off-site impact or calculating the total loss (i.e. by multiplying by the total runoff amount).

Similarly, analysis costs are prohibitive if all runoff samples are filtered and used to determine the water and sediment phase pesticide concentrations separately – analysis costs are doubled. In the rainfall simulator studies reported in this thesis, a ‘bulked’ runoff sample taken throughout the hydrograph was used to determine the water and sediment phase pesticide concentrations. The bulked filtered samples have several advantages: they provide a flow weighted mean concentration in a single sample, they define the dominant mode of transport (water or sediment), and allow an event average partition coefficient to be calculated. Processing of these filtered bulk samples involved more steps in the laboratory, more time between collection and extraction (with possible degradation of the pesticides), and some risk that at low concentrations, concentrations in the water and/or sediment will be below the detection limit (DL). This would give a lower total concentration than obtained using a total extraction method.

To check the reliability of the bulked runoff samples, their total concentrations were compared to the flow weighted mean concentrations calculated from samples taken through the hydrograph. This will indicate if bulk runoff samples can be used as the primary method for measuring pesticide concentrations in runoff from rainfall simulator plots. That is, one sample rather than say, six.

C.1 Methods

The bulked samples of runoff were taken by adding a portion of runoff to a single bottle (per plot) at a number of times during the hydrograph (e.g. 5). The sample must include the entire runoff stream to achieve the flow weighted averaging. The duration of sampling for each portion added to the bulked sample was kept constant, providing a flow weighted sample of runoff. This duration of sampling must be predetermined, based on the expected runoff rate, so that the final sample volume approaches but does not exceed (in my case) ~500mL (i.e. about a half-full 1L bottle). The number of sub-sample taken through time can vary (i.e. to provide a larger or smaller sample) but should be reasonably evenly spaced. The methods used for analysis of pesticides in runoff samples (taken at discrete times through the runoff hydrograph) and in the bulked filtered samples are given in Chapter 2. Data from rainfall simulator studies at Emerald and Jondaryan are presented. Data for pyrithiobac sodium at Jondaryan are not included because different methods were used as part of a related project.
C.2 Results and discussion

C.2.1 Emerald

Concentrations from bulked runoff samples were highly correlated with mean flow weighted total concentrations, particularly for the endosulfan compounds and all data combined (Fig. 9.1). Prometryn, trifluralin and DDE each had a limit range in concentrations with which to compare the methods using regression. However, there is a certain amount of error involved for any individual sample. Average absolute error for the bulked method was 16.7%, or 12.7% when trifluralin was excluded. Bulked runoff samples had 27% greater concentrations of trifluralin on average (yet another example of the deviousness of trifluralin!). Alpha endosulfan was 16% lower in bulked runoff samples than in flow-weighted runoff. This is believed to be due to degradation in the laboratory analysis of the sediment phase in the bulked samples, a problem that was avoided in other studies. All other pesticides in bulked samples had average concentrations within ±6%, average error of −1.5% and average absolute error of 11.7%.

Fig. 9.1. Total pesticide concentrations in bulked runoff samples and flow weight concentrations, for runoff from rainfall simulator plots at Emerald.

C.2.2 Jondaryan

Concentrations from bulked runoff samples were highly correlated with mean flow weighted total concentrations (Fig. 9.2). Concentrations from bulked samples were 13% lower than those from mean flow weighted concentrations, with an average absolute error of 11.3% (N=60). However, the largest differences were for the most recently sprayed plots (2d after spraying) where mean flow weighted concentrations were 21% higher than bulked samples (Fig. 9.3). The regression is dominated by the more soluble herbicides (metolachlor, fluometuron, diuron and prometryn), which had high concentrations compared with most of the other pesticides. When data for this plot are
excluded, concentrations from the two methods are within 6% on average (Fig. 9.2), with an average absolute error of 10.2% (N=46).

Fig. 9.2. Total pesticide concentrations in bulked runoff samples and flow weight concentrations (log-log plot), for runoff from rainfall simulator plots at Jondaryan.

Fig. 9.3. Total pesticide concentrations in bulked runoff samples and flow weight concentrations (linear plot), for runoff from rainfall simulator plots at Jondaryan. BP_5 was 2 days after band spraying.
APPENDIX D. PESTICIDE ANALYSES – QLD HEALTH SCIENTIFIC SERVICES

Pesticides in soil and runoff from the rainfall simulator and dissipation studies at Jondaryan were analysed by the following methods by Queensland Health Scientific Services (Mary Hodge, pers. comm.). Analysis was requested for the following multi-residue groups, which included the listed pesticides:

- OC group - α-endosulfan, β-endosulfan, endosulfan sulfate, total endosulfan, metolachlor, pendimethalin, trifluralin, DDE, DDD, DDT, total DDT, heptachlor. Endosulfan lactone, alcohol and ether were also detected in some samples.
- Herbicide group - diuron, fluometuron, prometryn.
- OP group - profenofos, chlorpyrifos, dimethoate, monocrotophos, parathion-methyl.

The following description of the methods was supplied by Mary Hodge, Supervising Chemist, Organic Chemistry, Queensland Health Scientific Services.

**Water**: The method used is solvent extraction in which 60 gm of sodium chloride is dissolved in the water and then the water is extracted with dichloromethane according to EPA Method 3510. Concentrated extracts were quantified using gas chromatography and electron capture detection for the OC pesticides, endosulfan and the herbicides trifluralin, metolachlor and pendimethalin. Quantitation is based on EPA 8080 for OC pesticides. Quantitation for the OP pesticides is based on EPA method 8140 using gas chromatography and nitrogen phosphorus detection. This detector was also used for the herbicide, prometryn. The OP pesticides were confirmed using Flame photometric detection. References for prometryn and trifluralin is EPA method 507. Quantitation for diuron and fluometuron was by an in house method using HPLC with UV detection. Column is Hypersil MOS C8 5micron column and mobile phase with gradient elution using acetonitrile and water.

**Sediments**: Method was based on AOAC 15th edition (1990) No 970.52M for extraction and quantitation was the same as for the water. Filter papers were analysed using an in house method using acetone solvent, concentration and quantitation again as for the waters.

Detection limits were:

<table>
<thead>
<tr>
<th>Group</th>
<th>Water (µg/L)</th>
<th>Soil (µg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>OP</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>Hericides</td>
<td>0.1</td>
<td>10</td>
</tr>
</tbody>
</table>

Monocrotophos was not analysed in soil samples.

**D.1 References on which the methods were based.**


