1

General introduction

1.1 INTRODUCTION

Arsenic (As) contamination of soil is a major environmental threat due to the toxic and carcinogenic nature of As compounds (Mandal and Suzuki 2002). Both natural (weathering, volcanism) and anthropogenic processes cause widespread As contamination of soils and sediments across the globe (Smith et al. 1998; Smedley and Kinniburgh 2002). Agricultural use of arsenical pesticides and herbicides, copper-chromium-arsenate (CCA) treatment of timber and pesticides manufacturing processes are the major anthropogenic causes of soil As contamination (Mandal and Suzuki 2002; Smith et al. 2006a; Smith et al. 2006b). The inappropriate and repeated use of the As-based chemicals in the past has contaminated large expanses of soils surrounding the agricultural and urban areas. There are thousands of As-contaminated sites throughout the world where contamination has occurred due to the historical application of As-based pesticides and herbicides. In Australia alone, there are more than 2500 (disused) cattle-dip sites where arsenical pesticides were used to control the spread of cattle tick (*Boophilus microplus*) across New South Wales (NSW) and Queensland states, from the early 1900s to 1955 (Smith et al. 2003; Smith et al. 2006a). Over 1600 dips were constructed only in northern part of NSW and over 60% of these were in operation until 1990 (Smith et al. 1998). The distribution of total As content in soils around these cattle-dip sites has been found to be high and extremely variable, with As concentrations of up to 14,000 mg

kg^{-1} (McLaren et al. 1998). The spatial heterogeneity in soil As concentration around these sites is thought to be associated with the cattle dipping process, removal of the As-contaminated sludge material from the dip and draining out of the dipping fluid from the dip bath within the dip-yard (Kimber et al. 2002).

Considering the toxic and mobile forms of As present in soil, considerable research has been done for the restoration and rehabilitation of these sites. Traditional techniques used for the remediation of As-contaminated soils include excavation, capping, and stabilisation or immobilisation. These methods are costly and do not remove the contaminant from the soil. In recent years, *phytoremediation* has emerged as a low-cost and environmental friendly *in situ* remediation technology for the restoration of As-contaminated soils (Ma et al. 2001). This technology utilises plants (ferns) to *phytoextract* As from contaminated soils; thereby reducing its threat to the ecosystem, human and animal health. The plants that can accumulate exceptionally high concentrations of As into aboveground biomass are referred to as *hyperaccumulators*. All As-hyperaccumulators identified so far have been ferns (Gonzaga et al. 2006; Xie et al. 2009). Since the discovery of the first As-hyperaccumulator, *Pteris vittata* L. several other ferns in *Pteris* and non-*Pteris* genera (e.g. *Pteris longifolia*, *Pteris umbrosa*, *Pityrogramma calomelanos*, *Pityrogramma calomelanos* var. *austroamericana*) have been reported to hyperaccumulate As (Ma et al. 2001; Gonzaga et al. 2006; Kachenko et al. 2007; Xie et al. 2009). The fern, *P. calomelanos* var. *austroamericana* which is naturalised in Australia was recently identified as an As-hyperaccumulator in the glasshouse experiments (Kachenko et al. 2007). This lesser-known As-hyperaccumulating species can be well-suited for phytoextraction of As under field conditions.

In addition to high As concentrations, large variability in the soil As content around the cattle-dip sites is a major problem for the restoration and management of these sites. Cattle-dip sites are point-sources of As contamination. Arsenic contamination in the soil has occurred from various processes such as splashing of solution during cattle dipping process, disposal of As-containing waste material near to the dip. Hence, the variation of As in soil needs to be defined for the management and remediation purposes of these sites. Geostatistical methods may be used to describe the spatial variability of As in soil surrounding the cattle-dip sites, so far no such research has been conducted to delineate the spatial variability of As in soil in the vicinity of the cattle-dip sites.

Arsenic was applied in the form of As^{III}-based pesticides (as sodium arsenite) at the cattle-dip sites, which is a highly toxic and mobile form of As. Once in the soil environment, the fate of As is determined by soil environmental conditions. Arsenic may be adsorbed to the surfaces of soil minerals or could be precipitated into a mineral form (Paktunc et al. 2003; Cances et al. 2005; Cances et al. 2008; Meunier et al. 2010). The valence form of As in soils could vary depending on soil moisture conditions (Masscheleyn et al. 1991; Smith et al. 1998; Grafe and Sparks 2006). The forms of As in soils control its potential mobility and (phyto)availability; therefore, the knowledge of both solid-phase and solution-phase speciation of As is important to determine its (phyto)availability and mobility in soil environment.

The thesis starts with this general introductory chapter (Chapter 1) which is followed by a review of the relevant literature (Chapter 2). The results from the research work are presented in Chapters 3–7.

1.2 AIMS

This thesis presents the following aims:

1. To evaluate the spatial variability in soil As in the vicinity of a cattle-dip.
2. To determine the solid-phase speciation and phytoavailability of As in a wide range of contaminated soils.
3. To compare the phytoremediation potential of *P. calomelanos* var. *austroamericana* against the well-known As hyperaccumulator *P. vittata* under field conditions.

1.3 OBJECTIVES

The specific objectives of the work presented in this thesis were:

1. Evaluation of the spatial variation in soil As concentration adjacent to a cattle-dip site using a model-based geostatistical approach (Chapter 3);
2. To compare the phytoextraction efficiency of *P. calomelanos* var. *austroamericana* and *P. vittata* at a highly variable As-contaminated cattle-dip site – comparison based on short- and long-term data (Chapters 4 and 5);
3. Application of mid-infrared (MIR) spectroscopy and partial least-squares (PLS) regression to estimate total As content in soil (Chapter 6);
4. Determine the speciation and phytoavailability of As in historically contaminated soils and soils spiked with As using a sequential extraction procedure (SEP) and X-ray absorption fine structure (XAFS) spectroscopy (Chapter 7);

The final chapter of this thesis (Chapter 8) provides a summary of the results presented in the research chapters (Chapters 3–7), and suggest ideas for future research in this field.

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