CHAPTER 1 - INTRODUCTION

1.1. ANTIMONY

Antimony has been known to human civilisation for several thousand years. Early alchemists valued it for its purifying properties, and it was known by several names such as 'the wolf of metals', which was a reference to its ability to scavenge other metals and impurities during metallurgy procedures (Nriagu 2005). The name antimony itself is suspected to have been derived from the greek *anti* = opposed and *monos* = solitude (EnvironmentalChemistry.com 2005). It has been used both as a 'cure-all' and a poison throughout the last several hundred years, and was even heralded as one of the 'twelve keys to the most secret fountain of health' by Basil Valentine (Anon 2005). Antimony is still the treatment of choice for several bacterial-based diseases and has been recently used in the treatment of HIV (Fowler and Goering 1991). It also has various industrial uses, and is a component in lead batteries, car brake pad liners, fire retardants, ammunition, and semi-conductors (Filella *et al.* 2002a).

Antimony is increasingly recognised as an inorganic contaminant of concern. The mining, smelting, and subsequent uses of Sb have resulted in increasing anthropogenic inputs of this metalloid into the environment (Shotyk *et al.* 2005). Coupled with this, its chemical similarity to As and the limited toxicological data available suggest Sb enrichment has the potential to detrimentally affect both natural and human systems (Filella *et al.* 2002a). There is a dearth of information on the environmental fate and behaviour of this metalloid.

1.2. METALLOIDS IN THE STUDY SITE

Geochemical sampling of stream sediments and waters in the Macleay River catchment in northeastern NSW, Australia has identified a 300 km long dispersion train with elevated Sb and As concentrations. This dispersion emanates from the Hillgrove SbAu mining area, which is located above Bakers Creek in the upper Macleay Catchment (Ashley and Graham 2001). The dispersion of metalloids into the stream system was initiated by historic mine waste disposal between the 1870s and

1970s. As a consequence, the upper reaches of the Macleay River system are highly contaminated, with concentrations of Sb and As in stream sediments and waters in Bakers Creek downstream of the mine exceeding current guideline values by one to three orders of magnitude (Ashley *et al.* 2003). This contamination has been transported down the high energy Macleay system and spread across the coastal floodplain and estuary. Previous limited sediment sampling has indicated that surface Sb and As concentrations within the floodplain were up to 18 and 3.5 times regional background levels (1 and 7.5 mg kg⁻¹ respectively). Previous sediment core sampling at 20 and 40 cm depth intervals indicated variable surface enrichment of Sb and As within 20 - 40 cm of the surface (Ashley and Graham 2001).

The coastal floodplain system is dominated by modern swamp (relict estuarine) and alluvial flood related depositional landscapes (e.g. levees). Alluvial landscapes are characterised by silty clay loams and loams, with infrequent or no waterlogging, and generally low organic matter in surface layers. Swamp landscapes are seasonally flooded and are characterised by a predominance of silty clay to clay soils with high (6 - 30 %) organic matter in surface layers, commonly overlying potential or actual acid sulfate subsoils (PASS or AASS). Areas of the swamp landscapes are actively generating acid, and undergo large pH, redox and solid phase fluctuations seasonally and with management changes.

These soil properties and processes may influence metalloid mobility and availability within the system. Investigating the extent of transfer of Sb(As) between soil, water and biota systems has been recognised as a specific research need to elucidate risks to humans and the environment in the floodplain system. Investigations into the role of environmental parameters such as redox and pH changes upon metalloid mobility are needed, as well as research into the influence of management changes upon these interactions (Ashley and Graham 2001; Duck 2000; Mundell 2000).

1.3. THE AIMS AND STRUCTURE OF THIS THESIS

This thesis has two main objectives. Firstly, this thesis aims to improve the understanding of some aspects of the biogeochemistry, fate and behaviour of Sb within the environment. The lack of knowledge regarding Sb behaviour in the environment is of concern, and while this thesis does not systematically address any particular area of Sb behaviour, some investigations into Sb behaviour are made in the context of the project and study site that have general implications. Secondly, this thesis aims to investigate the fate and behaviour of Sb (and As) within the Macleay coastal floodplain system. The extent of the contamination and the site-specific issues are addressed. This involves quantifying some aspects of Sb fate and behaviour, such as concentrations in soil, water and pasture systems of the study area.

This thesis has several further objectives that are addressed and reflected within its structure. Firstly, the extent of information regarding the behaviour of Sb in the environment is reviewed in Chapter 2, with particular emphasis given to the soil environment. Comparisons are made to similar information that is available on As behaviour, in an effort to emphasise the lack of information that is available for Sb, and to compare and contrast results for elements with chemical similarities. Several recommendations for necessary further work into aspects of Sb chemistry and cycling are made.

The characteristics of the study site, the Macleay coastal floodplain, are outlined in Chapter 3. Previous Sb and As analyses in the area are discussed, as are some of the specific attributes of the floodplain that may affect the mobility and availability of both of the metalloids. These include both acid sulfate soil processes and the seasonal flooding of some areas. Building on the generic recommendations of Chapter 2, several site-specific needs are identified.

Chapters 4 and 5 address the necessary precursors to any floodplain investigations, namely the development of appropriate analytical techniques for the detection of both metalloids at the University of New England. Chapter 4 deals with the determination of a digestion method for analysis of the metalloids and other elements via ICP-OES. Chapter 5 details the development of a sequential extraction scheme to fractionate the metalloids in the floodplain soils, which contain significant amounts of non-crystalline Fe and Al oxyhydroxides.

Chapters 6, 7 and 8 address some of the specific research needs identified in Chapters 2 and 3. Chapter 6 includes a detailed survey of As and Sb enrichment in the

floodplain soils, pastures and waters. Estimates of local background calculations are also undertaken. The concentrations of both metalloids within the floodplain environments are related to flood patterns, ASS areas and sediment deposition, and there are indications of relatively high metalloid availability and mobility.

In Chapter 7, the availability and mobility of both metalloids in acid sulfate affected soils of the floodplain are investigated under controlled and field conditions, as well as the interactions of the metalloids with soil phases and environmental conditions such as flooding. The possibility of using measured variables and chemical extracts as predictors of availability of the metalloids to pastures is also examined.

Chapter 8 addresses a particular knowledge gap in the known environmental behaviour of Sb, namely the adsorption behaviour of Sb(V) onto the floodplain soils examined in Chapter 7, and the dominant soil phases of amorphous $Fe(OH)_3$ and solid humic acid. The findings of this chapter are related to the predictions of availability and solid phase partitioning as determined in Chapter 7.

Finally, Chapter 9 summarises the important findings of this thesis. In addition, an attempt is made to integrate some of the findings of the thesis into a limited risk assessment. Specifically, a limited exposure assessment and risk characterisation is undertaken for 2 possible floodplain scenarios, using the currently accepted concepts of risk assessment and some of the previously determined values of metalloid concentrations in the floodplain. Some dominant exposure pathways are identified, and basic recommendations are made to minimise risk using this limited assessment.

CHAPTER 2 - THE ENVIRONMENTAL CHEMISTRY AND BEHAVIOUR OF ANTIMONY WITH COMPARISONS TO ARSENIC

2.1. INTRODUCTION

Antimony (Sb) and arsenic (As) are elements that occur naturally in the environment at trace levels. Arsenic has long been recognised as a potentially harmful element, evidenced through its historic use as a popular poison (Azcue and Nriagu 1994). Recently, similarities between the chemical properties of As and Sb, and the limited data on the toxicity and environmental behaviour of Sb have raised concerns over the enrichment of this metalloid in many environments. Filella *et al.* (2002a) state the problem succinctly; "little information is available on the transformation and transport of antimony in different environmental compartments. Even information on antimony speciation and total content in the various media is scarce and often contradictory. This lack of understanding of antimony behaviour and fate in the environment hinders further research."

This review focuses on the scarcity of environmentally relevant Sb data, while comparing and contrasting the available data with similar work on As. Specific aspects of the environmental chemistry of Sb are reviewed and compared to that of As. The extent of information on Sb in environmental media including soils, water and terrestrial herbaceous plants is also discussed and contrasted with that of As. Characteristics of the Sb (and As) - soil system are reviewed in detail, with an emphasis on sorption and phase associations under neutral to acidic conditions. Finally, the limitations of information available regarding the fate and behaviour of Sb in environmental systems is summarised.

2.2. USES AND PRODUCTION

Arsenic as arsenic trioxide (As_2O_3) is used industrially in manufacturing numerous products including glass, ceramics, electronics, cosmetics, and fireworks (Smith *et al.* 1998). In the latter half of the 20th century As was also widely used in pesticide and herbicide formulations, and was widely applied in many agricultural systems,

although such use is now declining (Azcue and Nriagu 1994). Conversely, its woodpreserving ability has seen its use as such increasing globally in recent times. World production of As as As_2O_3 between 1985 and 1990 was estimated at 50000 tonnes per annum (Loebenstein 1993 cited in Smith *et al.* 1998).

Antimony is used in the making of semiconductors, diodes, flameproof retardants, lead hardener, batteries, small arms, tracer bullets, automobile brake linings, and pigments. Antimony also remains the treatment of choice for several tropical protozoan diseases, such as leishmaniasis, and more recently, HIV (Fowler and Goering 1991). World production of Sb stands around 140000 tonnes per annum (Filella *et al.* 2002a). Enrichments of both elements occur naturally and anthropogenically in the environment due to mineralisation, mining and industrial emissions, historical site contamination and agricultural uses (for As). Of these, mining and industrial emissions will be focussed upon in the following comparative review, as the majority of Sb contamination appears to originate from these sources.

2.3. CHEMICAL PROPERTIES

Antimony and As are of special interest in terms of environmental chemistry and contamination. Their uniqueness stems from their elemental properties. Both Sb and As are classed as metalloids, with properties intermediate between metals and non-metals. The important environmental characteristics of Sb and As are illustrated in a comparison of metal and non-metal chemical characteristics (Table 2.1).

Table 2.1. Some chemical property differences between metals and non-metals (adapted fromWhitten *et al.* 1996).

Metals	Nonmetals
Outer orbitals contain few electrons, usually 3 or less	Outer orbitals contain 4 or more electrons
Tend to form cations	Tend to form anions
Form ionic compounds with nonmetals	Form ionic compounds with most metals,
	covalent compounds with nonmetals
Solid state characterised by metallic bonding	Form covalently bonded molecules (noble gases
	are monatomic)

Both As (atomic number 33) and Sb (atomic number 51) have partially filled outer p orbitals, with their highest energy electrons in the configuration s^2p^3 . Although both As and Sb may form species with formal redox states of 3- to 5+, the tendency of these elements to maintain a full outer orbital means species of these elements in the environment tend towards either the 3+ (III) or 5+ (V) state (although the 3- redox state may be dominant under strongly reducing conditions, such as in AsH₃).

2.4. SPECIATION AND TOXICITY

It has been repeatedly shown that the environmental reactions of As are governed by oxidation state, and as such are largely dependent on both redox conditions and pH (Sadiq 1997; Smith *et al.* 1998). Less is known about the environmental forms and reactions of Sb, but the chemical similarities between Sb and As, and the work on Sb completed to date (e.g. Mok and Wai 1990; Takayanagi and Cossa 1997), indicates some broad similarities in environmental behaviour.

The dependency of Sb (and As) oxidation states on environmental conditions is important in assessing environmental toxicities and related work, such as setting realistic and scientifically based guidelines for contamination assessment. The toxicities of Sb and As in the environment strongly depend upon speciation (Filella *et al.* 2002a; Gebel 1997; Smith *et al.* 1998). In environmental systems both metalloids may occur in the (III) and (V) oxidation state and in organic or inorganic form. The form of As and Sb in the environment is oxyanionic, with speciation determined by protonation and organic or inorganic complexing. The general speciation order of toxicity for As is:

Organoarsenicals (e.g. methylated species) < arsenates (As(V)) < arsenites (As(III)) (Yamauchi and Fowler 1994).

Similar species toxicity has been found for Sb (Filella *et al.* 2002a; Gebel 1997; He and Yang 1999), and may be broadly stated as:

Organoantimonials (e.g. methylated species) < antimonates (Sb(V)) < antimonites (Sb(III)).

It is debatable whether or not As is essential to human health, but there is no known human requirement for Sb (Bhattacharya *et al.* 2002; Shotyk *et al.* 2005; Smith *et al.* 1998). Both metalloids are clastogenic in the trivalent state, and have carcinogenic potential (Gebel 1997). Both have a strong affinity for thiol groups and they may substitute for P in biological reactions, which explain their inhibitory role in DNA replication and metabolic processes (ATSDR 1992; ATSDR 2000; Shotyk *et al.* 2005). There is less evidence that Sb is detoxified via methylation in biological systems, and while there is some question as to the detoxifying role of methylation for As, it is often accepted more readily than for Sb (Gebel 1997). Currently the World Health Organisation has set the Acceptable Daily Intake (ADI) of As at 2 μ g kg⁻¹ day⁻¹ kg of body weight⁻¹ (WHO 1989) and the Tolerable Daily Intake (TDI) of Sb at 6 μ g kg⁻¹ day⁻¹ kg of body weight⁻¹ (WHO 2003).

The dependence of the speciation of both As and Sb on environmental conditions will be elucidated in the following sections.

2.4.1. pH and redox as master variables

pH is often referred to as a 'master' variable in inorganic contaminant discussions (Stumm and Morgan 1996). Specifically, the pH of an environmental system or phase such as water or soil gives an indication of the species of contaminant present and possible reactions with system constituents. As a measure of protonation, pH determines the degree of dissociation of weak acids in aquatic systems, and affects precipitation, adsorption and solution chemistry in soil systems. pH and redox potential, another 'master' variable, do not operate independently of each other in environmental systems.

The oxidising or reducing state of a system can determine the species present (specifically the oxidation state of the element in a particular form). Assessment of a system's redox status can be done via Eh (or pe) values (Stumm and Morgan 1996), although these values are difficult to equate to actual quantitative chemical changes in a heterogeneous environmental system (Bartlett 1999). As the toxicity of As and Sb depend on the species present, pH and pe (characterising system redox conditions) are

important to determine in an environmental system. Important environmental redox half reactions are given in Table 2.2, showing that redox reactions of inorganic As and Sb fall within the redox limits of natural environments (Brookins 1988; Lindsay 1979). Due to the natural phenomena of sequential reduction/oxidation, the species of As and Sb present depends upon the amounts of co-occurring reductants and oxidants in any given system.

2.4.2. pH, redox, and species of As and Sb

As stated, pH, redox potential, and speciation of As and Sb are interdependent in environmental systems. Reactions of many As species are well understood in such systems (e.g. Smith *et al.* 1998), the reactions of Sb species less so. Similar to phosphorus, the properties of As and Sb (Table 2.1) ensure their close association and strong bonding with oxygen and hydroxide in the environment (e.g. Table 2.2). The oxyanionic form plays a central role in most As and Sb species in the environment.

Table 2.2. Some pertinent redox reactions in natural systems (adapted from Aylward and Findlay 1994, Stumm and Morgan 1996 and Whitten *et al.* 1996).

Reaction	pe ^{0 †}	$\operatorname{Eh}^{0}(V)$
$1/4O_2(g) + H^+ + e^- = 1/2H_2O(l)$	20.8	1.23
$1/5NO_{3}^{-}(aq) + 6/5H^{+} + e^{-} = 1/10N_{2}(g) + 3/5H_{2}O(l)$	21.1	1.25
$1/2MnO_2(s) + 2H^+ + e^- = 1/2Mn^{2+} (aq) + H_2O(1)$	20.4	1.21
$Fe(OH)_3 (am) + 3H^+ + e^- = Fe^{2+} (aq) + 3H_2O (l)$	16.6	0.98
$Fe(OH)_3 (s) + 3H^+ + e^- = Fe^{2+} (aq) + 3H_2O (l)$	15.7	0.93
α -FeOOH (s) + 2H ⁺ + e ⁻ = Fe ²⁺ (aq) + 2H ₂ O (l)	13.1	0.77
$1/2Sb(OH)_{6}(aq) + 3/2H^{+} + e^{-} = 1/2Sb(OH)_{3}(aq) + 3/2H_{2}O(l)$	12.9	0.76
$1/2H_3AsO_4(aq) + H^+ + e^- = 1/2H_3AsO_3(aq) + 1/2H_2O(l)$	9.7	0.57
$1/8SO_4^{2-}$ (aq) + $5/4H^+$ + e ⁻ = $1/8H_2S$ (g) + $1/2H_2O$ (l)	5.3	0.31
$1/8SO_4^{2-}$ (aq) + $9/8H^+$ + e ⁻ = $1/8HS^-$ (aq) + $1/2H_2O$ (l)	4.3	0.25
$1/8CO_2(g) + H^+ + e^- = 1/8CH_4(g) + 1/4H_2O(l)$	2.9	0.17
$1/3As(s) + H^+ + e^- = 1/3AsH_3(g)$	-4.0	-0.24
1/3Sb(s) + H ⁺ + e ⁻ = $1/3$ SbH ₃ (g)	-8.6	-0.51

[†] $pe^0 = Eh^0/0.059V$ at 25 C and Eh^0 is the equilibrium redox potential relative to the oxidation of H₂(g).

Inorganic forms of As and Sb

Inorganic As and Sb compounds predominate over organic forms in most environmental systems (e.g. Table 2.10). The pK_a values of inorganic As and Sb species are given in Table 2.3. Using the values of arsenic acid protonation listed in Table 2.3, a thermodynamic stability diagram over a range of pH values can be calculated (Figure 2.1).

Table 2.3. Equations and pK_a values for inorganic As and Sb species (Puigdomenech 2002; Smith *et al.* 1998; Zakaznova-Iakovleva and Seward 2000).

Arsenic (V)	pK _a
$H_3AsO_4_{(aq)} + H_2O_{(l)} = H_2AsO_4^{-}_{(aq)} + H_3O^{+}_{-}$	2.20
$H_2AsO_4^{-}(aq) + H_2O_{(1)} = HAsO_4^{-}(aq) + H_3O^{+}$	6.97
$HAsO_4^{2^-}(aq) + H_2O_{(1)} = AsO_4^{3^-}(aq) + H_3O^+$	11.53
Antimony (V)	
$Sb(OH)_{5 (aq)} + 2H_2O_{(1)} = Sb(OH)_{6 (aq)} + H_3O^+$	2.72
Arsenic (III)	
$H_3AsO_3_{(aq)} + H_2O_{(l)} = H_2AsO_3_{(aq)} + H_3O^+$	9.22
$H_2AsO_3^{-}(aq) + H_2O_{(l)} = HAsO_3^{-}(aq) + H_3O^{+}$	12.13
$HAsO_{3}^{2}(aq) + H_{2}O_{(1)} = AsO_{3}^{3}(aq) + H_{3}O^{+}$	13.4
Antimony (III)	
$Sb(OH)_{3 (aq)} + H_2O_{(l)} = Sb(OH)_{2 (aq)}^+ + H_3O^+$	11.9



Figure 2.1. Thermodynamically predominant species of protonated As(V) (arsenic acids) across a range of pH values.

Table 2.3 and Figure 2.1 show the most stable inorganic As(V) species over a typical environmental pH range (4 - 8) are $H_2AsO_4^-$ and $HAsO_4^{2-}$. Similarly the most thermodynamically stable As(III) species is H_3AsO_3 . The lack of charge on the As(III) species compared with the successive deprotonation of the As(V) species has implications for charge dependent associations with solid phases, such as clay minerals and oxyhydroxides in soils (see section 2.5.3). A generalisation made from this is that As(V) species are less mobile than As(III) species in many environmental systems (Bhattacharya *et al.* 2002).

Pauling (1933) stated that the coordination of Sb(V) with oxygen differs to that of As (and P) due to a larger ionic radius and lower charge density. Antimony (V) is octahedrally coordinated with oxygen, whereas As and P are tetrahedrally coordinated, and have very similar pK_a values (Aylward and Findlay 1994). Thus, the deprotonated form of antimonic acid, $Sb(OH)_6^-$, is the dominant Sb(V) form over most environmentally relevant pH values, and is resistant to successive protonation changes, unlike arsenic acid. This is shown by the lack of successive protonation changes as indicated in Table 2.3. The first dissociation constant of Sb(OH)₃ (Sb(III)), similarly, has been given as 11.9 (Zakaznova-Iakovleva and Seward 2000), showing its resistance to protonation changes within normal environmental pH ranges (Table 2.3). Thus, the mobility of Sb(III) may be higher than Sb(V), as in the case with As. Furthermore, while successive protonation changes with pH complicate As(V) binding to particulate matter in oxygenated systems (along with changes in pHdependent charges on solids), the influence of pH-dependent binding of antimonic acid (Sb(V)) on solid phases should be a more general pattern of solid charge influence.

Conditions necessary for species stability of both Sb and As can be illustrated using simple Eh(pe)-pH diagrams, as Vink (1996) and Takayanagi and Cossa (1997) have shown. Such diagrams are an extension of the pH stability determinations as shown in Figure 2.1, including redox potentials, and are a convenient way of summarising often-extensive thermodynamic work. They are limited to the number of species considered, calculated or published thermodynamic data, and the number of elements incorporated into the system.



Figure 2.2. pe-pH diagram for the As-O-H system (a), and Sb-O-H system (b), assuming Σ As and Sb = 0.1 mM. Possible oxide and hydoxide precipitates have been removed. (c) = crystalline, (g) = gas. All other species are aqueous. Dashed lines are the environmental redox limits imposed by the dissociation of water into H₂ (g) and O₂ (g). Computed using HYDRA (Puigdomenech 2004) and MEDUSA (Puigdomenech 2002) for windows.

Figure 2.2 shows the simplified systems of As-O-H and Sb-O-H under redox and pH conditions experienced in natural systems. The differences between predominant As and Sb aqueous species across different pH values reflects the differences in protonation tendencies mentioned previously. As supported by Masscheleyn *et al.* (1991), Figure 2.2a also shows that under oxidising conditions As(V) is the predominant form of As occurring. Under moderately reducing conditions across a wide pH range, As exists as the uncharged aqueous species H₃AsO₃, and in slightly more complex pe-pH diagrams, As is coprecipitated with Fe oxyhydroxides, for

example, as scorodite (Mok and Wai 1990) (for a discussion of adsorption tendencies, see section 2.5.3). In the presence of S, sulfides of As(III) are the most stable As form under reducing conditions (Vink 1996), causing the formation of arsenopyrite at high As concentrations, and the scavenging of As at lower concentrations by Fe sulfides (Bowen 1979).

Some generalisations may be made based on investigations into Sb solution chemistry, as summarised by Filella *et al.* (2002b). The simplified pe-pH diagram of the Sb-O-H system proposed by Brookins (1988) shows that Sb may precipitate as oxides across a range of pe-pH, while a soluble form is limited to more oxidising conditions at low pH. Vink (1996) included the oxyanionic form SbO₃⁻ due to its inclusion as the basic Sb oxyanion for the formation of various Sb minerals, and the soluble commercial Sb(V) product of KSb(OH)₆. Incorporating this or the hydrated antimonic acid anion Sb(OH)₆⁻ into the calculations increases the solubility of Sb(V) in mildly acidic to alkaline conditions (Figure 2.2b). Furthermore, the inclusion of Sb(OH)₃ as an soluble uncharged species (due to the pH independent solubility of Sb₂O₃, (Filella *et al.* 2002b)) increases the solubility of Sb(III) when compared to the earlier pe-pH diagrams. This more closely aligns Sb stability predictions with those for As, as well as supporting findings of dissolved Sb(III) in aqueous systems (section 2.6). This shows that:

pe(Eh)-pH diagram interpretation is limited to the range of data available, and;
Sb may be more soluble over a wider pe-pH range than previously suspected.
Further evidence of this solubility of both Sb(III) and Sb(V) is given in section 2.6.

More complex pe-pH diagrams suggest that like As, sulfides are the predominant Sb mineral formed under reducing conditions (i.e. stibnite (Vink 1996)), but, extrapolating from laboratory conditions, soluble complexes such as SbS_2^- may form in more alkaline reducing conditions (Takayangi and Cossa, 1997). Antimony (V) as SbS_4^{3-} has also recently been observed under anoxic conditions (Filella *et al.* 2002b). In contrast to S, Cl complexing is suspected to play a minimal role in seawater (Strohal *et al.* 1975), although complexes of both Sb(V) and (III) with Cl have been found following high experimental additions of Cl (Filella *et al.* 2002b), and this has not been confirmed at more realistic concentrations of Cl (or Sb). The lack of data on

Sb complexing by inorganic ions such as Cl and S affects thermodynamic predictions of speciation (see Chapter 7). Despite this, and as the above pe-pH adaptations show, at environmentally relevant concentrations and conditions Sb exists as a soluble species regardless of oxidation state (Takayanagi and Cossa 1997) (excluding the scavenging potential of solid phases). Much like As, the general solubility of Sb infers the importance of adsorption-desorption mechanisms and charge dependent processes in complex environmental systems when examining the mobility of inorganic species.

Organic forms of As and Sb

Organic forms of As and Sb are poorly understood compared to inorganic forms. Organic As species are usually associated with methylation reactions in soil, water and biota (the more complex forms such as arsenosugars, arsenobetaine, arsenocholine and arsenolipids will be excluded from this discussion). Methylation of As and Sb is a poorly studied transport pathway for these contaminants. It may enhance mobilization through volatilisation or the formation of soluble compounds, such as methylated acids (Jenkins *et al.* 1998; Salomons and Forstner 1984). Some volatile compounds generated via methylation, such as methylated species of arsine, may increase the element's toxicity (Maeda 1994). Some common methylated species are listed in Table 2.4.

As Species Name	Formula	Sb equivalent	Formula
Monomethylarsonic acid	CH ₃ AsO(OH) ₂	Methylstibonic acid	(CH ₃)SbO(OH) ₂
(MMAA)		(MSA)	
Dimethylarsinic acid	(CH ₃) ₂ AsO(OH)	Dimethylstibonic acid	(CH ₃) ₂ Sb(O)OH
(DMAA)		(DMSA)	
Dimethylarsine	(CH ₃) ₂ AsH	Trimethylstiboxide	(CH ₃) ₃ SbO
Trimethylarsine	(CH ₃) ₃ As	Trimethylstibine	(CH ₃) ₃ Sb

Table 2.4. Common methylated forms of As and Sb (common abbreviation in parentheses).

Biomethylation of As has been known to occur since the 1930s work of Challenger *et al.* (1933). Various methylation processes are now known. While bacterial biomethylation may occur to di- or trimethylarsine (which is stable in the absence of oxygen), fungal biomethylation can produce arsine gas (which may also be produced

inorganically) (Gao and Burau 1997). While attempts to ascertain whether Sb methylation occurs began soon after confirmation of As methylation, results have commonly been inconclusive or contradictory. Gurleyuk *et al.* (1997) attributes much of this to poorly comparable analytical methods of Sb speciation, such as the different behaviour of Sb under hydride generation conditions as compared to As (Dodd *et al.* 1992). The lack of certified methylated Sb compounds for calibration, ad hoc approaches to standard synthesis and detection methodologies also complicates analysis.

Despite these difficulties, recent investigations have confirmed the existence of biologically mediated Sb reactions, but almost nothing is known regarding solution chemistry of the methylated Sb compounds that have been identified in the environment. Gurleyuk *et al.* (1997) found biologically mediated reduction and methylation of Sb compounds in *Pseudomonas fluorescens* bacterial cultures and soil samples respectively, using a capillary GC-fluorine-induced chemiluminescence detection system. Expanding on this work, Jenkins *et al.* (1998) determined biological production of Sb may occur under reducing conditions. This suggests biomethylation of Sb may occur under reducing conditions in the environment, such as in waterlogged soils. Conversely, mono- and dimethyl Sb compounds have been detected in oxidised seawaters (Andreae *et al.* 1981), and Brannon and Patrick (1985) found unidentified Sb volatiles could be lost from sediments regardless of oxygen status. The toxicity of these volatile Sb species has not been determined.

In comparison to Sb, there has been a large amount of work on methylated As compounds in the environment, including studies on adsorption, mobility, redox transformations, and toxicity. However, as the abundance of both methylated As and Sb compounds appears to be low compared to the more toxic inorganic forms (e.g. Table 2.10), and as data on the occurrence of methylated Sb compounds in soils are particularly scarce (Filella *et al.* 2002a), these forms have been omitted from further detailed discussion in this review.

Kinetic aspects of speciation

Biogeochemical cycling is more complicated than any brief discussion of pH, redox and speciation at equilibrium implies. For example, reduced species of As and Sb can occur in oxic systems, while oxidized species may persist in anoxic environs (Masscheleyn *et al.* 1991; Mok and Wai 1990). Kinetic stabilization of thermodynamically unstable species is usually invoked as the possible cause (Filella *et al.* 2002b).

Slow reaction rates may account for the continued existence of Sb(III) in natural, oxidised waters. Although Cutter (1992) suggested photochemical reduction may play a role in oxic systems, after finding no correlation between Sb(III) and biotic tracers (in marine systems), he has recently questioned his own findings following methodology re-evaluation (Cutter and Cutter 2005). Some authors invoke biological activity as a cause. It is known that Sb(III) can be stabilized in aquatic systems by organic matter, such as tartaric acid (Sun *et al.* 1982), and that the rate of Sb(III) oxidation to Sb(V) decreases with pH (Belzile *et al.* 2001). Inorganic processes may also play a role. Belzile *et al.* (2001) found oxidation of Sb(III) by Mn oxyhydroxides took 3 days, but 5 days by the Fe equivalent. The relative importance of these mechanisms in Sb speciation has not been elucidated, but, similar to the lack of knowledge on inorganic complexation effects, these unknowns introduce uncertainties into predictions of Sb behaviour in soils, waters and biota.

2.5. ARSENIC AND ANTIMONY IN SOIL

2.5.1. Background levels

Both As and Sb occur naturally as trace elements in soil, their main source being the weathering of soil parent materials. Both elements are typically enriched in the early stages of magmatic differentiation, and often occur in hydrothermal metal and sulfide deposits, either co-precipitated and associated with metal ores, or as separate mineral ores (Gilligan *et al.* 1992; Yan-Chu 1994). Typical As minerals include As sulfides such as arsenopyrite (FeAsS), orpiment (As₂S₃), or realgar (AsS), while various oxides, metal oxides and metal sulfides of arsenic also commonly exist (Azcue and Nriagu 1994; Yan-Chu 1994). Stibnite (Sb₂S₃) is the chief ore of Sb, with valentinite (Sb₂O₃, an oxidation product of stibnite) also widely occurring (Filella *et al.* 2002a).

Some typical non-mineralised concentrations of both elements in geological media are given in Table 2.5.

	Granite	Basalt	Shale	Limestone	Sandstone	Earth's crust
As	1.5	1.5	6.0	13	1.0	1.5
Sb	0.2	0.2	1.5	0.3	0.05	0.2

Table 2.5. Typical average concentrations (mg kg⁻¹) of As and Sb in various lithological media (Bowen 1979).

How background concentrations of trace elements in soils should be derived is a topical issue. Single guideline values for contaminants in soil do not account for regional variation in mineralisation, soil type, or adaptations of biota. Thus, determinations of regional and local soil background concentrations of trace elements have become an integral part of site risk assessment and determination of the extent of contamination. Zillioux (2001) defines background concentrations as either:

'Natural' background, including a natural geological component as well as an unknown diffuse historical contribution from human activities;

'Anthropogenic' background, characterised by a higher average background level, often found in urban environments, and;

Point sources, which are associated with discrete activities that have caused distinctly elevated levels of soil (As) within limited areas.

The difficulty in determining appropriate background levels is due to problems in separating 'natural' from 'anthropogenic' backgrounds, either of which may be influenced by trace element point sources. Methods ranging from semi-qualitative (Gough 1993) to robust statistical modelling of mixed contaminant populations (Portier 2001) have been devised to evaluate background concentrations of contaminants in soil. Background derivations of As concentration far outweigh similar work on Sb (Chen *et al.* 1999; Chen *et al.* 2001; Crommentuijn *et al.* 2000; Zillioux 2001).

Some background and baseline values of As and Sb are listed in Table 2.6. Baseline values are usually calculated from spatially selected 'background' samples (which

may include both natural and anthropogenic influences), and the upper and lower limits of the 'background' range of concentrations is quantified statistically, using either geometric distribution properties or stated confidence limits to define the distribution (Chen *et al.* 1999; Chen *et al.* 2001; Gilbert 1987; Gough 1993; Ma *et al.* 1997). In a series of papers concentrating on background derivations Chen *et al.* (1999; 2001) determined baseline values of different elements, including As and Sb, in Florida soils. Across seven soil orders, the As and Sb baseline ranges were 0.02 -7.01 mg kg⁻¹ and 0.06 - 0.79 mg kg⁻¹ respectively. These values typify the trend of Sb background concentrations in soils being much lower than the corresponding values for As.

Background concentration		Study comments	Reference
As	Sb		
<12.8	-	Natural occurrence sampled to 33 m	Anawar et al. (2003)
		depth	
<1 - 8	-	Australian rural soils	Tiller (1992)
0.2 - 8.1	-	Melbourne urban soils	
0.6 - 11	-	Sydney urban soils	
2 - 45	< 0.2 - 22	Hobart urban soils	
0.02 - 7.01	0.06-0.79	Across seven soil orders	Chen et al. (1999)
		(ranging from Spodosols (Podosols)	
		to Histosols (Hydrosols))	
29	3	Used in generic hazard assessment in	Crommentuijn et al. (2000)
		the Netherlands	
-	6.9	English grassland for comparison to	Ainsworth et al. (1990a)
		smelter site	
6.0	1.0	Generic soil background	Bowen (1979)

Table 2.6. Background ranges and values for As and Sb in surface soils (mg kg⁻¹).

Variations in background concentrations reflect mineralisation, parent material differences, varying degrees of anthropogenic influence, and different sampling strategies. For example, the high background ranges of As and Sb in the urban soil of Hobart are associated with localised metal refinery practices (Tiller 1992). The above variations in background values undermine the acceptability of generic guideline values for contamination assessment, which has been increasingly recognised in the

approaches to investigating contamination in Australia (ANZECC and NHMRC 1992; NEPC 1999a).

2.5.2. Anthropogenic enrichment of As and Sb in soils

Due to the variations in background concentrations (Table 2.6) and differences in contamination guideline levels between countries and regions, concentrations of As and Sb deemed to be anthropogenic enrichment or contamination vary greatly. A general trend is that studies are being carried out more often in areas of gross industrial, agricultural or mining related contamination (Table 2.7).

High concentrations of As and Sb in soils may be associated with mineralised areas (Table 2.7). In these areas, metalloids are typically related to primary mineral occurrence, such as those mentioned in section 2.2. In the case of mining or smelting, extraction and processing can selectively concentrate metalloids in waste material and subsequently in areas surrounding the mine. Other anthropogenic additions of metalloids to soils may include industrial or agricultural contamination such as residual As in cattle dip locations in north-eastern NSW (McLaren *et al.* 1998). The source of anthropogenic contamination affects the mobility and retention of the metalloids in the soil. Examples of this will be given in section 2.5.3, in the discussion of metalloid mobility.

2.5.3. Retention mechanisms

The retention mechanisms of As and Sb in soils have been the focus of substantial investigation. Some investigations into As retention mechanisms have included the methylated forms, due to their commercial uses and subsequent dispersion into the environment. However, the majority of investigations into both As and Sb retention by soils has concentrated on inorganic forms, due to their prevalence. The following discussion will be limited to these.

Concentra	tion range	Contamination source	Comments	Reference
As	Sb			
30 - 1920	-	Cattle dip sites	0 - 10 cm soil	McLaren et al.
				(1998)
1.0 - 3000	-	Mining and smelting	38 sites in Austria	Wenzel et al.
		(and mineralisation)		(2002)
-	< 1490	Smelter site	8-336 mg kg ⁻¹ in grasses,	Ainsworth et al.
			related to plant-surface	(1990a)
			deposition	
-	11.9 - 710	Previous mining	Low levels of water soluble	Flynn et al.
		activities	Sb	(2003)
-	27.7 - 15100	Previous mining	Shoots and leaf accumulation	Baroni et al.
		activities	for 3 species of up to 1160	(2000)
			and 1370 mg kg ⁻¹	
1 - 14	35 - 17500	Shooting range	< 0.5 mm soil fraction. High	Johnson <i>et al</i> .
			concentrations associated	(2005)
			with Sb in bullets	
2220	80200	Smelter site	From 1 sample classified as	Wilson et al.
			soil	(2004)
191 - 38600	2.5 - 237	Previous mining	Soils classified as strongly	Ashley and
		activities	contaminated	Lottermoser
				(1999)

Table 2.7. Examples of total soil concentrations of As and Sb found in soils contaminated by anthropogenic activities (mg kg⁻¹).

Specific retention mechanisms include both adsorption and precipitation/coprecipitation. The interaction of these with other variables such as pH, pe, and organic matter determines the importance of each mechanism for metalloid retention (Smith et al. 1998). Retention mechanisms of As and Sb in soil have also been investigated through the use of chemical extractions. In this approach, fractionation of the metalloids between operationally defined soil 'pools' is determined and binding attributes are inferred. A brief overview of each mechanism and its importance in the retention of As and Sb in soil follows, with an emphasis given to investigations into and mechanisms operating within neutral to acidic pH ranges.

Adsorption

In general terms, adsorption is the accumulation of a substance at the common boundary of two phases (Manahan 2000), while the generic term sorption is used when the actual mechanism of association of the substance with the boundary is unknown or unclear. Within soil, adsorption refers to the association of ions and molecules from the soil solution with solid phases of soil, such as clay minerals, oxides and hydroxides of metals, or organic matter. Adsorption can be either nonspecific (electrostatic) or specific (chemisorption). The discussion below incorporates both specific and non-specific adsorption, due to the dearth of information on the different mechanisms involved in Sb adsorption.

Adsorption has been identified as one of the most important mechanisms for As and Sb retention in soil (Bhattacharya *et al.* 2002; Dudas 1987; King 1988; Peryea 1998; Smith *et al.* 1998), albeit most often through inferences developed from studies of pure mineral phases (Fendorf *et al.* 1997; Huang 1975; Thanabalasingam and Pickering 1990). While As and Sb may exist as soluble species under environmentally relevant conditions (section 2.4.2), the strong adsorptive tendencies of both metalloids may control their mobile or dissolved concentrations. Adsorption may be on clay minerals, calcite, oxides and hydroxides, or organic matter, and may be affected by competitive ions as is the case with P and As (Matera and Le Hecho 2001), or ionic strength. The characteristics of adsorption processes are unique to the As and Sb species present (see the following sections), and as such the interpretation of species-sorption-pH-pe-phase (soil) interactions can often be confounded, particularly when species conversion is not considered.

Clay Minerals

Matera and Le Hecho (2001) emphasised the importance of pH when considering anion adsorption sites on clay minerals. Such sites are associated with broken clay particle edges, and utilise protonation as given in the following arsenic acid example of inner sphere complex formation:

 $-M-OH + H_2AsO_4 = -M-H_2AsO_4 + OH^2$

The adsorptive properties of clay minerals in relation to anionic forms of As and Sb depends heavily upon pH and the point of zero charge (PZC) of the mineral, as well as the species of metalloid present. Studies of As adsorption confirm this. An environmental solubility minimum for As(V) around a pH of 4 - 6 (Mok and Wai 1990) relates well to adsorption maximums of arsenate (around a pH of 5) by minerals such as kaolinite and montmorillonite (Goldberg and Glaubig 1988). Frost and Griffin's (1977) findings supported this, and also showed arsenite adsorption by these minerals increased with increasing pH between 3 and 9 (with a possible peak around a pH of 7). Differences in pH adsorption optima were attributed to protonation of As species in solution, while the higher adsorption of arsenate compared to arsenite was attributed to soluble species configuration and bonding strength differences. However, problems with stabilities of standard solutions (ie. As(III) oxidation) possible confounded these results.

Huang (1975) investigated the retention of As by micaceous minerals including biotite, muscovite and vermiculite. Adsorption was found to depend on surface coatings of hydroxy-Al across a wide range of pH (2 - 7). This data also suggests that surface coatings of Fe oxides, such as in precipitation reactions following acid soil processes, would also increase adsorption, in view of the relative importance of these phases for As adsorption (see section 2.5.3 - Oxides and hydroxides).

There have been no specific investigations of Sb adsorption by clay minerals to date. There is some indication of a general solubility minimum around a pH of 4, similar to As (Ashley *et al.* 2003; Edwards *et al.* 1995), but the importance of clay minerals in determining this minimum cannot be separated from the effect of oxides and hydroxides (see below), or other soil phases, at this stage.

Oxides and hydroxides

The adsorption of As by oxides and hydroxides has been studied much more comprehensively than Sb. As with clay minerals, adsorption by oxides and hydroxides depends on pH and the oxidation state of the metalloid. Pierce and Moore (1982) found that arsenite sorption by a synthetic amorphous $Fe(OH)_3$ was at a maximum around a pH of 7, while arsenate sorption peaked around a pH of 4. Sorption

maximums were related to pK_a values of arsenous and arsenic acids (Table 2.3). Both arsenite and arsenate were adsorbed quickly (90 % of added As in less than 2 hours), and the adsorption kinetics suggested different types of binding sites for As, depending upon the concentration of As added in solution. This was confirmed by Waychunas *et al.* (1993) and Manceau (1995), who found that As formed a bidentate binuclear complex when binding to ferrihydrite. Both studies also found other binding formations of As onto ferrihydrite, and following data re-evaluation, Waychunas *et al.* (1995) proposed the existence of a monodentate complex. This was in agreement with the later findings of Fendorf *et al.* (1997), who found that 3 complex formations existed, depending upon metalloid loadings, for As binding to goethite.

Most often the binding relationships between Sb and various oxides and hydroxides have been inferred through chemical extractions (section 2.5.3 - Phase associations). The studies on As-oxide relationships and some similarities between As and Sb chemistry (sections 2.3 and 2.4) give an indication of the importance of oxides and hydroxides for Sb adsorption. One study of Sb(III) sorption on oxides found that the sorption capacity decreased in the order MnOOH > $Al(OH)_3$ > FeOOH, with the amount sorbed decreasing gradually as pH rises above 6, but with all 3 phases retaining over 80 % of added Sb(III) below a pH of 6 (Thanabalasingam and Pickering 1990). Specific adsorption of Sb(III) by Al and Fe oxides peaked around a pH of 7 - 8. Thus, the amount of non-specific adsorption occurring appeared to shift the adsorption maximum downwards by a pH of 1 - 2 units. They concluded that while the Al and Fe hydrous oxides showed the smallest relative amount of adsorption, their predominance in environmental samples meant they should govern Sb(III) retention in natural waters. Possible oxidation of Sb(III) to Sb(V) in the addition solutions, or due to the oxidative effect of the adsorbents, was not considered. Ambe (1987) undertook the only known published study on Sb(V) sorption by an Fe oxide. He found the sorption behaviour of Sb(V) on hematite was possibly due to a combination of surface binding sites, similar to As (Pierce and Moore 1982). There have been no investigations into adsorption of Sb(V) by noncrystalline Fe hydroxides (e.g. ferrihydrite).

Organic matter

The adsorption of both As and Sb by organic matter has been limited to investigations of humic acid-metalloid interactions. Thanabalasingam and Pickering (1986) investigated the adsorption of both As(III) and (V) by humic acid. This is the only published study on As sorption by humic acid, and there are discrepancies in the results. For example, the sorption curves show a maximum sorption of As of approximately 85 mmol kg⁻¹ following an addition of 5 μ mol L⁻¹ As (see Figure 2D; Thanabalasingam and Pickering 1986). However, with this initial As concentration, 25 ml total volume and 15 mg of humic acid, the maximum sorption possible is 8.3 mmol kg⁻¹. Such discrepancies make the calculated maximum adsorption of As(III) and As(V) of 70 and 90 mmol kg⁻¹ questionable, although the general patterns of adsorption appear to be acceptable. The maximum adsorption of both As(III) and (V) occurred around a pH of 5.5, and adsorption decreased with further increases in pH. Thanabalasingam and Pickering (1986) suggested this was due to enhanced deprotonation and competition with OH at higher pH, although physical loss of binding sites with humic acid dissolution at higher pH values was not considered. They also inferred the importance of electrostatic attraction for As by humic acid due to the displacement of adsorbed As by a range of other anions, and hypothesised an anion exchange mechanism to explain this. Binding of As by natural organic matter has been invoked as an As retention mechanism in several environmental studies, and will be briefly discussed in section 2.5.3 - Organic associations.

Experimental information on Sb sorption by organic matter is scarce. Pilarski *et al.* (1995) investigated Sb(III) and Sb(V) sorption by humic acid. They found an adsorption maximum of 23 μ mol g⁻¹ and 53 μ mol g⁻¹ for inorganic (Sb₂O₃) and organic (antimonyl tartrate) based solutions. The difference was attributed to the effect of the tartrate on Sb(III) binding. Antimony (III) adsorption from the inorganic source was affected by pH changes between 3.1 and 5.4, which the authors attributed to a combination of protonation changes on the humic acid and changes in the dominant form of aqueous Sb(III) by the following reactions:

 $Sb_2O_3 (s) + 3H_2O = 2Sb(OH)_3 (aq)$ $\frac{1}{2} Sb_2O_3 + \frac{1}{2} H_2O = SbO^+ (aq) + OH^-$

$\frac{1}{2}$ Sb₂O₃ + $\frac{1}{2}$ H₂O = SbO₂⁻(aq) + H⁺

Thus, changes in the proportion of Sb sorbed were attributed partly to protonation of aqueous species. However, thermodynamic modelling (Puigdomenech 2002; Puigdomenech 2004) indicates the concentration of Sb(III) is governed by $HSbO_2$ or its hydrated form, $Sb(OH)_3$ in the pH range of 3 - 6 (due to the dissociation constants of SbO^+ and SbO_2^- with $Sb(OH)_3$ (Schecher and McAvoy 2003)). Maximum adsorption occurred at a pH of 3.8, with an average of around 70 % of added Sb(III) sorbed. At higher pH values this decreased to around 55 %, suggesting that the sorption of Sb was related to the species predominating around a pH of 3.8, namely Sb(OH)_3. A possible alternate explanation for sorption changes with pH is competition with other aqueous ions for binding sites, or aqueous complexing of Sb that reduces its affinity for the surface (i.e. by organic complexes).

The same authors found no retention of Sb(V) by humic acid at these pH values and with Sb concentrations less than 10 μ mol L⁻¹, which was attributed to the structure of the Sb(OH)₆⁻ anion, although this statement was not elaborated upon. Presumably this was a reference to the negative charge on both the ion and the binding sites that are dominant on solid humic acid.

Filella *et al.* (2002a) stated that little interaction is expected between natural organic matter and Sb due to the predominantly negatively charged sites available on the organics in the pH ranges of natural systems. However, this does not appear to be fully justified when bonding of oxyanionic forms of As to humic acid has been observed (Thanabalasingam and Pickering 1986). The effect of protonation and specific adsorption at acidic pH values in soil has not been explored, nor has the predicted ability of dissolved Sb to hydrolyse and form polymers (Filella *et al.* 2002b), thus interacting with protonated organic groups. Furthermore, Sb is known to form complexes with various low molecular weight organic ligands (a fact that has been exploited in trace element analysis for several years (Sun *et al.* 1982)), which themselves form many of the reactive functional groups of humate compounds. Thus, like much of the behaviour of Sb in soils, the interaction of Sb with organic phases is largely undetermined.

Soils

Adsorption studies of As and Sb in whole soils are fewer in number than studies of pure phases. As with investigations of inorganic phases, the effects of metalloid species and surface charge and the PZC of the soil on binding are important. Elkhatib *et al.* (1984) found that As(III) sorption by soils was largely irreversible, and was governed by Fe oxides and pe. They postulated that the formation of binuclear bridging complexes might explain the strong sorption of As(III) and the importance of the Fe oxide phase. This and other inner-sphere complexing has since been determined as an As binding mechanism onto oxides and hydroxides (section 2.5.3 - Oxides and hydroxides). Similarly, Wauchope (1975) found arsenate binding by alluvial soils was strongly correlated with clay and Fe oxide content (as determined by an oxalate based extract) of the soils, but was independent of organic matter content. This author assumed simple anion exchange at positively charged sites, and the possibility of specific adsorption was not considered.

More recently, Smith *et al.* (1999) investigated the sorption of arsenate and arsenite by Australian soils with pH values of 4.97 - 6.90. They found that the soils generally sorbed more As(V) than As(III), and the proportions of each species sorbed differed in response to pH changes. Arsenate sorption increased as pH decreased, while arsenite sorption increased as the pH approached neutral. Crystalline and noncrystalline Fe oxides were important predictor variables for the amount of arsenate adsorbed, and the proportions of both As(V) and As(III) sorbed approached 100 % in oxidic soils at optimum pH values for adsorption. These authors also postulated oxidation of As(III) to As(V) by Fe or Mn minerals as a possible mechanism affecting the As(III) adsorption profiles (e.g. Manning and Goldberg 1996), although this was not supported by their analysis of spiked soils.

The adsorption behaviour of Sb in whole soils is almost completely unknown. In the only known study to date, King (1988) equilibrated a range of US surface and subsoils with 26.4 μ M of Sb. He found that 50 - 100 % of the added Sb was sorbed to the soils, and 57 - 99 % of the sorbed Sb was non-exchangeable, as determined by a 1 M KC1 extract. Sorption increased as the sand content of the soils decreased (or as the silt + clay fraction increased), although he found no relationship found between the

amounts of Sb sorbed and the amounts of non-crystalline or crystalline oxide phases in the soils. King (1988) also found that the relative sorption of Sb was higher in mineral soils compared to organic rich soils. Whether Sb(III) or (V) have different adsorption behaviour in soils is unknown, although oxidation of Sb(III) to Sb(V) in the presence of some hydroxides, similar to that for As, is known to occur (Belzile *et al.* 2001). This needs to be taken into account during any investigations of Sb(III) adsorption, but does not appear to have been recognised apart from in studies of oxidation kinetics.

Effects of ionic strength and competition

The effect of ionic strength on anion adsorption depends upon the PZC of the soil, and whether the adsorption is specific (inner-sphere complexing) or non-specific (outer-sphere complexing). There is little research on the effect of ionic strength on adsorption, and poor understanding of surface bonding mechanisms, particularly for Sb, complicates this.

While investigating the adsorption of As(III) and As(V) by soils, Smith et al. (1999) also studied the effect of ionic strength on As adsorption. Increasing ionic strength decreased sorption below the PZC of the soils, and increased it above the PZC. This was attributed to a decrease in electrostatic potential a small distance from the surface, which increased the repulsion of anions below the PZC, and decreased repulsion above the PZC. This was put forward by Bowden et al. (1980), based on the work of van Olphen (1963), as a mechanism affecting specifically adsorbing anions. However, a lack of effect on sorption following ionic strength changes is often used to infer specific adsorption (Sparks 2003). This may be the case, but if both specific and nonspecific adsorption is taking place, the effect of one may mask the effect of the other below the PZC, resulting in the appearance of no over-all effect of ionic strength. This is possible as the general effect of increasing salt concentration is to increase net surface charge. This results in greater ionic exchange and outer-sphere complexing, which would counteract the increased repulsion of specifically binding anions below the PZC. The effect above the PZC would be additive for anion adsorption, so the increase in sorption with ionic strength at pH values above the PZC may not necessarily be solely due to specific adsorption as is sometimes implied (e.g. Smith *et al.* 1999).

The only reference to ionic strength effects in regards to Sb sorption is that made by Thanabalasingam and Pickering (1990) during their investigations into Sb(III) sorption by hydrous Al, Mn and Fe oxides. They found that the addition of an acetate buffer reduced sorption, and this was attributed to the minimisation of ion exchange at the surface. However, the actual effect of reduced ion exchange on the uncharged Sb(OH)₃ species was not discussed, nor was the effect of probable aqueous complexing of Sb(OH)₃ with the buffer, nor was the effect of ionic strength and PZC interactions for the adsorbates discussed. The predominance of the uncharged Sb(III) species and the singly deprotonated Sb(OH)₆⁻ Sb(V) species across environmentally relevant pH values would appear to make Sb an ideal trace element to use in further investigations of adsorption effects following ionic strength changes, although this has not been explored to date.

Competitive effects on adsorption of contaminants like As and Sb are important as environmental systems usually contain high levels of other inorganic or organic anions such as phosphates or humates, which can affect the adsorption behaviour of metalloids. Livesey and Huang (1981) found that chloride, nitrate and sulfate had little effect on As(V) sorption at concentrations typical of saline soils, but phosphate (and in other studies, sulfate) has been shown to desorb As(V) from or reduce adsorption of As(V) by soils, pure mineral phases and Fe(OH)₃ (Livesey and Huang 1981; Manning and Goldberg 1996; Smith *et al.* 2002). Smith *et al.* (2002) found that this competitive effect of phosphate on arsenate retention was severely reduced in soils with high levels of free Fe oxides (a Vertisol and Oxisol), but this retardation was limited as P additions increased. A similar effect of P addition was also observed on As(III) adsorption. Competition between the anions appeared to be limited by the very high number of sorption sites available. Similar results were reported by Waltham and Eick (2002) for adsorption of arsenate onto goethite in the presence of silicic acid.

Recently there has been increasing interest in the competitive effects of organic acids on As retention by soils and soil phases. Grafe *et al.* (2002) studied the adsorption of As(V) and As(III) by ferrihydrite in the presence and absence of humic, fulvic, and citric acids across a wide pH range (3 - 11). They found that As(V) adsorption by ferrihydrite was only decreased in the presence of citric acid, while citric and fulvic acids both decreased As(III) adsorption. Humic acid had no effect. These differences were attributed to the low affinity of dissolved organic carbon for ferrihydrite surface sites, and the increased relative binding of carboxyl groups in the smaller citric and fulvic acids. Conversely, Saada et al. (2003) found that humic acid coatings on kaolinite at a pH of 7 increased As(V) adsorption at low initial As concentrations. They concluded that the humic acid had a higher affinity for As than the kaolinite, and that protonated amine groups were responsible for the increased As adsorption in the presence of humic acid. This is similar to the anion exchange mechanism proposed by Thanabalasingam and Pickering (1986) for As sorption by humic acids. Saada et al. (2003) stated that organic matter content of soils may govern As adsorption if the hydrous Fe oxide content is low, and findings such as those above support this. The interaction of dissolved As and organics such as humates and fulvates remains unclear.

To date, there have been no published studies on the effects of anion competition on the adsorption of Sb by either pure materials or whole soils. Similarly, there have been no investigations into the interactions of dissolved or adsorbed organic matter on Sb retention by solid phases.

Precipitation, co-precipitation and dissolution

Dissolution of As and Sb bearing primary minerals is typically a mechanism of metalloid mobility cited in studies of mineralised areas and areas affected by mining and smelting contamination (Ashley *et al.* 2003; Ashley and Lottermoser 1999). However, dissolution is often accompanied by an abrupt change in environmental conditions that leads to attenuation of the mobile metalloids. For example, scorodite (FeAsO₄.2H₂O) is known to precipitate following dissolution of As bearing sulfides, if conditions are acidic and oxidising (Vink 1996). Subsequent dissolution of scorodite releases As, the soluble concentration of which may then be controlled by freshly formed hydroxides such as $Fe(OH)_3$ (Zhu and Merkel 2001). Similarly, dissolution of stibnite (Sb₂S₃) has been shown to produce up to 55 mg L⁻¹ of Sb in

solution at active mining sites, although some attenuation occurs due to adsorption and co-precipitation with amorphous hydroxides both on site and immediately downstream (Ashley *et al.* 2003). A metalloid-solid phase association that has been shown to be of particular importance in neutral to alkaline calcareous soils is the binding/precipitation of As with Ca phases, particularly carbonate (Matera and Le Hecho 2001). Similarly, in a highly contaminated alkaline soil, Johnson *et al.* (2005) found the solid Ca(Sb(OH)₆)₂ was controlling the concentration of dissolved Sb(V).

In general, the processes described above are only important in areas of gross contamination, where the concentrations of As and Sb are high enough to initiate precipitation, or where primary As or Sb minerals occur, and control dissolved concentrations of metalloids. In soils with lower total concentrations of metalloids, adsorption and co-precipitation are the processes governing mobility (Matera and Le Hecho 2001). Some residual, or recalcitrant As or Sb usually exists in these soils, however, and along with other phase associations, can be operationally defined through chemical extraction methods. Some associations of importance in acidic conditions will be discussed below.

Phase associations

The associations of As and Sb with solid phases in soil have most often been determined through the use of single or sequential chemical extractions. While most work refers to a link between extractions and speciation, what is actually being analysed is the partitioning of trace metals between soil phases (Tessier *et al.* 1979), or a measure of the binding capacity of operationally defined soil 'pools'. The ongoing difficulties and controversies associated with applying chemical extracts to soils will not be discussed here, but are summarised succinctly in several reviews (Butler *et al.* 2005; Gleyzes *et al.* 2002; Hill *et al.* 2002; Hirner 1991). While there are obvious disadvantages when compared to direct speciation measures (e.g. HPLC-ICP-MS), the additional phase information and lower cost of sequential extraction procedures has seen their continued use and development (Butler *et al.* 2005). The discussion below is limited to the description of several extracts used either singly (Table 2.8) or sequentially (Table 2.9) to determine the phase associations of As and/or Sb in soil (Table 2.8). A detailed discussion of difficulties and mechanisms

involved is beyond the scope of this review, but it is necessary to point out that the examples given here are only a small proportion of the extracts in use, and the suitability of extracts should be determined before applying them to a particular soil (Chapter 5). Similarly, difficulties in determining the specificity of extracts means that while reference is made to the soil phase that is targeted by each extract, this is done for convenience only. While the mechanism of extraction in some cases is well known (Gleyzes *et al.* 2002), the concept of 'operationally defined' fractionation must also be considered (Hirner 1991).

In addition, there appears to be a trend towards coupling soil extractions and inferred fractionation with methods of advanced aqueous speciation (De Gregori *et al.* 2005). At this stage, the undefined natures of most extract mechanisms, gross inferences of metalloid soil fractionation, and uncertainty in analytical applications results in poor analytical efficiencies and ambiguous results. This application will not be discussed further here.

There are a few general trends of As and Sb fractionation in soil evident in Tables 2.8 and 2.9. These include the low mobility of both As and Sb and the high proportion of both metalloids associated with the oxyhydroxide fraction of the soil, as well as the possible lower proportions of both metalloids associated with soil fractions defined as 'organic'.

Dissolved, soluble and labile concentrations

Concentrations of dissolved or soluble As and Sb may be high in grossly contaminated soils, but typically remain a small percentage of the total metalloid concentration in the soil (Table 2.8). Advances in speciation analysis have also resulted in improved identification of the oxidation states of both metalloids in the dissolved fraction, which can reflect both the redox status of the soil and possible kinetic effects. Wenzel *et al.* (2002) found that > 99 % of soil solution As in a range of oxidised Austrian soils was present as arsenate, and that the concentration of dissolved As ranged from 0.05 - 171 μ g L⁻¹, which was related to total soil As (1 - 3000 mg kg⁻¹). Hamon *et al.* (2004) found that conversion of As(V) to As(III) in the dissolved fraction did occur in anaerobic soils and was dependent on organic matter

additions and redox effects on labile As (i.e. desorption coupled with redox changes). Onken and Hossner (1996) found that conversion of arsenate to arsenite in the soil solution of a flooded acid soil (pH = 4.89) was incomplete after 60 days, even though the measured pe indicated arsenite would be the stable form. Total soil solution As approached 900 μ g L⁻¹, depending on the form and amount of As added during the experiment (up to 45 mg kg⁻¹).

Targeting	Extract	Metalloid	Total soil	Proportion	Study	Reference
			concentration	of total	details	
			$(mg kg^{-1})$	extracted		
				(%)		
Dissolved	Soil	As	66	0.005	pH 5 - 6	Tyler and
	solution					Olsson
						(2001)
			5 - 45	0.6 - 1.8	pH 4.9	Onken and
						Hossner
						(1996)
		Sb	0.40	< 0.25	pH 5 - 6	Tyler and
						Olsson
						(2001)
	Water-		73 - 196	0.7 - 1.5	pH 3.5 - 4.6	Lintschinger
	soluble					et al. (1998)
Labile or	NH ₄ H ₂ PO ₄	As	725 - 4770	2.6 - 12	pH 4.9 - 8.3	Hamon et
mobile						al. (2004)
	NH ₄ NO ₃	Sb	7.8 - 159	0.06 - 0.59	Sandy loam,	Hammel et
					pH 4.0 - 7.3	al. (2000)
Non-	$C_{2}H_{2}O_{4} +$	As	30 - 3540	35 - 82	Cattle dip	McLaren et
crystalline	$(NH_4)_2C_2O_4$				soils,	al. (1998)
oxyhydroxides					pH 4.8 - 6.2	
		Sb	73 - 196	62 - 92	pH 3.5 - 4.6	Lintschinger
						et al. (1998)

Table 2.8. Typical single extracts used to determine As and Sb soil associations, and the proportions of metalloids extracted.

		As			S	sb	
Pool Targeted	Extract	Proportion of metalloid	Study details	Pool Targeted	Extract	Proportion of metalloid	Study details
		extracted				extracted	
		(%)				(%)	
Freely exchangeable	Anion exchange	0.8 - 5.4	Cattle dip surface soils < 10 cm.	Carbonates	CH ₃ COOH	< 0.5	3 residential soils
	resin		Total soil As 30 -3540 mg kg ⁻¹				contaminated from
Non-exchangeable but	NaHCO ₃	0 -7.8 [†]	pH 4.83 - 6.16	Mn oxides with	NH ₂ OH-HCl	3.9 - 6.1	industry.
readily labile			(McLaren et al. 1998)	little attack on Fe	and HNO_3 (pH 2)		Total Sb 73 - 196 mg kg ⁻¹
				oxides			pH 3.5 - 4.6
Chemisorbed to Fe and	NaOH	22 - 71		Organic and	H ₂ O ₂ and NH ₄ OAc	1.1 - 4.1	(Lintschinger et al. 1998)
Al and held at the				sulfides			
internal surfaces of							
aggregates							
Ca-associated As	HCl	0 - 19					
Residual or highly	Aqua regia	0 - 43					
recalcitrant							

Table 2.9. Examples of two sequential extraction procedures for As and Sb fractionation and the proportions of metalloids extracted.

[†] One outlier of 35 %.

Measurements of dissolved Sb concentrations in soil exist (e.g. Table 2.8), although speciation of Sb in soil solution is rare. Johnson *et al.* (2005) found that Sb(V) usually accounted for > 99% of water soluble Sb (up to 5 mg L⁻¹) from contaminated shooting range soils (up to 13.8 g kg⁻¹ soil Sb). Similarly, Lintschinger *et al* (1998) found only Sb(V) in the water-soluble fraction of oxidised soils (although sample preparation issues and resulting Sb oxidation were not addressed). The soluble fraction never accounted for more than 1.5 % on average of the total soil Sb (Table 2.8). Measurements of dissolved Sb concentrations, or speciation of this fraction does not appear to have been attempted in flooded soils.

The exchangeable or weakly bound As is also typically a small proportion of total concentrations. The freely exchangeable and labile proportions found by McLaren *et al.* (1998) were less than 10 % of the total As in the soil (Table 2.9), similar to that reported by Hamon *et al.* (2004), although the latter investigators also found that organic matter additions and anaerobic conditions increased the labile proportion of As. Similarly, the few reported data for exchangeable or weakly bound Sb indicate this fraction is small. Hammel *et al.* (2000) classified less than 0.59 % of total soil Sb as mobile, as determined by a weak anion exchange mechanism, while Lintschinger *et al.* (1998) measured approximately 0.20 % of the total soil Sb in the same fraction, and < 6 % as EDTA extractable (an extract often associated with plant available trace element concentrations). While little work in relating Sb extractable concentrations with plant availability has been reported, the low proportions of total Sb considered to be or mobile reflect the low transfer factors of Sb from soils to plants (section 2.7.1).

Oxyhydroxides

The previous discussion of adsorption emphasised the importance of hydroxides and oxides for metalloid retention in soils. Data from both single and sequential extractions (Tables 2.8 and 2.9) reflect this. Additionally, As or Sb that are presumed to be associated with oxides or hydroxides on the basis of extract data, are often considered to be unavailable or immobile (e.g. Lintschinger *et al.* 1998), which is probably only correct under specific pe-pH conditions.

Arsenic has been found to be strongly associated with both non-crystalline and crystalline oxyhydroxides. Wenzel *et al.* (2001) developed a sequential extraction scheme for As and applied it to 20 soils. They found that 12 - 73 % of total As was associated with the amorphous to poorly crystallised hydrous oxides of Fe and Al (using an oxalate extract), while 13 - 39 % was associated with the crystallised forms of these oxides (oxalate + ascorbic acid at 96°C). Tareq *et al.* (2003) and Anawar *et al.* (2003) found that the mobility of As in Bangladesh sediments was controlled by reducible Fe oxyhydroxide phases as determined by an NH₂OH.HCl extraction. Furthermore, Smith *et al.* (1999) found that the non-crystalline and crystalline Fe oxyhydroxide soil contents (determined by oxalate and citrate-dithionite extracts) were strongly related via a stepwise regression analysis to the retention of As in the 10 soils studied by these authors.

Reports of single and sequential extractions for fractionating soil Sb are limited, but the association of Sb with oxyhydroxides defined fractions is common in the studies that do exist. In an early study, Crecelius et al. (1975) found that an oxalate reagent extracted 48 % of Sb from sediments with only 0.5 - 1.0 mg kg⁻¹ total Sb. A citrate dithionite - bicarbonate extract targeting the crystalline Fe and Al compounds removed an additional 31 % of the Sb. Such associations are also evident in soils with higher total concentrations of Sb. Lintschinger et al. (1998) found that 62 - 92 % of Sb in 3 industrially contaminated acidic urban soils was extractable with an oxalate reagent, and additionally < 6.1 % of the total Sb was associated with Mn oxides (Tables 2.8 and 2.9). Brannon and Patrick (1985) found the majority of Sb from 10 US harbour sediments occurred in the oxalate extractable phase, and interpreted this as being an immobile fraction (presumably under the normal environmental conditions of the sediments). Recently Johnson et al. (2005) used an oxalate extract to determine the proportion of Sb associated with Fe oxyhydroxides in firing range soils that contained up to 13.8 g kg⁻¹ total Sb. They found approximately 50 % of the total Sb was extracted in this fraction.

Typically the proportions of both As and Sb extracted with reagents assumed to target the non-crystalline and crystalline oxyhydroxide fractions of soils are high. However, to assert that this fraction is 'immobile' assumes that the phase does not interact with environmental variables. The mobility of both metalloids is known to depend on oxidation state and on pH (Bhattacharya *et al.* 2002; Corwin *et al.* 1999), as well as the source of contamination and solid phase associations. Desorption and/or reductive dissolution of the oxyhydroxide soil phase may occur with redox or pH changes. Considering that the mobility and toxicity of both metalloids depends largely on oxidation state and pH, as well as solid phase binding, the interaction of oxyhydroxide binding and metalloid mobility following changes in redox and pH is an area of research that has been neglected.

Organic associations

The extraction of soil As and Sb associated with organic material has been attempted with various reagents. Discussion of the relative specificity of extracts will not be attempted here, except for comments on NaOH that are pertinent to Chapter 5.

There is some indication that the proportions of As and Sb removed from soils by extracts targeting the organic fractions are relatively small. Jones *et al.* (1997) used a hydrogen peroxide + ammonium acetate solution to extract the organic fraction of mining derived soils and tailings. They found that slightly over 10 % of the total As was associated with this fraction. Lintschinger *et al.* (1998) used the same reagent to extract a mix of organic and sulfide phases (Table 2.9), and found less than 4.1 % of Sb in this fraction.

Sodium hydroxide has been used to extract organic associated metals and P in soils (Hedley *et al.* 1982a; Hedley *et al.* 1982b; Sposito *et al.* 1982) and was implicitly acknowledged as containing organic P in the harmonised extraction procedure developed by the Standards, Measurements and Testing program of the Commission of the European Communities (Pardo *et al.* 2003). The mechanism for this is clear, and it is a method commonly employed to characterise organic content of soils (Schnitzer 1971). Addition of NaOH to soil results in pH induced deprotonation of long chain organics, such as humic acid (Senesi and Loffredo 1999). Thus, this extract solubilizes metals or metalloids bound to these organics. However, the pH change also induces desorption of anions from variably charged surfaces such as hydroxides. Both As and Sb adsorption are pH dependent (section 2.5.3 - Oxides and hydroxides). Thus, metalloids extracted with NaOH may be either desorbed from inorganic

surfaces, or dissolved along with organics, and the amount of NaOH-As associated with either phase is unclear. For example, Jones *et al.* (1997) used NaOH to determine As associated with oxides in mine tailings, and the hydrogen peroxide solution later in the scheme to determine As oxidised and dissolved with organic matter. While the NaOH dissolved 30 - 60% of the total soil As, the peroxide step also contributed over 10 %. McLaren *et al.* (1998) used NaOH to determine As sorbed to hydroxides in soils contaminated from cattle dip operations (Table 2.9), but did not include an extract for organic matter in the scheme. Use of NaOH to extract Sb from soils has not been documented.

While there is some indication of the organic-associated As and Sb in soils being relatively small (Jones *et al.* 1997; Lintschinger *et al.* 1998), this is one area where the difficulties in applying extracts is obvious, and further investigation is required.

Residual As and Sb in soil

The proportion of metalloids in this fraction is usually determined with a strong acid digest (Gleyzes *et al.* 2002; Hirner 1991). Residual or highly recalcitrant As and Sb in soil may or may not reflect the source of contamination, but does give an indication of the 'unavailable' fraction of metalloids in a soil. The proportion of As in residual form in tailings from smelting activities has been found to be as high as 60 % (Jones *et al.* 1997). Conversely, Pfiefer *et al.* (2004) measured only 15 % of total As in the residual fraction of soils that contained detectable arsenopyrite and pyrite in a mineralised area.

Specific estimates of recalcitrant Sb in soils have not been published, although Crecelius *et al.* (1975) noted that two contaminated sediments near smelters retained 'most' of the Sb (and As) in a chemically stable form, which they speculated as being associated with slag particles. This contrasts with their findings of Sb associations in 'noncontaminated' sediments, in which 97 % of the Sb was associated with non-crystalline and crystalline hydroxides. Similarly, Brannon and Patrick (1985) found that practically all of the native Sb was extracted in the moderately reducible soil phase of US marine sediments (using an oxalate extract).

Presumably the proportion of residual As and Sb depends not only upon the contaminant source, but interactions with variables that control mobility. These include dissolution of primary phases, adsorption of the metalloids by other soil phases, and interactions of these with other variables such as pH, redox, and competing ions. These interactions require further investigation, especially in the case of Sb, in which sequential extraction attempts, and calculation of residual proportions in particular, are limited.

2.6. ARSENIC AND ANTIMONY IN WATER

As with other environmental compartments, there is a preponderance of data on As concentrations in water compared to Sb. Predictions based on assumptions of chemical similarities between the metalloids are more scarce in water related work than in soil investigations, probably due to the existence of thermodynamic and kinetic solution chemistry data that serves to emphasise both the similarities and differences between As and Sb. Such data are summarized for Sb by Filella *et al.* (2002a) and Filella *et al.* (2002b). This discussion will not attempt to reproduce these comprehensive reviews, but will be limited to a brief overview of information (and lack of) on Sb in waters, and how this compares to salient data for As.

2.6.1. Occurrence and speciation

Some measured concentrations of As and Sb in waters are given in Table 2.10. Bowen (1979) states that typical concentrations of As in freshwater are around 0.5 μ g L⁻¹. Concentrations measured in marine, estuarine and freshwater systems are similar, but may be orders of magnitude higher in areas affected by mineralisation or anthropogenic As inputs (Bowen 1979; Xiankun *et al.* 1994). Similarly, Filella *et al.* (2002a) state typical Sb concentrations in unpolluted systems are less than 1 μ g L⁻¹, but can increase greatly in waters affected by contamination.

Concentrations of As are usually slightly lower in freshwater compared to marine systems, with mean values of 0.5 and 3.7 μ g L⁻¹ in these media, respectively (Bowen 1979). Surface waters contain a much higher proportion of As(V) than As(III), although this ratio can change depending upon redox and pH conditions, and the source of contamination (Table 2.10). For example, Mok and Wai (1990) found

higher As(III) than As(V) in surface waters of the Coeur D'Alene River, Idaho US (Table 2.10). They attributed this to preferential adsorption of As(V) by hydroxides in the sediments. Similarly, Braman and Foreback (1973) measured 2.74 μ g L⁻¹ As(III) and 0.41 μ g L⁻¹ As(V) in a lake in Florida, but did not propose an explanation for the differences in the concentrations of the As species found.

In aerobic coastal marine systems, arsenate is the dominant inorganic form of As, although there is some indication that As(III) may be maintained as a relatively higher proportion of the total As in marine compared to freshwaters. As with freshwaters, specific areas may be dominated by As(III). For example, Xiankun *et al.* (1994) found up to 76 % of the inorganic As in Chinese estuaries and coastal seas could be present as As(III). These As(III) values were related to terrestrial contamination sources.

In freshwater systems the distribution and speciation of Sb has not been extensively studied. Total concentrations in 'unpolluted' systems range from a few ng L⁻¹ to a few μ g L⁻¹, with concentrations of orders of magnitude higher in anthropogenically affected systems (Filella *et al.* 2002a). Where the oxidation states have been determined there is also a wide range of dissolved Sb(III) and Sb(V) concentrations. Antimony (III) concentrations increase in ground and anoxic water systems but generally Sb(V) is still also present (Table 2.10).

In marine systems, Sb(III) and Sb(V) coexist in anoxic and oxic conditions, indicating a lack of thermodynamic equilibrium. Some form of kinetic stabilization is required to retard the redox reactions, and various mechanisms have been suggested (section 2.4.2 - *Kinetic aspects of speciation*). Where Sb(III) has been analysed for in marine waters, it generally forms a higher proportion of total Sb (even in surface layers) compared to freshwaters, although this is variable. Gohda (1975) found 30 - 240 ng L⁻¹ Sb(III) compared to 180 - 490 ng L⁻¹ Sb(V) in surface marine waters, while Andreae *et al.* (1981) found much lower Sb(III) compared to Sb(V) (Table 2.10). The variability in the published results may reflect the limited amount of data available or environmentally relevant speciation trends, and meaningful inferences cannot be made at this stage. For both As and Sb, the concentration of methylated or organic species in waters usually appear to comprise a small proportion of the total (Filella *et al.* 2002a; Maeda 1994). Methylated stibonic acid (MSA) and dimethylated stibonic acid (DMSA) have been detected at trace levels in some studies. Andreae *et al.* (1981) found that monomethyl species were more abundant than dimethylantimony species in river, estuarine and ocean water samples, with methylated species accounting for < 10% of the total dissolved Sb.

The issues of standard use, calibrations and variable analysis methods for methyl detection have been mentioned in section 2.4.2, and additionally, there is an obvious lack of environmentally relevant Sb - organic complexation studies. For example, although it is known Sb forms complexes with various alcohols, phenols and hydroxy acids (Sun *et al.* 1982), a lack of correlation between Sb and DOM has been found in some oceanic waters (Filella *et al.* 2002b). The organic forms and reactions of Sb, in particular, need much more investigation.

The processes that govern As and Sb retention in soils determine their mobility as measured by their dissolved concentrations in aqueous systems. For example, the high levels of dissolved As in groundwater samples from Bangladesh are hypothesised to have resulted from reduction of adsorptive Fe hydroxide phases at depth, subsequent release of As, and transport to surface water with well operation (Anawar *et al.* 2003; Tareq *et al.* 2003). Similarly, the mobility of both contaminants determines to some extent their availability to plants, and thus entry in to the food web (section 2.7.3).

Reference	Details	Dimethylated	Monomethylated	(V)	(III)	Total	Metalloid
Ellwood and	New Zealand	0.002 - 0.03	0 - 0.003	2 - 1.5 (III + V)	1.	n/a	
Maher (2002)	marine waters< 25						
	m in depth						
Andreae et al.	Estuary in Portugal	s only	Trace level	1.20 - 6.39	0.06 - 0.94	1.26 - 6.65	
(1983)							
Mok and Wai	River in Idaho, US	n/a	n/a	0.031 - 0.276	0.039 - 0.816	0.125 - 0.902	A a
(1990)							AS
Braman and	Lake Echols,	0.32	0.11	0.41	2.74	3.58	
Foreback (1973)	Florida US						
Pfiefer et al.	Groundwater with	n/a	n/a	0 - 88.6	0 - 368	0 - 368	
(2004)	As rich sediments,						
	Switzerland						
Andreae et al.	Gulf of Mexico	0.0032	0.0053	0.164	0.0044	0.177	
(1981)	Estuary in Florida,	ND-0.0015	0.0008-0.013	0.042-0.136	0.003-0.0111	0.046-0.162	
	US						
	Five US rivers	ND	ND-0.0023	0.013-0.311	< 0.0003-0.0032	0.139-0.313	Sb
Sun et al. (1993)	Groundwater	n/a	n/a	0.012	0.008	0.02	
Ulrich (1998)	Water from a		ND^{\ddagger}	28	2	31	
	contaminated site						

Table 2.10. Typical concentrations of As and Sb ($\mu g \ L^{\text{-1}}$) in natural waters.

ND = Not detected.

[‡] Trimethylstiboxide analysed for only.

2.7. ARSENIC AND ANTIMONY IN PLANTS

While several studies on both As and Sb accumulation and possible uptake mechanisms for biota such as algae and bacteria exist, this section will be restricted to the current level of understanding of uptake and accumulation of Sb (and comparatively As) in terrestrial plants, specifically herbaceous crop, pasture and vegetable species. Furthermore, while the availability and plant concentrations of methylated As species have been found to be important in areas with industrial or agricultural applications of these compounds (Lepp 1981), they have been less well studied and are lower in abundance than inorganic forms in most systems (e.g. Table 2.10). The existence of Sb methylation in environmental systems has only recently been confirmed and research such as that investigating methylated As species has not been carried out (section 2.4.2 - *Organic forms of As and Sb*). The following discussion will be limited to plant interactions with inorganic As and Sb.

2.7.1. Plant concentrations and soil concentrations

The concentrations of both As and Sb in plants are usually low. Transfer factors (ratios of trace elements in plants to their concentrations in soil) are low for As, typically around 0.20 (Kabata-Pendias 2000). Kabata-Pendias (2000) also state that the concentration of As in plants growing on uncontaminated soils ranges from 0.009 to 1.5 mg kg⁻¹ (dry weight). Sandberg and Allen (1975) cited in Lepp (1981) gave an average As concentration in Couch (Cynodon dactylon) of 1.23 mg kg⁻¹, while Thoresby and Thornton (1979) cited in Kabata-Pendias (2000) stated that pasture As did not exceed 0.5 mg kg⁻¹ until total soil As was > 250 mg kg⁻¹. However, some crops and pastures may accumulate greater concentrations of As at lower total soil As concentrations than these. For example, soils with $25 - 50 \text{ mg As kg}^{-1}$ accumulated 6 -12 mg As kg⁻¹ in alfalfa and pastures (Bhumbla and Keefer 1994). In highly contaminated soils, concentrations of As may be orders of magnitude greater than these values. While hyperaccumulation is rare, accumulation to extreme concentrations is common in plants growing on grossly contaminated sites. For example, Porter and Peterson (1975) found Agrostis tenuis growing in mine wastes in England accumulated As up to 3470 mg kg⁻¹ in soils with total As concentrations of up to 26500 mg kg⁻¹. In this instance, plant concentrations of As were positively correlated with total soil As.

Plants vary in their response to As. Some highly tolerant species and ecotypes like the example given above may be exceptions, but in agronomic systems growth reduction is usually expected before As accumulation to phytotoxic levels in plants. Some predictions of critical As concentrations that indicate reductions in growth are available. Lepp (1981) lists several of these, including 10 mg kg⁻¹ (dry weight) for spinach, and 0.7 mg kg⁻¹ (dry weight) for the fruit of the tomato plant. Kabata-Pendias (2000) state the residue tolerance for As in plants is 2 mg kg⁻¹ (dry weight). Accumulation of As in herbaceous plants generally follows the trend of:

As in roots > As in shoots and leaves > As in seeds and fruits (Kabata-Pendias 2000; Lepp 1981).

Even compared to investigations targeting the soil and water systems, there is a dearth of information on Sb concentrations within and uptake into terrestrial plants. In regards to the few studies on Sb, there is little evidence for terrestrial biomagnification (Ainsworth *et al.* 1990a; Ainsworth *et al.* 1990b), but some uptake is known to occur. This is in direct contrast to studies on As, which shows hyperaccumulation in selected species, although this difference may be due to the scarcity of data on Sb uptake by different plant species. There is some limited evidence that concentrations of Sb in plant components follows the same trend as that for As (Hammel *et al.* 2000).

Kabata-Pendias (2000) state typical transfer factors of Sb from soil to plant are around 0.01, approximately 20 times lower than As. Hammel *et al.* (2000) investigated Sb uptake from historic mine dump soils (up to 500 mg kg⁻¹ total soil Sb) into 19 vegetable and crop species. They found higher Sb levels in leaves and shoots than fruits or grains, with the highest accumulation (up to 2.2 mg kg⁻¹) in endives, parsley and spinach. These low uptake values were related to the fraction of soil Sb defined as being mobile (see section 2.7.2). Similarly, Baroni *et al.* (2000) also found Sb accumulated in pasture species growing in soils with up to 15100 mg kg⁻¹ total soil Sb was lowest when the extractable fraction of Sb was low (defined with an acetic acid

extract). Research in mining-contaminated areas in China also showed greater enrichment of Sb in leaves and shoots than grain in rice, with root concentrations of Sb being higher again (He and Yang 1999). This study also identified toxic effects on rice at soil Sb levels > 300 mg kg⁻¹, with effects on biomass, root development, and grain production under controlled conditions. Critical concentrations were estimated at 150 and 300 mg kg⁻¹ for Sb(III) and Sb(V) in soil based on a 10 % yield reduction, or 182 and 206 mg kg⁻¹ respectively based on a rice grain Sb content of 1 mg kg⁻¹.

Ainsworth *et al.* (1990a) investigated pasture uptake of Sb near an Sb smelter with up to 1489 mg kg⁻¹ total soil Sb. They found that while pasture concentrations of Sb were elevated (up to 336 mg kg⁻¹ dry weight), most of this was surface deposition, evidenced by poor pasture uptake (up to 2.23 mg kg⁻¹ dry weight) using the same soils under controlled conditions. Generally, the impact of atmospheric deposition onto pastures could be expected to be minor in areas not in close proximity to an active smelter (or mine).

In general, there is a lack of species-specific plant uptake data for Sb, and only limited understanding of the processes that may govern availability. This is reflected in the lack of work attempting to predict Sb availability, compared to P, As (section 2.7.2), and other metals (e.g. Krishnamurti and Naidu 2000) through the application of single and/or sequential extractions to the soils.

2.7.2. Extracts as predictors of availability

Similar to P, there has been some success in relating chemical extracts of soil As to plant growth traits. Woolson *et al.* (1971) found significant correlations between growth reduction and both mixed acid and bicarbonate extractable As in selected soils. Walsh and Keeney (1975) suggested either a NaHCO₃ or a mixed acid extract could be used to predict phytotoxicity effects of As based on the success of these extracts in measuring available P (e.g. Coventry *et al.* 2001). Similarly, there has been some success in using the oxalate based extract (see section 2.5.3 - *Phase associations*) in predicting plant available P. Guo and Yost (1999) found that the oxalate extractable P was generally available in highly weathered acid soils, and was linearly related to actual available P ($R^2 = 0.81$). This finding has not been applied to

predictions of metalloid availability, even though large proportions of the total soil As and Sb are known to be associated with the oxalate extractable phase (section 2.5.3 - *Phase associations*).

There has been almost no work relating Sb soil extracts to measures of availability or toxicity. As mentioned earlier, Hammel *et al.* (2000) found low plant uptake values corresponded to low mobility in soil (determined by an NH₄NO₃ extraction), while in artificially contaminated soils higher mobility correlated well (R = 0.91) with increases in spinach uptake under controlled conditions. Baroni *et al.* (2000) also found acetic acid-extractable soil Sb was significantly correlated with Sb in either the basal leaves or roots of 3 pasture species (R varied from 0.468 to 0.801). While both of these studies attempted to address the differences in mobility depending on the form of Sb in the soil, there has been no work investigating the effects of environmental conditions, such as the pe-pH status of the soil, on the availability of Sb. For example, the conclusions of Hammel *et al.* (2000) regarding the minor role of pH in Sb mobility do not consider pH changes that may be extreme enough to affect Sb bound to oxyhydroxides or organic matter.

2.7.3. The effects of environmental conditions on plant uptake

There have been several attempts to relate factors affecting mobility of As to plant availability. In particular, the interacting effects of redox and pH changes and rhizosphere oxidation processes have been examined in flooded soils. For example, Otte *et al.* (1991) found that while flooding salt marsh soils increased the mobility of As as arsenite, oxidation in the rhizosphere converted this to the less mobile arsenate, and increased the amount of Fe (III) plaques in the root zone. This would result in a higher concentration of As in the root zone, which may in turn result in increased availability if the plant can access this pool of As. While Otte *et al.* (1991) and Doyle and Otte (1997) found increases in Fe (III) plaques and As in the root zone may have increased As availability, others have found that the presence of such a plaque decreased availability (Blute *et al.* 2004). These differences were attributed to species-specific uptake mechanisms. For example, Grossl *et al.* (2004) found that radish still accumulated As in the presence of added Fe oxide, while lettuce did not. They proposed that Fe oxide plaques on lettuce roots provided a preferential sorption surface for As, thus preventing its movement into the plant.

Other environmental factors known to affect As availability include soil texture and competition from other ions for uptake. Jacobs and Keeney (1970) found As in corn was 10 times higher when the crop was grown in a sand rather than a silt loam (with commensurate soil As loadings). Similarly, Woolson et al. (1973) found that growth reduction of corn occurred at a much higher As concentration in a vermiculitic clay than a lighter kaolinitic soil. The effect of competiting ions, such as phosphate, is variable. Pervea (1998) found monoammonium phosphate increased As phytoavailability by releasing it from the soil. Presumably this was via competition for adsorption sites on the solid phase. However, the uptake pathways in many plants are assumed to be analogous for P and As, and Kabata-Pendias (2000) state that As is less toxic to plants that are well supplied with P. There is apparently a complex interaction between soil type, plant species, competing ions, and the availability of As.

More commonly, the effect of environmental conditions on plant uptake has been studied indirectly, via comparisons of uptake of the different As species. The uptake of As(V) has been noted to be more rapid and to greater concentrations than As(III) (Asher and Reay 1979). Work on organoarsenicals has emphasized uptake via leaves and stems following agricultural applications of As compounds (Lepp 1981), but this would be of minimal importance in areas with no history of agricultural application of As and with typical proportions of the methylated species (section 2.4.2 - *Organic forms of As and Sb*, and Table 2.10).

Applied studies into the effects of redox and pH changes on the plant availability of Sb, such as those indicating the importance of rhizosphere oxidation and Fe (III) plaques for As availability, have not been undertaken based in the data reported to date. Furthermore, the relative availability of Sb to plants in different soils, or in the presence of competing ions has not been investigated. He and Yang (1999) did show that the phytotoxic effect of Sb(III) on rice was greater than Sb(V) in a pot trial, and that the content of each species in the rice was correlated with the application rate of Sb. Interactions between the pe-pH system, soil type and binding phases with the

availability of Sb to plants is an area that has been neglected and emphasises the dearth of information on Sb across the various environmental media.

2.8. SUMMARY – THE LACK OF KNOWLEDGE REGARDING ANTIMONY IN ENVIRONMENTAL SYSTEMS

This review has concentrated upon the extent of information available on the fate and behaviour of Sb in environmental systems, with particular emphasis on the soil environment. Comparisons were made with As to emphasise the lack of environmental data for Sb. In most instances the inorganic forms of As and Sb were emphasised, as current research indicates their predominance in environmental media, and because of the paucity of information on methylated Sb. The extent of research on Sb, and critical knowledge gaps, can be summarised as follows.

The relative toxicity of different Sb species in the environment needs confirmation. The thermodynamic stability of Sb(V) and Sb(III) species in different environments requires measurement (particularly for Sb(OH)₃). Thermodynamic data needs to be further incorporated into environmental considerations of Sb mobility and species interchange. An extension of this is that more work is required on the thermodynamic and kinetic effects of complex formation for Sb, with, for example, low molecular weight organics, chlorides and sulfides, under environmentally relevant conditions. These data are a prerequisite for developing a better understanding of Sb behaviour in soil, water and plant systems.

In comparison to As and other trace elements, further work is required for Sb in soils. Particularly:

Calculations of regional and local background concentrations for Sb need to be undertaken, in light of the increasing use of these values in assessments of contamination (Chapter 6). Such measurements need to be made across a range of soils and environments, to produce comparative values for future investigations into Sb in the environment. This is also required of many other metals and metalloids, such as As.

The adsorption behaviour of Sb by pure phases and whole soils needs further investigation. Specifically, the binding characteristics of Sb(III) and Sb(V)

require elucidation, in particular the relative importance of inner and outer sphere complexing by different solid phases. Basic adsorption characteristics of Sb(V) by hydroxides and organic matter have not been examined to date, including the effects of pH on binding (Chapter 8). The effects of ionic strength and competing ions on Sb adsorption have been almost completely overlooked at this stage.

The use of chemical extractions for metalloid fractionation in soils, and in particular Sb, needs evaluation for each soil and phase being investigated. The use of certain extracts needs to be justified based on the soil to be extracted, the chemical mechanism of extraction, and the aims of the research (Chapter 5). The extension of extract use into predicting the availability of Sb to plants needs to be pursued (Chapter 7).

In water, the areas of Sb behaviour requiring further research resemble those stated for the general chemistry of Sb in the environment. Specifically:

Measurements of concentrations of Sb in the various water media should be continued. This will ensure a comprehensive database of comparative values for further environmental research (Chapter 6).

The mechanisms of kinetic stabilisation of Sb(III) in oxic and Sb(V) in anoxic water systems need to be determined.

Related to the above, the types and extent of aqueous complex formation (inorganic and organic) with Sb in marine, fresh and groundwater systems needs further examination. Such complexing may explain kinetic effects, mobility, and availability of Sb in these systems. This may also have consequences for thermodynamically based modelling of Sb speciation (such as that used in Chapter 7).

Regarding plant-Sb interactions, basic research into the links between mobility, availability, and environmental conditions for different plant species is lacking.

Determining the concentrations of Sb in a range of terrestrial plants needs to be ongoing. This will aid in building a knowledge base of 'typical' and 'enriched' values of Sb in environmental media (Chapters 6 and 7). In relation to plant availability, the links between soil binding, dissolved or mobile Sb concentrations, and plant uptake needs to be examined (Chapter 7). The potential use of chemical extracts for soil Sb fractionation as proxy measures of plant-available Sb needs to be examined. In particular, bicarbonate or oxalate based extracts, that have been related to plant available As and/or P, should be investigated (Chapter 7).

In general, the development of methods for quantifying organic and methylated Sb species needs to continue. There is a great deal of variability in the methods applied and the investigation conclusions for methylated Sb, even in the limited available literature. In the remainder of this thesis, possible methylated forms of Sb (and As) will not be discussed, and are assumed to be minimal.

CHAPTER 3 - STUDY SITE DESCRIPTION AND PREVIOUS RESEARCH

3.1. INTRODUCTION

This chapter details the study area of the Macleay coastal floodplain, and also briefly summarises the geochemical work that led to recognition of As and Sb enrichment in the area, and defined the needs for the investigations described in this thesis. The initial findings investigations previous to this work are detailed, as well as recommendations for further work.

In addition, some site specific characteristics that may influence the environmental behaviour of As and Sb are discussed, particularly the acid sulfate soil (ASS) attributes of parts of the floodplain. Additional recommendations for further investigations into the fate and behaviour of As and Sb are made in relation to these processes and possible redox-pH-soil binding interactions that may occur.

3.2. STUDY SITE DESCRIPTION

3.2.1. Location

The Macleay catchment coastal floodplain is located in north-eastern New South Wales, Australia, where it forms the major terrestrial depositional and estuarine environments of the Macleay catchment and contains the second largest river on the NSW north coast, the Macleay River. The floodplain comprises around 5 % of the catchment's 11500 km² (Department of Public Works 1989) (Figure 3.1).

3.2.2. Urban areas

The town of Kempsey is the major urban area in the floodplain (pop. 10235), (lat = $31^{\circ} \ 05' \ 00''$ S, long = $152^{\circ} \ 50' \ 00''$ E (UTM); Easting = 485000 m, Northing = 6561000 m (WGS84)) with several smaller towns occurring along the Macleay River and coast (ABS 2003). These include Smithtown (pop. 584), Gladstone (pop. 389), and Fredrickton (pop. 903). Several coastal towns fringe the floodplain proper, including South West Rocks (pop. 4359), Stuarts Point (pop. 781), and Hat Head (pop. 322) (ABS 2003).



Figure 3.1. Location of the study site. A = NSW, B = Macleay Catchment (Eastings and Northings (m) datum ref. WGS84), C = Macleay floodplain. See Figure 3.3 for floodplain details.

The local government area has a population of 26430. The projected population growth for the region over the 5 year period 2001-2006 shows a growth of a little over 20 %, with an estimated 2006 population of 31800 (ABS 2003).

3.2.3. Climate and flooding

The climate of the floodplain is temperate to sub-tropical, with an average maximum monthly temperature of 29.2° C in January, and a minimum of 5.7° C in July (CBM 2003). The average annual rainfall at Kempsey is 1220 mm, with the highest falls occurring December to April (Atkinson 1999; CBM 2003) (Figure 3.2).



Figure 3.2. Average monthly rainfall (columns) and average daily temperature (line) at Kempsey (CBM 2003).

The floodplain is approximately 20 km wide (east to west) and slightly more than 20 km north to south. The Macleay River is the central feature, with an average hydrological gradient of 0.0001m m⁻¹ eastward of Kempsey (Ashley and Graham 2001). Small tributaries input water to the Macleay seasonally from the surrounding hills, and the Belmore River and Kinchela Creek are major tidally-affected tributaries flowing from the low-lying Belmore and Swan Pool localities in the south of the floodplain. The area experiences frequent flooding, with a 1 in 100 year flood

covering an estimated 56 000 hectares in the Kempsey Shire boundary (Laurie *et al.* 1980), almost 100 % of the defined floodplain area. Smaller floods of 5 and 10 year recurrence intervals cover almost the same area as the larger floods, but to a shallower depth (Department of Public Works 1989; Laurie *et al.* 1980).

3.2.4. Floodplain depositional environments and surroundings

A very brief summary of the local and regional geology influencing the floodplain is given here, taken from Gilligan *et al.* (1992) unless referenced otherwise. A more detailed description of the local and regional geology may be found in Ashley and Graham (2001); Duck (2000); Gilligan *et al.* (1992); and Mundell (2000).

The geological overview is followed by a brief outline of the recent development of the contemporary floodplain. Further detailed investigation into this aspect was undertaken by Duck (2000); Hails (1968); Mundell (2000); and Walker (1970; 1972).

Surrounding geology

The Macleay floodplain and coastal fringe lie in the southern part of the New England Oregon. Both the regional and more localised geology play a role in the composition of the floodplain and estuarine sediments and soils. The regional geology will be briefly mentioned in the context of previous catchment geochemical work relevant to this study.

Paleozoic

The floodplain is bordered to the north-west and south-west by the Nambucca block, a major component of the New England Fold Belt, which faults against the Coffs Harbour Block and the Hastings Block to the north and south respectively. The Nambucca Block is comprised of late Carboniferous to early Permian metasediments. The Nambucca Beds of the Nambucca Block, comprised of diamictite (Parrabel Beds), fringe much of the floodplain to the north and west, including sections of the Yarrahapanni area. The Kempsey beds of the Nambucca block border much of the floodplain to the south and west, while parts of the south-west of the floodplain proper are bordered by the Beechwood Beds of the Hastings Block. Geology in these

areas is comprised predominantly of interbedded lithic sandstone, siltstone, mudstone, and some conglomerate (Atkinson 1999).

These parent materials have produced shallow soils, with Lithosols in upper slope areas, and Red, Yellow and Brown Chromosols and Kandosols in intermediate to lower slope areas. Locally, swales and depressions have developed deeper Kandosols and Ferrosols (Atkinson 1999; Eddie 2000; Isbell 1996).

Mesozoic

Small granitoid bodies (probably of Triassic age) have intruded the Nambucca Block in the floodplain locality. These include the leucocratic and biotite adamellite of the Yarrahapanni area, and the leucocratic adamellite and granophyre of the Smoky Cape area.

These localities have produced soils similar to the Paleozoic strata, with a tendency towards even shallower soils with well-delineated horizons in the mid to lower slope positions (i.e. chromosols) due to the local steep slopes and related drainage (Atkinson 1999; Eddie 2000).

Cenozoic

The majority of the floodplain proper may be defined as Quaternary sediments (< 1.6 million years B.P.), and are an amalgamation of the local Mesozoic and Paleozoic sediments and eroded material from the upper catchment (Ashley and Graham 2001). Quaternary sediments fringing the floodplain also constitute the modern estuarine environment in the east, and barrier dune systems of Pleistocene and Holocene age (Hails 1968).

Recent floodplain development and soils

The modern environments that comprise the study area are the direct result of recent eustatic and sedimentary coastal processes that are typical of the northern coast of NSW (Flood and Frankel 1989; Hails 1968; Thom and Roy 1985). A detailed discussion of the broad principles and processes of coastal sedimentology is unnecessary for this project, but an overview of local coastal and alluvial processes will aid in describing the modern floodplain environment.

The modern floodplain is the result of the end of the last global ice age (18000 yrs B.P.) and the subsequent postglacial marine transgression (PMT). During the last glacial period, sea levels along the eastern coast of Australia were 110 - 130 metres lower than the modern mean sea level (MSL) (Hails 1968). The lower sea level during this period resulted in widespread erosion of the continental shelf, and deep incision by the historical Macleay River into the coastal bedrock. During the PMT, the MSL rose until a still-stand period @6500 yrs B.P., estimated at 1-1.5 m above modern MSL (Hopley and Thom 1983).

An important factor in the development of the Macleay floodplain during and following the PMT was the presence of a relict (Pleistocene age) coastal dune system (Figure 3.3), which gave the receding estuary system a wave-dominated aspect with associated facies (Hails 1968). Presumably, this lessened the deposition of larger particles, reduced storm effects, and rapidly increased the importance of alluvial as opposed to estuarine processes following the still-stand period (Thom and Roy 1985; Thurman 1997). This relict dune system ensured the floodplain would develop from an embayed barrier estuary, and the floodplain system today is essentially the final stage of a barrier estuary's evolution, with a small and receding active estuary system.

These processes have had several impacts on the floodplain morphology. Relict beach sites are evident in the south and west of the floodplain (Atkinson 1999; Eddie 2000), and are indicative of depositional processes predominant during the still-stand. Basal dates of these structures have been given as 6860 ± 190 yrs B.P. (Walker 1970). Alluvial material that was initially deposited in the Gladstone area 3295 ± 95 yrs B.P. is now at a depth of 2.7 m (Walker 1970), implying the central area of the floodplain was estuarine dominated until that time. The current broad scale morphology of the floodplain is a variable layer of this recent alluvial sediment (< 3295 ± 95 yrs B.P.) ranging from 6 m in depth adjacent to the Macleay River to nonexistent in the swamp areas of the Seven Oaks and Belmore areas in the north and south of the floodplain, respectively (Walker 1970; Walker 1972). Alluvial material grades into relict coastal sand and swamp deposits on the landward side of the Pleistocene dune barrier system.

At a broad morphological scale, the coastal floodplain system is dominated by modern swamp (relict estuarine) and alluvial flood-related depositional landscapes (e.g. levees). These areas have been delineated based on previous investigations (Atkinson 1999; Eddie 2000; Hails 1968), aerial photography, and the profile sequences detailed by Walker (Walker 1970; Walker 1972). This study focuses upon the central 35 000 hectares of these floodplain landscapes as depicted in Figure 3.3, and all references to the floodplain from this point forward refer to this area.

Swamp landscapes are seasonally waterlogged and are characterised by a predominance of silty clay to clay soils with high (up to 30%) organic matter in surface layers, commonly overlying potential or actual acid sulfate subsoils (PASS or AASS) (Table 3.1). Alluvial landscapes are characterised by silty clay loams and loams, with infrequent to no waterlogging, and generally low organic matter in surface layers (Table 3.1). The estuary forms a complex interplay between Pleistocene and modern (Holocene) barrier dune systems, mangrove-fringed tidal channels and swampy alluvial islands.

	Modern swamp	Modern alluvium
Soil	Deep, poorly drained humic gleys and acid	Uniform well drained to imperfectly
	peats, solonchaks (Hydrosols and Organosols).	drained loams, chernozems, euchrozems,
		yellow earths, yellow and grey podzolics
		(Dermosols, Ferrosols, Chromosols and
		Kurosols).
Details	High surface layer organic matter (< 20 cm),	More uniform organic matter, Fe and S
	abrupt decrease in organic matter with depth.	distributions with depth. Higher sand/silt
	Variably reduced/oxidised soils in acid sulfate	contents. Little evidence of waterlogging
	generating areas. Evidence of Fe and S	or mottling. No acid sulfate soils.
	mottling. Increase in S with depth.	

Table 3.1.Typical soil types of the depositional environments of the floodplain. Adapted from Hails (1968), Walker (1970) and Atkinson (1999).

3.2.5. Landuses

Aboriginal landuses

The aboriginal language groups of the Dunghutti and Ngaku occupied the Macleay valley prior to European settlement. These Aboriginal groups mainly occupied the riverine and coastal localities, and extensive shell middens around the Yarrahapinni locality to the north of the floodplain indicate a long period of Aboriginal occupation. There are also several other sites of aboriginal cultural significance in the area. The first European settlers entered the region in the 1820s and 1830s as timber harvesters (Eddie 2000).

Contemporary landuses

Around the eastern fringe of the floodplain, particularly South West Rocks, tourism is an important landuse. The estuaries and lower Macleay also supports commercial fishing and oyster farming enterprises as well as recreational boating, fishing and other activities. Areas of the surrounding hills are owned by State Forests and logged commercially.

Horticulture and cropping is practised along the river levees, with small market gardens operating in the Austral Eden and Gladstone areas. The majority of cropping is for fodder, particularly corn. Some commercial tea tree and flower production occurs in the low hills adjacent to the floodplain proper, as well as quarrying to supply predominantly local road base and sand. Dairy farms are located in more productive areas, particularly around Smithtown and Kinchela. The majority of the remainder of the floodplain comprises dry to wet beef cattle grazing land.

3.2.6. Vegetation

The following is a brief summary of the floodplain vegetation associations as given by Atkinson (1999) and Eddie (2000). Across the floodplain proper, the majority of land has been cleared for agricultural pursuits. Swamp sclerophyll forest remnants occur in low-lying floodplain areas of poor drainage. They consist of stands of swamp oak (*Casuarina glauca*) and/or broad leaved paperbark (*Melaleuca quinquenervia*).

Mangrove (*Avicennia marina*) forest and woodland occurs in estuarine areas, with chenopod shrubland occurring on estuarine mudflats. Subtropical and dry rainforest pockets occur in some sheltered, south facing slopes in the hillsides to the north and south west of the floodplain, in areas of more fertile soils. Littoral rainforest occurs in depressions within the coastal headlands and Holocene dune system to the east. The majority of the hills fringing the floodplain are comprised of dry to wet sclerophyll forests, made up of blackbutt (*Eucalyptus pilularis*), grey gum (*E. propinqua*), grey iron bark (*E. paniculata*), white mahogany (*E. carnea*) and other trees typical of these associations.

Kikuyu (*Pennisetum clandestinum*), paspalum (*Paspalum dilatum*), broad leaved paspalum (*Paspalum wettsteinii*), Rhodes grass (*Chloris gayanna*) and phalaris (*Phalaris* sp.) comprise most of the improved pastures in dry grazing areas with couch (*Cynodon dactylon*) and swamp couch (*Paspalum distichum*) dominating the shallow (< 0.3 m) wet grazing lands. Deeper (> 0.3 m water) wetland areas are dominated by various sedges and rushes, such as maritime rush (*Juncus kraussii*), twine rush, chord rush and zig-zag bog rush (*Leptocarpus tenax*, *Restio pallens*, *Schoenus brevifolius*).

3.3. PREVIOUS GEOCHEMICAL WORK

3.3.1. The contaminant source in the upper catchment

Three recent studies have given some indication of enrichment of both As and Sb within the Macleay floodplain (Duck 2000; Graham 2000; Mundell 2000), and have been largely amalgamated in the report of Ashley and Graham (2001). The catchment-wide geochemical characterisation survey undertaken by Graham (2000) also identified the major contamination source as the Hillgrove mineralised area that ultimately produces the metalloid enrichment in the floodplain.

The mineralised area of Hillgrove in the upper Macleay catchment occurs in the Bakers Creek sub-catchment in the upper Macleay catchment. The geology is comprised mainly of granite and metasediment of Paleozoic age, specifically the Permo-Carboniferous Hillgrove Adamellite, Early Permian Bakers Creek Diorite, and the Late Carboniferous Girrakool Beds (Gilligan *et al.* 1992).

Mineral deposits occur in mainly shear and fracture zones, as stibnite - gold - quartz - arsenopyrite mixed assemblages of mesothermal vein deposits in low-grade metamorphic belts. Hillgrove mineralisation comprises both steeply dipping veins and hydrothermal breccia systems, and the immediate host rock contains disseminated As bearing minerals such as arsenopyrite. Vein systems also contain enough carbonates to buffer acid production from arsenopyrite, stibnite and pyrite oxidation, which results in circum-neutral pH values in soils and waters of the local system (Ashley *et al.* 2003). One hundred and ninety four deposits have been noted in the area, and have been chiefly mined for Sb, Au and W. Total production of Sb is noted at over 60000 tonnes (Ashley and Graham 2001).

Mining occurred periodically between 1877 and the 1970s without notable environmental regulations. During this period, waste rock, tailings and unused ore were deposited in the gully beds of the local gorges (Figure 3.4). Subsequent erosion has produced a contaminated slug of sediment moving through the Bakers Creek subcatchment and into the trunk Macleay. Metalloid concentrations in sediments range from 14 - 4640 and 16 - 1490 mg kg⁻¹ of As and Sb respectively within the Bakers Creek subcatchment. As far as the confluence with the trunk Macleay, the values of dissolved As and Sb in Bakers Creek were found to be 41 and 705 μ g L⁻¹ (Ashley and Graham 2001). Using average metalloid concentrations of waste material and estimates of missing material, Ashley and Graham (2001) calculated that several thousand tonnes of As and Sb may have been lost from the area and be active within the catchment-water system.

There are several other minor trace element dispersion patterns in sediments throughout the catchment (Ashley and Graham 2001), but the concentrations of As and Sb in sediments follow a clear pattern from the Bakers Creek source to the Macleay floodplain. Following limited sediment and water sampling, concentrations of both metalloids were found to be enriched above catchment-wide background within the floodplain, with values greater than the recommended environmental health guideline value for Sb in sediments (ANZECC and ARMCANZ 2000b).

Figure 3.4. An example of mine waste disposal within Bakers Creek at Hillgrove, circa 1900. This waste dump has subsequently been partly removed by erosion (taken from Ashley and Graham 2001).

3.3.2. Indications of As and Sb enrichment in the floodplain

Enrichment of As has been known in some areas around the Macleay floodplain for several years. The identification of As (unrelated to the Hillgrove related dispersion) in the groundwater used for residential purposes in the coastal locality of Stuarts Point (Smith *et al.* 2003) did much to increase awareness of the issue in the region. Arsenic concentrations in reticulated water is now routinely analysed for and results are accessible via the local council web site (KSC 2005).

The studies mentioned in section 3.3.1 and detailed in the report of Ashley and Graham (2001) outline the initial determinations of As and Sb enrichment in the floodplain. Twenty sediment cores (up to 3.5 m in depth, sectioned at either 20 or 40 cm) and 15 additional surface sediment samples were taken from the floodplain and analysed for As, Sb and several other elements of interest. These investigators found that the majority of surface sediments contained As and Sb of up to 25.9 and 18.4 mg

 kg^{-1} respectively. There was some indication that surface sediments contained higher As and Sb in the southern areas of the floodplain. Both As and Sb were enriched in the top 20 - 50 cm of sediment cores, with concentrations of up to 2.7 and 16 times background values of As and Sb (taken as 7.5 and 1.0 mg kg⁻¹ respectively (Ashley and Graham 2001)). Cores taken in the northern backswamp areas did not display pronounced surface enrichment like those in southern backswamp areas (section 3.3.3), although there was some indication of anomalous As and Sb in surface samples of levee cores taken on both sides of the Macleay.

One Macleay River water sample taken at Fredrickton contained 3 μ g L⁻¹ As and 4 μ g L⁻¹ Sb, which, for Sb, was greater than the drinking water guideline value of 3 μ g L⁻¹ (NHMRC and ARMCANZ 1996). While water taken from core holes in the floodplain did not show any mobilisation of Sb (all samples < 0.5 μ g L⁻¹) in ASS areas, dissolved As ranged from < 0.5 to 16.5 μ g L⁻¹ (up to 2.4 times the drinking water guideline concentration for As).

Specifically, the highest sediment concentrations of Sb in the floodplain breached the ISQG low and high sediment quality guidelines of 2 and 25 mg kg⁻¹ (ANZECC and ARMCANZ 2000b), while the concentrations of Sb in the Macleay surface water sample and As in the core waters suggested the metalloids may be relatively mobile in the floodplain.

3.3.3. Acid sulfate soils in the floodplain

The estuary infilling of the floodplain during the Holocene laid the foundations for the acid sulfate processes evident in the contemporary floodplain (section 3.2.4 - Recent floodplain development and soils). Walker (1970; 1972) identified the problems that would be associated with draining areas of the floodplain with high sulfide levels in the subsoil, but his advice appears to have gone initially unheeded. The low lying areas of the floodplain that are overlain by little or no recent alluvium can be classified as areas of moderate to high ASS risk (Naylor *et al.* 1998). The Macleay floodplain also contains one of the largest acid sulfate scalds in NSW, near the Seven Oaks drain in the northern backswamp area of the floodplain. Both descriptive and ameliorative studies have focused on this site, with the area now being managed as a

shallow bunded area to retain water and acid and encourage reduction processes (Smith and Yerbury 1996; Willet and Bowman 1990).

The generation of acid from active acid sulfate soils can result in poor water quality, toxic effects to aquatic life and aquaculture, degradation of soil, and mobilisation of soil contaminants. There are numerous reviews on ASS processes, but these will not be reiterated here (Bloomfield and Coulter 1973; Creagh 1993; Dent 1986; Dent and Pons 1995; Willet and Bowman 1990). A short summary of the reduction and oxidation based processes that occur in ASS areas will be given, with specific reference to the Macleay floodplain.

Reduction processes

Potential acid sulfate soils form in areas that were geologically recent (i.e. Holocene) estuarine sediments. The formation of pyrite occurs via the overall reaction (Lin *et al.* 1995):

$$Fe_2O_3 + 4SO_4^2 + 8HC_2O + 1/2O_2 = 2FeS_2 + 8HCO_3 + 4H_2O_3$$

This requires:

Organic matter for bacterially based sulfate reduction A source of sulfate Available Fe Reducing conditions (Dent 1986).

During the sea level fluctuations in the Holocene, organic matter and sulfate accumulated in the estuarine sediments, while Fe was typically sourced from eroded sediment (Dent 1986; Dent and Pons 1995). The gradual burial of these sediments provided the necessary reducing conditions, and pyrite formation was initiated.

There are several intermediate steps in the above process. Sulfate needs to be reduced to H_2S , while Fe-monosulfides such as mackinawite and greigite are metastable precursors to pyrite formation (Bush and Sullivan 1997). The persistence of these phases indicates that pyrite formation is not immediate, and recently the Fe-

monsulfide phase has been recognised as an important pool affecting water quality during redox transformations in ASS areas (Bush *et al.* 2004a; Bush *et al.* 2004b).

In the south of the floodplain cores exhibited an increase (> 10000 mg kg⁻¹) of S at a depth of 120 cm, which typically marked the redox boundary (Duck 2000). Sediments below this depth contained pyrite, and in general, these areas have high acid sulfate potential but are not actively producing acid. These samples exhibited enrichment of Sb in the top 40 cm (up to approximately 5 mg kg⁻¹), with a sharp decline in concentrations below this (to below the catchment background value), and a similar pattern in As concentrations, although decreases with depth were not as pronounced with this metalloid (Duck 2000).

Oxidation processes

Acid generation occurs following oxidation of the pyrite rich subsoils discussed above. This happens when the reduced sediments are exposed to oxygen following drought, or in many cases, artificial drainage for land reclamation. The Macleay floodplain has undergone several series of agricultural drainage improvements as recently as the 1970's (Department of Public Works 1978) that have resulted in sulfide oxidation and the genesis of active acid sulfate soils.

While there are several intermediate steps involved, and oxidation may be biologically or chemically based (Bloomfield and Coulter 1973), Figure 3.5 shows the general reaction products of pyrite oxidation. Important products and associated processes are given in Table 3.2.

Apart from the initial production of sulfuric acid (Table 3.2), there are several effects of oxidation. The oxidation of Fe (II) (Table 3.2) can occur at a distance from the initial pyrite oxidation, resulting in off-site acidification and Fe hydroxide flocculation in waterways (Kabata-Pendias 2000).

The precipitation of jarosite (Table 3.2) is favoured over Fe (III) hydroxide or goethite at pH values less than approximately 4, and is dependent upon adequate concentrations of its constituent elements (and Na in the case of natrojarosite). Even more so than the Fe oxides and hydroxides, its presence is an indicator of active acid sulfate processes (Dent and Pons 1995).

Figure 3.5. pe-pH diagram for the Fe-K-S-O-H system. Assuming Σ K⁺, SO₄²⁻ and Fe³⁺ = 0.01 M. (c) = crystalline. (am) = amorphous. All other species are aqueous. Dashed lines are the environmental redox limits imposed by the dissociation of water into H_{2 (g)} and O_{2 (g)}. Calculated using HYDRA (Puigdomenech 2004) and MEDUSA (Puigdomenech 2002) for windows. Amorphous Fe(OH)₃ was assumed to be the dominant Fe (III) phase. The log K values for Fe(OH)₃ and jarosite as given by Lindsay (1979) were used.

The generation of acidity also increases the dissolution of clay minerals. Kaolinite formation is favoured at acidic pH values, while the dissolution of smectite and illite type clays may release both exchangeable bases and Al^{3+} into solution (Dent and Pons 1995). In acidic conditions Al exists as a hydrated ion in solution, making it very mobile and possibly toxic (Brookins 1988). However, high mobility of Al^{3+} may decrease its content in these acid soils. For example, van Breeman (1976) found that in acid sulfate soils of Thailand, areas with the lowest pH also contained the lowest Al^{3+} , due to leaching.

Reaction name	Reaction	Environmentally relevant
		products
Pyrite oxidation	$FeS_2 + 7/2O_2 + H_2O =$	2 moles of sulfuric acid for
	$Fe^{2^+} + 2H^+ + 2SO_4^{2^-}$	every mole of pyrite oxidised
Ferrous iron oxidation	$Fe^{2+} + 2H^+ + 1/4O_2 =$	Precursor to below
	$Fe^{3+} + 1/2H_2O$	precipitation reactions.
		Consumes 2 moles of acidity
Precipitation of Fe (III) hydroxide	$Fe^{3+} + 3H_2O =$	Generates 3 moles of acidity
	$Fe(OH)_3 + 3H^+$	
Precipitation of goethite	$Fe^{2+} + 1/4O_2 + 3/2H_2O =$	Generates 2 moles of acidity
	$FeOOH + 2H^+$	
Precipitation of jarosite	$FeS_2 + 15/4O_2 + 5/2H_2O + 1/3K^+ =$	Generates 3 moles of acidity
	1/3KFe ₃ (SO ₄) ₂ (OH) ₆ + $4/3$ SO ₄ ²⁻ + 3H ⁺	

Table 3.2. Reactions and reaction products associated with pyrite oxidation (Bloomfield and Coulter 1973; Dent 1986; Lin *et al.* 1995).

Three cores taken in the northern backswamp area of the floodplain Mundell (2000) identified pyrite towards the base of a periodically oxidised (mottled) zone and within the permanently reduced zone below this (> 1.5 m depth). Above this, these cores exhibited extensive Fe hydroxide (ferrihydrite), goethite and jarosite mottling, indicative of ongoing oxidation. This area was classed as having a very high acid sulfate potential (Naylor *et al.* 1998), and is still an active acid sulfate area. pH values are routinely maintained at < 4.0, and this has been the subject of recent management trials focusing on retention of acidity and encouraged reduction following bunding and shallow flooding (Smith and Yerbury 1996). These samples exhibited As and Sb concentrations close to background values (section 3.3.2).

3.3.4. The interaction of ASS and metalloid binding

The formation of poorly ordered oxides, hydroxides, and sulfate containing minerals in acid sulfate affected areas has implications for retention of the oxyanionic forms of As and Sb (Chapter 2, section 2.5.3 Retention mechanisms). Furthermore, the mobility of Al, dissolution of clay minerals, and favouring of kaolinite formation under acidic conditions may influence the role of the different soil phases in metalloid binding. Even more complex are the known speciation changes of As and Sb with redox and pH fluctuations (Chapter 2), and the effects redox changes have on the oxidation and reduction products of acid sulfate soils. For example, what is the effect on As or Sb mobility in a soil that has a pe low enough to reduce $Fe(OH)_3$ to Fe^{2+} , compared to a soil that has a pe low enough to also convert As and Sb(V) to the uncharged (III) form?

Similarly, the potential changes in pH that accompany oxidation of acid sulfate soils will affect the retention of As and Sb. While the adsorption of both metalloids may be high in the pH range of 4 - 6 under oxidised conditions (Chapter 2), acid sulfate soils in the area may become even more acidic than this. At pH values less than 2.2, even the oxidised form of inorganic As is uncharged, while the dissolution of clay minerals and the instability of some hydroxides at such low pH values may further increase mobility. Similar processes may affect Sb binding in very acidic conditions, as the uncharged Sb(OH)₅ may predominate (Chapter 2). Furthermore, even if these areas are not extremely acidic, flooding may initiate reduction at the typical pH values (3 - 6) which may increase the proportion of uncharged As and Sb(III) species, again increasing metalloid mobility.

3.4. CONCLUSIONS AND RECOMMENDATIONS

Several recommendations for further research have been made based on the findings of Duck (2000), Mundell (2000) and Graham (2000) as amalgamated and extended upon in the report of Ashley and Graham (2001). These, and some other recommendations based on the discussion above are given below.

The initial indication of As and Sb concentrations in the surface sediments of the floodplain being highest within the backswamp areas has great implications for the interactions of the metalloids with the ASS processes and soil constituents. Specific research needs that have been addressed in subsequent chapters of this thesis are as follows.

The limited sampling regime in the floodplain required extension. Previous discussion of the concentrations of As and Sb in the different areas of the floodplain have been based on limited (n = 35) surface sediment samples taken in an area of 35000 hectares. The possible trends of high metalloid deposition

in backswamp areas compared to levee areas required elucidation. In particular, previous surface sampling concentrated on sediments. The extent of As and Sb enrichment in agriculturally productive soils of the floodplain needed to be determined (Chapter 6).

Similarly, the depth dispersion of As and Sb has been based on limited sediment sampling, and amalgamation of large depth intervals (i.e. 20 and 40 cm) for analysis. This may have led to dilution of metalloid concentrations, particularly in the shallower depths of the profiles. Further analyses of soil profiles at narrower depth intervals (e.g. 10 cm) were required (Chapter 6).

The availability and concentrations of both of the metalloids to pastures needed to be determined as an initial indication of possible movement of these contaminants into the food chain (Chapters 6 and 7).

The previous surface water sampling was very limited. Extension of surface water sampling into the different water strata of the floodplain (e.g. the trunk Macleay and tributaries, agricultural drains and swamp waters) was required to determine the dissolved concentrations of As and Sb in the floodplain (Chapters 6 and 7), and to provide comparisons to relevant guideline values.

The mobility of As and Sb in relation to acid sulfate processes, including pH changes, redox processes, and soil phase binding (such as amorphous Fe hydroxides required examination to aid in understanding the mobility and availability of these metalloids (Chapters 7 and 8).

CHAPTER 4 - DEVELOPMENT OF ICP-OES MULTIELEMENT ANALYSIS, OPTIMISED FOR ARSENIC AND ANTIMONY

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