

Modelling the fate of molinate herbicide in rice paddies of South Eastern Australia using RICEWQ

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Report Title: *Modelling the fate of molinate herbicide in rice paddies of South Eastern Australia using RICEWQ*

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Executive Summary

Contamination of drainage channels and creeks with pesticides used in rice production is of concern in south eastern Australia. Of major concern is the herbicide molinate that is detected in over 25% of water samples. This pesticide has been the focus of researchers and environmental protection authorities due to continuing frequent detection off farm despite improved application methods and water management guidelines.

The objective of this study was to assess the rice pesticide model RICEWQ version 1.7.2 for its applicability in simulating pesticide in runoff in south eastern Australia. The model was successfully calibrated against field data on water depths and molinate concentrations from a rice field in the Murrumbidgee Irrigation Area. It was found that the calibrated model was able to simulate the field data in the supply bay adequately; however it is not capable of modelling rice fields with multiple bays, which are much more complex than a single bay situation.

Sensitivity analyses of the parameter values on molinate concentrations in ponded water, sediment and foliage were performed. Overall the application efficiency has a major impact and this impact is carried throughout the entire simulation. In ponded water the bulk density, mixing velocity, release rate for slow release formulation, pesticide solubility and water/sediment partition coefficient were relatively sensitive. In the sediment the release rate and the mixing , soil bulk density, degradation rate in the sediment, water/sediment partition coefficient and mixing velocity have large sensitivities. On the foliage only three parameters have non-zero sensitivities, the application efficiency, the wash off coefficient and the degradation rate on foliage.

The calibrated model was used to investigate water and pesticide management for a single bay. It was found that water management was critical to minimising molinate runoff. Using a 41 year weather sequence for Griffith in the Murrumbidgee Irrigation Area it was found that if water levels were maintained 5 cm below the drainage outlet there was little likelihood of surface runoff occurring.

Simulation of the registered label application methods and rates for molinate were undertaken. These compared application onto a dry bay, a ponded bay and application by ground rig, aerial, and Soluble Chemical Water Injection In Rice Technique (SCWIIRT) low pressure system. The greatest maximum concentrations of molinate in the ponded water occurred when molinate was applied directly onto the water. The maximum concentrations for application onto a dry bay were an order of magnitude lower than for the applications onto a bay filled with water. However, the pesticide concentrations in water declined more rapidly for the application onto a water filled bay than for application onto a dry bay. Field trials are required to assess the accuracy of these results as no data comparing ponded water and dry bay applications is available.

The comparison of application methods was undertaken by adjusting the application efficiency parameter. This ranged from 60 % (assumed) for the aerial application on dry bay, to 70 % (assumed) for the ground rig, 95 % for aerial application, determined from the model calibration, and 100 % (assumed) for the SCWIIRT. The results showed that increasing the application rate by 60 % increased the period during which the water molinate concentration was above guideline level by 11 %. The results indicate that the application amount is only critical to the concentration of molinate in runoff if it occurs in about 30 days after application. The results regarding molinate concentrations in water with time and effects of different application rates suggest that poor application efficiency results in a major loss of chemical. If the application efficiency could be improved and application aimed at a target concentration then lower application rates of molinate could potentially be as effective as current label rates. This requires further research.

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1. Introduction

Irrigation provides the foundation for reliable agricultural production and economic security (Hillel 2000; Tanji 1990). There are 2.5 million hectares of irrigated land in Australia, of which up to 120,000 ha are sown to rice annually and about 500,000 ha are in a rice growing rotation. The rice growing areas are within the Murray Darling Basin on the Murrumbidgee and Murray Rivers in south western New South Wales and Victoria (Figure 1). This rice is grown as ponded (paddy) rice.

Figure 1. Rice growing region of Australia

In rice production a variety of pesticides are used, Westra (2002) found that there were about 18 different pesticides used in rice production in the Murrumbidgee Irrigation area in 2001. Paddy rice growing presents a challenging system for the management of pesticides due to rapid runoff from rainfall, variable management and often close proximity of rice fields to surface waters such as drains, rivers and wetlands. Thus the opportunity for pesticide movement out of the rice paddy into the wider hydrological system is large.

Contamination of surface waters by pesticides has been detected at various sites across the rice growing areas. The three main irrigation companies in their annual reports all show frequent detection of rice pesticides in surface drains, to the point where some chemicals

such as molinate are found more than 25% of samples (Coleambally Irrigation Environmental Report, 2003). This frequent detection of rice pesticides has led to concern from environmental regulators and the Australian Pesticides and Veterinary Medicines Authority (2003) when considering the re-registration of molinate. Molinate is a selective herbicide widely used around the world and its basic properties are given in Table 1.

To try to reduce the environmental effects of molinate and other pesticides a variety of regulations are imposed upon rice farmers to try to contain the chemicals on farm. The most important of these is the "withholding period" which is the period after pesticide application during which water must not be released from the farm. The length of this withholding period for molinate is 28 days in the Murrumbidgee Irrigation Area. Another suggested management measure is to construct high banks to ensure rainfall can be held within the rice bays.

Table 1. Basic properties of molinate

* Pesticide Action Network North America

Researchers have undertaken various studies to assess the dissipation rates of rice chemicals within rice fields. In south eastern Australia, Bowmer et al. (1998) found that molinate reduction was 99% within 19 days in bays near the irrigation supply but remained

much longer in bays at the drainage end of the field. Quayle and Oliver (2005) found a 99% reduction in molinate within 15 days in a bay near the supply, taking nearly 30 days for a 99% reduction in a bay at the drainage end of the field. The current guidelines set for water in surface drains by the New South Wales Environmental Protection Authority are 0.0034 mg/L as a Notification level and 0.014 mg/L as an Action Level (NSW EPA, 2004).

The large variability in biophysical and management conditions makes it very difficult to produce definitive guidelines. The experimental resources required to monitor a broad range of conditions are unavailable. As such the use of models to simulate varying biophysical and management conditions is useful in obtaining a broader spectrum of results that can be used to develop management guidelines.

Very few water quality modelling tools have been developed for rice production, and fewer still that deal with pesticides. There are two detailed process based models aimed at researchers - PADDY by Inao and Kitamura (1999) and RICEMOD by Linders and Alfarroba (2001). A less detailed model developed for pesticide registration purposes in USA is RICEWQ by Williams et al. (2004). The RICEWQ model was assessed by the Mediterranean-Rice (MED-RICE) group of the European Union and was found to be the most suitable of those named above for the assessment of exposure risk of surface waters neighbouring rice paddies (Karpouzas and Capri, 2004). RICEWQ has been validated for northern Italy where it simulated runoff processes adequately (Capri and Miao, 2002; Miao et al. 2003a, 2003b).

2. RICEWQ Model description

RICEWQ was developed to evaluate the fate and pathways of pesticides in rice paddies. It was developed by Waterborne Environmental Inc. in 1999 to address the main pesticide dissipation pathways whilst minimising input requirements. The model was developed specifically to simulate pesticide dissipation and runoff losses to receiving waters. The processes represented in the model are shown in Figure 2. The latest version 1.7.2 is used in this study.

Figure 2. Schematic of RICEWQ processes (Williams et al. 2004)

2.1. Water balance

Water balance algorithm in RICEWQ uses storage account method. The water balance equation in the paddy is given by Eq. (1).

$$
\frac{\partial S}{\partial t} = \sum I - \sum O \tag{1}
$$

where *S* is storage of water in the control volume, *t* is time, *I* is inflow, and *O* is outflow. Inflow sources include precipitation and irrigation whilst outflow includes evapotranspiration, seepage, and release and overflow from the paddy outlets. Irrigation is by user set amounts or an automatic irrigation facility that fills the bay to a set level when the water level in the bay drops to a critical level. The rate of filling is set by the user as an available irrigation flow rate. Drainage outflow occurs when the water level in the paddy field reaches a critical level and has an outflow rate given by the user. The model also allows for a constant rate seepage from the rice bay. For a detailed description see Williams et al. (2004).

2.2. Pesticide Fate

The model applies a conservation of mass approach to simulate the total mass of chemical residues in the paddy. RICEWQ tracks the fate of the chemical on the foliage, in the ponded water and in the sediment. The pesticide mass conservation equation in the control volume is given by Eq. (2).

$$
V\frac{\partial C}{\partial t} = \sum M_{\text{inf low}} - \sum M_{\text{outflow}} - \sum M_{\text{react}} \tag{2}
$$

where *V* is the control volume, *C* is pesticide concentration, *t* is time, *M* is pesticide mass, and subscript *inflow* means coming into the control volume, *outflow* going out of the control volume, and *react* is mass transformation from all processes. Pesticide mass balance equations for foliage, water, and soil are given below, respectively.

$$
\frac{\partial Mf}{\partial t} = Mf_{app} - Mf_{deg} + Mf_{tran} - Mf_{wash} - Mf_{harv}
$$
\n(3)

$$
\frac{\partial Mw}{\partial t} = Mw_{app} - Mw_{deg} + Mw_{tran} + Mw_{wash} - M_{volat} - M_{out} - M_{seep} - M_{bed} - M_{sell} + M_{resus} \pm M_{difus}
$$

$$
(4)
$$

$$
\frac{\partial M_S}{\partial t} = -M_{S_{\text{deg}}} + M_{S_{tran}} + M_{\text{bed}} + M_{\text{sell}} - M_{\text{results}} \pm M_{\text{diffus}}
$$
(5)

where *M* is pesticide mass, *Mf, Mw, Ms* are pesticide mass in foliage, water, and soil, respectively, and *t* is time, *app* is application, *deg* is degradation, *tran* is metabolite mass formed by transformation of the parent compound, *wash* is wash off from the foliage, *harv* is allocation of pesticide mass after harvest, *volat* is volatilisation, *out* is outflow, *seep* is seepage, *bed* is bed sediment, *setl* is particulate settling, *resus* is resuspension, *difus* is diffusion between the water and sediment, respectively.

The rate of chemical application is attenuated by an application efficiency to account for drift, off-site deposit, rapid volatilisation and other immediate losses that prevent the chemical entering the water column or depositing on foliage. The pesticide mass is then either volatilised, degraded (hydrolysis, photolysis, metabolism), partitioned to sediment or lost by mass transfer through surface runoff. Partitioning to sediment occurs by direct partitioning, diffusion and settling of chemical sorbed to suspended sediment. These processes are represented simplistically governed by rate terms input by the user. The model can track both parent and metabolite chemicals. For a detailed description of the model see Williams et al. (2004).

2.3. Inputs and Outputs

2.3.1. Inputs

Model inputs are provided through two files, a meteorological file and a parameter input file. The meteorological file has rainfall, pan evaporation and average temperature on a daily basis. The model assumes that evaporation is at that of open pan, this is appropriate for conditions in south eastern Australia (Humphreys et al.1994). The parameters required for the input file are listed in Table 2.

2.4. Outputs

The model provides outputs of the water balance and pesticide mass balance on a daily basis. Each partition is reported separately.

The water balance components reported in the output are irrigation, rainfall, water depth in a bay, outflow from the bay, seepage, and evapotranspiration. The pesticide mass balance

components reported in the output are effective amount of pesticide arrived at water, soil and foliage, wash off , volatilisation, seepage, diffusion, mass in water, soil and foliage, and concentration in water and soil. Therefore, the outputs are easy to compare with the field data which are generally provided as a concentration.

Table 3. Input parameters required for RICEWQ

3. Field data for model calibration

3.1. Location

Fieldwork was carried out on a commercial rice farm in the Murrami region of the Murrumbidgee Irrigation Area (MIA), approximately 35 km south east of Griffith in south western New South Wales, Australia. Field layout is shown in Figure 3.

Figure 3. Layout of the commercial farm

3.2. Soils

The soil at the site consisted of grey cracking clay, uniform across the entire extent of the field. These soils are known as self mulching grey clays. In the top 0.1m clay percentage is 60%, bulk density is 1250 kg/m³, the long term infiltration rate for these soils has been measured as 1-2 mm/day (Hornbuckle and Christen, 1999).

3.3. Crop and irrigation

The field layout consisted of a laser levelled paddock with bankless channel irrigation. The total area of the field was 15.72 hectares divided into 7 bays. Six bays were approximately 2.4 hectares each with the remaining bottom bay adjacent to the drain being 1.3 hectares. The slope of the field was 1:1429. Rice was planted as part of a 4 year rotation involving 1 year canola or oats, 2 years of clover/sheep and 1 year of rice. Flooding of the field was started on the 5/10/2001 followed by ground preparation and a 125 kg/ha urea application. Each bay took one day to fill. The field was aerially sown with the rice variety *Amaroo* at 140 kg/ha. Molinate was applied by plane with a 20 m swathe width and solid stream nozzles.

3.4. Climate

The local climate is described as "Mediterranean" with hot summers and cold winters and "semi-arid" as the annual average rainfall is 400mm, which is distributed evenly throughout the year. In this exercise climatic data was taken from the CSIRO Land and Water meteorological station in Griffith.

3.5. Field data

The sequence of water management and pesticide application are shown below. Irrigation timings were recorded but irrigation volumes were not. Field data were collected from October $5th$ to November 25th, 2001. After this date the molinate concentration in the paddy water was negligible.

3.5.1. Sequence of events for simulation period

3.5.2. Pesticide and water ponding depth

Quayle and Oliver (2005) sampled the water in three different bays of the rice paddock with three replicates at each sampling. They also tracked the water depth in the bays using six depth measurements across the bay and noted timing of irrigations. In order to calibrate the model as accurately as possible the data from bay 1 (nearest the irrigation supply) was used rather than averaging all measurements across all three bays, as there were large variations in water depths and pesticide concentrations. Of the six water depths two were not used as they were from a deep part of the bay considerably different from the other four positions. The data used for calibration is a shown in Table 3. The standard error of the pesticide samples and water depths are reported where possible.

Date	Average molinate concentration (mg/L)	Standard error (mg/L)	Average water depth (cm)	Standard error (cm)
18/10/2001	1.015	0.083	11.9	0.25
20/10/2001	0.756	0.006	11.1	1.00
22/10/2001	0.438	0.010	8.5	0.79
24/10/2001	0.228	0.010	14.7	0.25
28/10/2001	0.148	0.032	Na	
31/10/2001	0.072	0.010	Na	
2/11/2001	0.010	0.001	15.9	0.27
5/11/2001	0.006	0.002	Na	
7/11/2001	0.005	\star	13.7	0.25
14/11/2001	0.001	\star	10.7	1.45
19/11/2001	0.002	\star	10.5	1.06
23/11/2001			9.5	0.50

Table 4. Pesticide and water depth data, bay 1, 2001 (Quayle and Oliver, 2005))

* Only one sample with detection, Na – no measurement on that day

4. MODEL CALIBRATION

4.1. Water balance calibration

The model was calibrated in two steps, firstly the water balance and then the pesticide

balance. The basic input data used for the water balance calibration are shown in Table 4.

Parameter Name	Value	Source/comment
Simulation management		
Date simulation begins	5/10/2001	Field data
Date simulation ends	25/11/2001	Field data
Number of simulation time steps per day	24	
Crop		
Emergence date	19/10/2001	Field data
Maturity date	Not relevant	Model run finished prior
Harvest date	Not relevant	Model run finished prior
Maximum crop coverage	1	Full cover is usual
Deposition of pesticide residues at harvest	Not relevant	Model run finished prior

Table 5. Input parameters used for water balance calibration.

(removed or available)

In order to calibrate the water balance only the irrigation amounts were varied to match the observed ponded water depth. Initially irrigations were applied using the "Fixed volume" facility, which allows input of specified amounts, in order to make the water balance as accurate as possible. Evaporation and rainfall were not altered and it was observed that there was no surface drainage during this period. The results of the calibrated model were well matched to the observed water depth, Figure 4.

Figure 4. Water ponding depth using fixed volume irrigation method in RICE-WQ

The ponded water depths had an average error of 0.9 cm between modelled and observed and the maximum error was 1.8 cm, Table 5. The Root Mean Square Error (RMSE) was 1.3 cm.

Date	Observed (cm)	Modelled (cm)	Difference (cm)
18/10/2001	11.9	11.9	0.0
20/10/2001	11.1	10.4	-0.7
22/10/2001	8.5	8.4	-0.1
24/10/2001	14.8	15.1	0.3
2/11/2001	15.9	17.0	1.1
7/11/2001	13.8	14.8	1.0
14/11/2001	10.8	9.0	-1.8
19/11/2001	10.5	12.1	1.6
23/11/2001	9.5	7.8	-1.7

Table 6. Modelled and observed ponded water depths for fixed volume irrigation

The water balance for the fixed volume irrigation is investigated. Total inflow was 48.1 cm, of which 5.7cm was rainfall and 42.4 cm was irrigation. Total outflow was 48.5 cm, of which 35.4 cm was evapotranspiration and 7.7 cm was seepage, Table 6. The relative error was 0.8 %. At the end of simulation, the ponded water depth in the paddy was 5.4cm.

Table 7. Water balance for fixed volume irrigation simulation (05/10/2001 to 25/11/2001)

Irrigations were also applied using the "automatic" facility, which fills the bay to a set level when the water level in the bay drops to a critical level. For this simulation two periods were identified, before the end of the first week in November and subsequent to this, as it appeared from the observed data there was a regime change at around this time. Initially the critical depth to trigger refill was set as 8.0 cm and fill level set as 16.0 cm. After the $1st$ week in November these were changed to 6.0 cm and 12.0 cm. Again only the irrigation amounts were varied to match the observed ponded water depth. Evaporation and rainfall were not altered and it was observed that there was no surface drainage during this period. The results of the calibrated model were well matched to the observed water depth, Figure 5.

Figure 5. Water ponding depth using manual and automatic irrigation method in RICEWQ

The ponded water depths had an average error of 2.0 cm between modelled and observed, the maximum error was 4.4 cm, and RMSE was 2.7 cm, Table 7.

Table 8. Modelled and observed ponded water depths for automatic irrigation

The water balance for the automatic irrigation is investigated. Total inflow was 54.4 cm, of which 5.7 cm was rainfall and 48.7 cm was irrigation. Total outflow was 54.8 cm, of which 35.4 cm was evapotranspiration and 7.7 cm was seepage, Table 8. The relative error was 0.7 %. The differences in water balance between the fixed volume and automatic irrigation were irrigation depth and ponded water depth. The increased irrigation depth converted to ponded water in the automatic irrigation scheme.

4.2. Pesticide calibration

After the water balance was adequately calibrated the pesticide balance was calibrated. The basic input data used for the water balance calibration were again used and the soil and chemical parameters were added. Parameter values were taken from field data, literature, and general knowledge of rice growing. The specific pesticide parameters used for the calibration are shown in Table 9. Unsaturated sediment decay rate is assumed twice that of the saturated sediment considering soil half-life values given in Table 1, because unsaturated condition is aerobic and saturated condition is anaerobic.

We have field dissipation rate data specifically from this study. Dissipation half life for molinate in water was 2.7 days. Considering this half life, volatilization coefficient and decay rates in Table 8 are reasonable values. Only three parameters were completely unknown; the application efficiency, which is the fraction of pesticide mass applied not lost by drift, the mixing depth of sediment for direct partitioning and the mixing velocity which is associated with the mixing depth.

Table 10. Input parameters used for calibration of pesticide dissipation

Firstly calibration was undertaken to match the initial pesticide concentration sampled in the

bay for the fixed volume irrigation. This was done by altering the application efficiency.

During this process the mixing depth for sediment partitioning was set to zero as the partitioning process occurs after the chemical is in the water column and thoroughly mixed which will take about a day after application. The application efficiency reflects the drift loss and off-target deposit during initial pesticide application. The drift loss is mostly influenced by droplet size, application height and wind speed.

Calibration for application efficiency is necessary for most chemicals. Since molinate was aerially sprayed with solid stream nozzles with liquid concentrate the drift losses might be low. The field data here show high molinate recovery rate immediately after spraying. Calibration of the model led to a best fit value of 95% application efficiency to match the first sampling average concentration. This value is within the range of results of the previous drift loss studies (Riley and Wiesner, 1989; Bird et al., 1996; Hewitt et al., 2002; Spray Drift Task Force, 1997). The model results show that the molinate lost to volatilisation on the first day is about 14% of the total mass entering the water.

After calibration of application efficiency the mixing depth of sediment for direct partitioning was varied across the range from 0 to 0.5cm and a value of 0.1cm was selected with minimum error. The mixing depth and the mixing velocity, which is associated with the mixing depth, are linked parameters. Thus it was unnecessary to calibrate the mixing velocity once an appropriate calibration was achieved with the mixing depth.

The results of the model calibration for pesticide in the water are shown in Figure 6.. Note that the first water sample was taken one day after molinate application. It can be seen that the initial concentration in the water matches observed data well and the slope of the decay is similar to the observed.

Figure 6. Molinate concentrations in ponded water using fixed volume irrigation method

Analysis of the difference between modelled and observed concentrations is shown in Table 10. The largest differences occur soon after application, reducing to very small differences later. The maximum difference was 0.093 mg/L, the average difference was 0.032 mg/L, and RMSE was 0.048 mg/L.

Days after	Observed	Modelled	Difference
application	(mg/L)	(mg/L)	(mg/L)
1	1.015	0.941	-0.074
3	0.756	0.663	-0.093
5	0.438	0.467	0.029
7	0.228	0.177	-0.051
11	0.148	0.101	-0.047
14	0.072	0.06	-0.012
16	0.010	0.023	0.013
19	0.006	0.02	0.014
21	0.005	0.016	0.011
28	0.001	0.008	0.007
33	0.002	0.002	0.000

Table 11. Modelled and observed pesticide concentrations for fixed volume irrigation

The pesticide mass balance per ha for the fixed volume irrigation wais investigated, Table 11. Total effective application was 1.826 kg. Decay was 0.310 kg, volatilisation was 1.320, (which was 72% of the effective application) seepage loss was 0.172 kg and residue at the end of simulation was 0.120 kg, respectively. Relative error of the mass balance was 5.3 %.

Table 13. Pesticide mass balance for fixed volume irrigation simulation (05/10/2001 to 25/11/2001)

The calibrated model was tested using the automatic irrigation mode too. The resulting pesticide concentrations also closely matched the observed as the automatic irrigation mode closely reflects the fixed volume irrigation results, Figure 7.

Analysis of the difference between modelled and observed concentrations is shown in Table

12. The largest differences occur soon after application, reducing to very small concentrations later. The maximum difference was 0.133 mg/L, the average difference was

0.036 mg/L, and RMSE was 0.058 mg/L.

Table 14. Modelled and observed pesticide concentrations for fixed volume irrigation

The pesticide mass balance per ha for the automatic irrigation was also investigated, Table 13. The only difference from the fixed volume irrigation was decay in the water. Relative error of the mass balance was 5.1 %.

Table 15. Pesticide mass balance automatic irrigation simulation (05/10/2001 to 25/11/2001)

	Effective application		Decay			Residue			Volatili-	Seep-	Total	Relative		
											sation	age	outflow	error
water	foliage	total	water	soil	foliage	total	water	soil	foliage	total	(kg)	(kg)	(kg	(%)
(kg)	(kg)	(kg,	(kg)	(kg)	(kg)	(kg)	(kg	(kg)	(kg)	(kg)				
1.735	0.091	.826	0.145	.117	0.046	0.308	0.001	.109	0.010	0.120	.320	0.172	. 920	J.I

4.3. Calibration conclusions

The overall results from the model calibration were very encouraging. With minimum adjustment of the input parameters the results were able to adequately match the observed data from Quayle and Oliver (2005). However, it was fortunate that data for some key parameters such as degradation rates in water and partitioning to sediment were available from literature for the pesticide molinate. The calibration results indicate that the model is suitable for modelling pesticide dissipation in this environment. Analysis of the sensitivity of the model to the input parameter is provided in section 5.

5. SENSITIVITY ANALYSES

In order to assess the sensitivity of the model to the various input parameters a series of simulations were conducted using the calibrated fixed volume irrigation input file and varying

each parameter by ±50% of its original value except the application efficiency, which varied by \pm 5% of its original value. The sensitivity can not be defined by Eq. (6) for parameters with zero original values such as depth of incorporation, hydrolysis decay rate, photolysis decay rate, rate of release for slow release formulation and fraction of non intercepted chemical immediately lost. Since the original values have large impact on the sensitivities reasonable original values were carefully selected for these parameters. The results were analysed to create a sensitivity S:

$$
S = (dR/R) / (dP/P)
$$
 (6)

Where: d is differential,

R is the value of the dependent variable, and

P is the value of the independent variable

A sensitivity of 1 indicates that a unit relative change in the parameter value results in a unit relative change in the result. A sensitivity of zero indicates that changing the parameter value has no effect on the model results. The results for molinate concentrations were analysed at 0, 4, 15, 32 days after application, as the impact of a parameter change may occur early or late in the simulation. The results for sensitivity analysis are shown for water, sediment and foliage separately in Tables 14, 15 and 16, respectively. Results are given as absolute values and only for +50% (+5% for application efficiency) change of the parameter values as the results for most parameters were nearly linear. An exception to this is volatilisation coefficient which is shown separately in Table 17. Overall the application efficiency has a major impact and this impact is carried throughout the entire simulation.

Sensitivity of the parameters on molinate concentrations in ponded water is shown in Table 14. In order to assess these parameters and their effects early and late in the simulation they were ranked in Figure 8 and Figure 9. On the day of pesticide application the application

efficiency is the most sensitive followed by the release rate for slow release formulation and the fraction of pesticide intercepted by water and immediately transformed to innocuous product. Thirty two days after application, volatilisation coefficient is the most sensitive followed by application efficiency, bulk density, mixing velocity, release rate for slow release formulation, and water sediment partition coefficient. The release rate may be important for slow release pesticides.

Parameter		Days after application			
	$\mathbf 0$	4	15	32	
Application Efficiency (APPEFF)	1.00	1.00	1.00	1.00	1.00
Release rate for slow release formulation (RREAC)	0.78	0.17	0.43	0.41	0.45
Fraction of pesticide intercepted by water and immediately transformed to innocuous product (SNK)	0.11	0.11	0.11	0.09	0.11
Hydrolysis degradation rate in water (KWH)	0.00	0.01	0.02	0.03	0.02
Photolysis degradation rate in water (KWP)	0.00	0.01	0.02	0.03	0.02
Metabolism degradation rate in water (KWM)	0.00	0.09	0.27	0.27	0.16
Soil bulk density (BD)	0.01	0.04	0.17	0.74	0.24
Degradation rate in saturated soil (KSW)	0.00	0.00	0.00	0.15	0.04
Degradation rate in unsaturated soil (KSD)	0.00	0.00	0.00	0.00	0.00
Degradation rate on foliage (KF)	0.00	0.00	0.00	0.06	0.02
Water/sediment partition coefficient (KD)	0.00	0.04	0.12	0.40	0.14
Settling velocity (VSETL)	0.00	0.00	0.00	0.04	0.01
Mixing depth for direct partitioning to sediment (VBIND)	0.00	0.04	0.10	0.02	0.04
Mixing velocity (VMIX)		0.05	0.10	0.44	0.15
Wash off rate per cm rain (WO)	0.00	0.00	0.03	0.05	0.02
Pesticide solubility (SOLUB)	0.00	0.00	0.00	0.00	0.00

Table 16. Sensitivity of pesticide concentration in ponded water to input parameters

Figure 8. Ranking of parameter sensitivity for pesticide concentrations in ponded water, at application

Figure 9. Ranking of parameter sensitivity for pesticide concentrations in ponded water, 32 days after application The impacts of parameter change on pesticide mass in sediment and ranking early and late in the simulation are shown in Table 15 and Figure 10 and Figure 11. The application efficiency is the most sensitive. In the early stage the release rate and the mixing velocity have large sensitivities and in the late stage the soil bulk density, degradation rate in the sediment, water/sediment partition coefficient and mixing velocity have large sensitivities.

Table 17. Sensitivity of pesticide concentration in sediment to input parameters

Figure 10. Ranking of parameter sensitivity for pesticide concentrations mass in sediment, at application

Figure 11. Ranking of parameter sensitivity for pesticide concentrations in sediment, 32 days after application

The impacts of parameter change on pesticide mass on foliage and ranking early and late in the simulation are shown in Table 16 and Figure 12 and Figure 13. Only three parameters have non-zero sensitivities, the application efficiency, the wash off coefficient and the degradation rate on foliage.

Parameter	Days after application				Mean
	Ω	4	15	32	
Application Efficiency (APPEFF)	1.00	1.00	1.00	1.00	1.00
Wash off rate per cm rain (WO)	0.00	0.00	0.37	0.66	0.26
Degradation rate on foliage (KF)	0.01	0.08	0.27	0.60	0.24
All the others	0.00	0.00	0.00	0.00	0.00

Table 18. Sensitivity of pesticide mass on foliage to input parameters

The analysis outlined above does not include volatilisation, this is because the results for the volatilisation were found to be non linear as shown in Table 17. The volatilisation coefficient does not have any impact on the foliage pesticide mass, while it has large impact on the concentration in the water. The effect of reducing volatilisation coefficient by 50% was much greater than the effect of increasing it by 50%.

	Medium		Days after application	Mean		
Change		0	4	15	32	
	Water	0.16	1.11	5.69	11.22	4.55
50% decrease	Sediment	0.07	0.41	1.07	1.42	0.74
	Foliage	0.00	0.00	0.00	0.00	0.00
	Water	0.14	0.72	1.45	1.29	0.90
50% increase	Sediment	0.07	0.32	0.56	0.60	0.39
	Foliage	0.00	0.00	0.00	0.00	0.00

Table 19. Sensitivity of pesticide concentration to the volatilisation coefficient

6. SCENARIO MODELING

6.1. Water management

Water management is critical in preventing runoff from rice fields that may be contaminated with pesticides. In order to test the importance of water management a set of irrigation regimes was developed that varied the depth of water in the rice paddy when molinate is applied. The irrigation regimes tested were to have a target irrigation depth of 1, 2, 3, 4 and 5 cm below the paddy overflow depth of 20 cm. Tis value was called "Difference between Irrigation target and overflow depth" (DIOD). Thus the target irrigation depths were 19, 18, 17, 16 and 15 cm, respectively. The trigger irrigation depth to input water was set at 2.5cm below the target irrigation depth. The scenarios were run for 41 seasons between 1962/1963 and 2003/2004.

Changing the target water management depth altered the concentration of pesticide in runoff when the DIOD was 4cm or smaller, Figure 14. The results show that the maximum and average concentrations are above the NSW EPA Notification Level of 0.0034 mg/L when the DIOD was 4cm or smaller.

Figure 14. Daily average molinate concentrations in runoff water. This average was determined by running the model over 41 seasons

Changing the irrigation management also changed the total number of runoff days, Figure

15. The 5 cm DIOD was adequate to prevent runoff events with concentrations greater than

0.0034 mg/L. However, there were still days that contained some level of molinate.

Figure 15. Average annual number of days where runoff water was contaminated with molinate. This average was determined by running the model over 41 seasons

Average annual runoff volume and molinate loads were investigated, Figure 16. Both annual average runoff and molinate load to the drains decrease as the DIOD increases. These estimates of molinate pesticide leaving rice fields are for a single bay system. However, this is not the usual situation. Rice fields are made up of a number of bays and in most cases water moves not only along the bankless channel but also from one bay to the next until finally reaching the "bottom" bay. As such there is a process of chemical concentration as water moves through the bays as shown by the observed data in Figure 17. It is from this bottom bay that drainage water will leave the. Thus these modelling results will tend to underestimate the concentrations of pesticide in water that actually drains off a rice field.

Figure 16. Average annual runoff volume and molinate loads. This average was determined by running the model over 41 seasons

When looking at reducing chemical movement off farms it is these bottom bays that need to be considered. From a modelling perspective this means that the input water will have a concentration of the pesticide of interest. In the calibration phase, data from the rice bay closest to the supply water were used. This means that the irrigation water input to the bay is from the irrigation channel and has zero concentration of pesticide. The concentration of pesticide input into the bottom bay of a rice field will be time variant. In RICEWQ it is not possible to have a time varying input concentration of chemical.

To simulate a second bay the ponded water concentrations were calculated from the output of running the supply bay scenario. The evaporation from the bay is known. As such we assumed that the evaporation of the second bay would be replaced by water from the first bay on a daily basis with the concentration of pesticide on that day. Using this assumption the mass of pesticide to be introduced from the supply bay to the second bay was calculated on a daily basis. As RICEWQ does not have the facility for an input concentration the mass of pesticide was treated as a pesticide application with a 100% application efficiency. In this way the pesticide dissipation in a second bay was modelled. The modelled concentration difference between the supply bay and second bay is shown in Figure 18.

Figure 18. Modelled molinate concentration in supply bay and second bay

The results of the modelling for the second bay can be compared with observed data of the middle bay from Quayle and Oliver (2005). The observed and modelled results in Figure 19 show a very good fit. Note that the first water sample was taken one day after molinate application.

Figure 19. Modelled and observed molinate concentration for second bay

Quayle and Oliver (2005) also had data for the bottom bay in the sequence of bays they monitored, Figure 17, so the process of using the output data to calculate inputs to a third bay was used to try to match with the observed data in the bottom bay. However, we found little change from the 2^{nd} to 3^{rd} bay and repeating the process to simulate more bays resulted in changes in the order of 5 to 10 % and the shape of the modelled curve remained the same as the 2^{nd} bay, Figure 20, whereas the observed data shows a very different curve for the bottom bay, Figure 17. This indicates that there was a changed water regime in the bottom bay compared to the upper bays. It is often the case that the last bay does not receive as much water as the other bays. Assuming this was the case the irrigation target and trigger depths were arbitrarily reduced by 15% (2.4 and 1.2 cm, respectively). The simulation using these reduced irrigation triggers resulted in improvement in the match between modelled and observed data, Figure 21.

Figure 20. Modelled and observed molinate concentration for bottom bay, full irrigation

Figure 21. Modelled and observed molinate concentration for bottom bay, irrigation reduced by 15%

This scenario modelling indicates the importance of water management in the risk of pesticide movement off rice fields. To improve our predictive capability we need to be able to simulate multiple bays. This has to be supported by field data on the difference in water regimes between upper and lower bays.

6.2. Pesticide application management

In Australia pesticides can legally be applied by following the "Registered Label" directions. The registered label for the herbicide molinate directs that two rates (2.4 or 3.6 kg/ha actual ingredient)) can be used depending upon the age and type of grass weeds (Nufarm, undated). Molinate can be applied by normal ground rig to dry bays. When bays are flooded molinate can be applied by aircraft or alternatively by ground rig using a technique known as SCWIIRT. This is a low pressure (<200kPa) application technique that "dribbles" the pesticide into the ponded water. This technique is intended to minimise losses and drift compared to aerial techniques. These options are summarised very briefly from the registered label in Table 18.

Land surface	Application method	Application rate	Control comments
Dry bay	Ground rig or aerial spray	3.6 kg/ha	Pond water after spraying and do not drain water for at least 2 days
Ponded water	Aerial spray or SCWIRT	2.4 or 3.6 kg/ha	Minimum water movement through bays for 3 days

Table 18. Registered molinate application methods summarised from label, (Nufarm, undated)

 Using RICEWQ we can investigate the effect of these management options. The scenarios tested are outlined in Table 19. These scenarios require that the application efficiency of the ground rig, dry bay aerial spray and SCWIIRT methods be estimated. These were assumed to be 70%, 60%, and 100%, respectively. A low efficiency (60%) for the dry bay aerial spray was selected due to the observation of extensive pesticide presence on the ground beyond the application area. Aerial spraying used solid stream nozzles with liquid concentrate molinate.

Scenario	Application method	Application rate (kg/ha)	Application efficiency	Water management
A	Ground rig	3.6	70%	Dry bay at application, flooded next day, irrigate to maintain depth
B	Aerial dry	3.6	60%	Dry bay at application, flooded next day, irrigate to maintain depth
C	SCWIIRT3.6	3.6	100%	Ponded water at application,
				irrigate to maintain depth
D	Aerial ponded	3.6	95%	Ponded water at application,
				irrigate to maintain depth
E	SCWIIRT _{2.4}	2.4	100%	Ponded water at application,
				irrigate to maintain depth

Table 19. Scenarios for testing pesticide management options

These scenario simulations were made for the period 05/10/2001 to 31/03/2002, the same climatic conditions and parameters were used as for the initial calibration. For the dry bay scenarios, the irrigation was delayed until the day after spraying. The irrigation was controlled using the automatic mode in RICEWQ. The same irrigation control as in the model calibration was used. Initially the critical depth to trigger refill was set as 8.0 cm and fill level set as 16.0cm. After the 1st week in November these were changed to 8.0 cm and 14.0 cm. There were 2.0 cm rain on $23rd$ October and 1.8cm rain on $5th$ November.

6.2.1. Application method

Molinate concentrations in the ponded water for application to a dry bay by aerial and ground rig are shown in Figure 22, note log scale. The results show much higher concentrations for the ground rig application due to the assumed higher efficiency, 70%, as compared to the application efficiency of 60% for the aerial spray. The rise in concentration on day 18 is due to rainfall causing wash off of chemical from leaves into water.

Figure 22. Modelled molinate concentration in water for ground rig and aerial application to dry bay, Scenario A, B

The molinate concentrations in the ponded water for application to a ponded bay by aerial spray and SWIIRT method are shown in Figure 23, note log scale. The results show higher concentrations for the SCWIIRT application due to the assumed higher efficiency, 100%, as compared to the application efficiency of 95% for the aerial taken from the model calibration.

Figure 23. Modelled molinate concentration for SCWIIRT and aerial application to ponded bay, Scenario C, D

Appendices

Glossary

References

Reference lists should follow the author-date system (as described in the Style Manual for Authors, Editors and Printers 2002). Where a statement is referenced in the text, it should be cited by both author and date e.g. (Smith 1998).

References are to be listed alphabetically by author in the reference list. Where there are a number of references with three or more authors but the same first author, place in date order. Please follow the styles below:

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