CHAPTER 7 - THE EFFECT OF SHALLOW RESUBMERGENCE AND AN ACID SULFATE SUBSOIL ON METALLOID MOBILITY AND PASTURE UPTAKE

7.1. INTRODUCTION

The association of trace elements with soil solid phases is an important consideration when determining the extent of the environmental or human-health impact of inorganic contamination (Chapters 2, 5 and 6). As stated in Chapter 2, As and Sb may be found in soluble or exchangeable forms, bound to crystalline or non-crystalline hydrated soil phases, complexed with organic matter, or in strongly recalcitrant forms (Lintschinger et al. 1998; McLaren et al. 1998). In any system the proportion of the metalloid species present and their interactions with environmental variables (such as pH and redox potential) will govern mobility and phytoavailability (Masscheleyn et al. 1991; Smith et al. 1999).

The oxyanionic forms of As and Sb that are predominant in most soils result in a strong affinity of these metalloids with non-crystalline Al and Fe hydroxide soil phases. This is more evident as soil pH decreases and positive surface charge increases. The importance of the non-crystalline hydroxide phase for binding has been demonstrated in soils with 100 - 500 mg kg^{-1} total soil As and Sb (Lintschinger et al. 1998; McLaren et al. 1998), but the importance of this phase for element binding in soils with lower total metalloid concentrations has not been assessed. Changes in hydrolysis and charge of As and Sb species that accompany pH and redox fluctuations influence this affinity (Elkhatib et al. 1984; Pierce and Moore 1982; Smith et al. 1998; Thanabalasingam and Pickering 1990). Dissolution or precipitation of hydroxide phases in soils with large pH or redox fluctuations has been found to govern the mobility of some trace elements (Kashem and Singh 2004). While the non-crystalline hydroxide phase has been observed to play a major role in As retention in acid sulfate soils (ASS) (Dudas 1987), the effects of redox and pH changes are not clear.

One approach to determining these associations, described in Chapter 5, is to extract soil with a sequence of reagents, each designed to dissolve the element from a

particular operationally defined pool (Gleyzes *et al.* 2002; Kashem and Singh 2004; Pardo *et al.* 2003; Schoenau and Huang 1991; Wenzel *et al.* 2001). Some previous uses of this approach have been discussed in Chapters 2 and 5. Although attempts have been made to determine relationships between the availability of some metals and soil extracts (Gummuluru *et al.* 2002; Krishnamurti and Naidu 2000), any relationships between metalloid soil extract contents and plant availability in moderately contaminated soils have not been determined. While the chemical and practical interpretation of extractions are known to present problems in contrast with more direct measures of speciation, the extraction approach has the advantage of being relatively cheap and widely available to most, if not all, laboratories.

Additionally, measures of As and Sb in soil solution are relatively scarce, especially at environmentally realistic soil concentrations (Smith *et al.* 1999). Values for As can range from < 1 μg L^{-1} in soils with low (< 40 mg kg^{-1}) total As (Doyle and Otte 1997) up to mg L^{-1} levels in soils with several hundred mg kg^{-1} As (Hamon *et al.* 2004). Soluble Sb is typically lower than As, but can reach mg L^{-1} levels in soils with high levels of anthropogenic Sb (Johnson *et al.* 2005). While some investigation into As has taken place (e.g. Hamon *et al.* 2004; Otte *et al.* 1991), there does not appear to have been any attempt to link dissolved concentrations of Sb with either plant uptake or solid phase associations in soil. Such an attempt may greatly improve calculations of acceptable soil metalloid concentrations, as well as improving the understanding of processes governing mobility and availability of metalloids.

In this chapter, a glasshouse trial was undertaken to determine the effects of periodic flooding, a recognised management option for coastal floodplain acid sulfate soils, on the behaviour of As and Sb in soils containing moderate (< 30 mg kg^{-1}) concentrations of these metalloids. The effects on phytoavailability, solid phase associations and soil solution concentrations of the metalloids were investigated, as recommended in Chapter 6. Specific objectives of this experiment were to determine the importance of the 'non-crystalline hydroxide' and other soil phases for As and Sb retention in these soils, and to determine if any of the measured variables (such as redox potential or pH) played a role in governing mobility and phytoavailability of the metalloids.

7.2. MATERIALS AND METHODS

7.2.1. Glasshouse trial

Soil characteristics

Acid sulfate affected surface soils (low and moderate Sb levels) for the trial were sampled from two floodplain environments (Table 7.2). Subsoil high in sulfidic sediment was collected from the floodplain in one locality at a depth of 1 m. This subsoil was classified as 'ripe' (Dent and Pons 1995), having a general oxidised state, extensive mottling and an acid generating history based on previous studies (Naylor *et al.* 1998, Smith and Yerbury 1996).

Bulked soils were air-dried, thoroughly mixed and mechanically broken into aggregates of approximately 4 mm mean diameter. Triplicate sub-samples of each soil were ground to < 2mm and used for total aqua regia digestible element determinations (Al, Fe, As, Sb and S) (Chapter 4), loss on ignition (LOI) (400° C) organic matter, particle size distribution (pipette method (Day 1979)), pH (1:5 soil:water), electrical conductivity (EC) (1:5 soil:water), and X-ray diffraction analysis. As LOI is not an appropriate method for determining organic matter in soils with high amounts of non-crystalline hydroxide phases due to hydroxide decomposition at > 500° C (Schulte and Hopkins 1996), a lower temperature method (400° C) was used to counteract this. Nevertheless, LOI values should be taken as estimates of soil organic content only. Electrical conductivity (μS cm^{-1}) and pH were measured using a TPS-81 combination meter (TPS Pty. Ltd. Brisbane, Australia). X-ray diffraction analysis was performed using an automated Philips diffractometer. The surface soils were extracted using the oxalate-based extraction detailed in Chapter 5 to determine oxalate extractable Al and Fe. Oxalate extract spiked sample recoveries and precisions were commensurate with those given in Chapter 5, and no adjustments were made. Additionally, spike analysis of Mn in the oxalate extract gave recoveries of 97 - 105 %. Aqua regia elemental recoveries for NIST SRM 2711 and duplicate sample precisions were commensurate with those given in Chapter 4.

Experimental design

The glasshouse trial consisted of an incomplete confounded block design with three replications. Orthogonal contrasts between blocks were limited to the 2nd order

interactions, with the 3rd and higher order interactions being deliberately confounded, to allow a reduction in trial size. This complicated analysis of the pasture biomass effect, as it was confounded between flooding and soil type effects, as is illustrated in section 7.3.2.

The trial consisted of the following factors:

- 2 soils of differing characteristics (Table 7.2) with low (L) and moderate (M) levels of Sb (and varying levels of As).
- Presence (+S) or absence (-S) of an acid sulfate generating subsoil.
- 2 wetting regimes. Non-flooded (-W) and flooded (+W).
- 2 dominant floodplain pasture species. Couch (*Cynodon dactylon*) and swamp couch (*Paspalum distichum*).

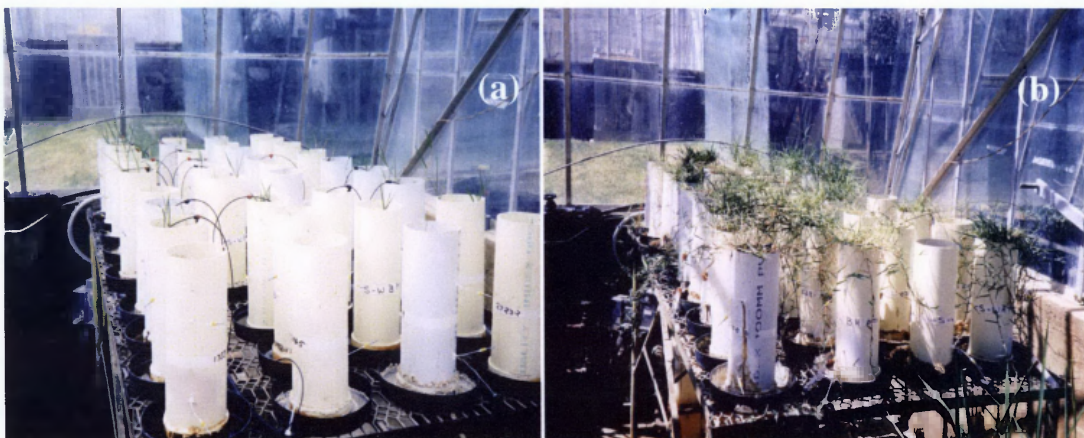The trial at 0 and 20 weeks is depicted in Figure 7.1.

Figure 7.1a, b. The glasshouse trial at 0 (a) and 20 (b) weeks.

Pots consisted of 10 cm diameter polyvinylchloride (PVC) piping 30 cm in length (see Figure 7.1). Subsoil (+S) treatments consisted of 15 cm of sulfidic material overlain by 10 cm of surface soil. -S treatments consisted of the appropriate field soil only; to a depth of 25 cm. Soils were not packed to a specific density as initial investigations showed no discernable compaction upon soil wetting to field capacity or greater. Micro-fibre soil solution samplers were inserted in the surface soil of each pot at a depth of 5 cm, and left for *in-situ* solution sampling following the method of Menzies and Guppy (2000).

Swamp couch (*P. distichum*) was propagated from cuttings, with 3 cuttings allocated per pot. Couch (*C. dactylon*) was surface sown at a rate of 10 plants per pot. All pots were watered to field capacity 3 times weekly.

Flooding was imposed after 4 weeks, and flooded treatments maintained the soil-saturated zone within 2 cm of the soil surface thereafter. Pots in the flooded treatments were sealed at the base to stop leaching losses. The trial was run in a temperature-controlled environment, with watering to maintain water levels in flooded treatments, and moist, oxidising conditions (minimum of approximately 60 % field capacity by weight) in non-flooded treatments.

Monitoring, sampling and analysis

The trial was run over 20 weeks. Soil solution was collected every 4 weeks and soil solution pH, EC, and redox potential (Platinum electrode) were recorded immediately following extraction, using a hand-held TPS WP-81 combination meter. Redox measurements were corrected using Zobell's solution (Nordstrom 1977; Stumm and Morgan 1996) and a measured value of 0.203 V. Electrode potentials were converted to pe for analysis and presentation as per Stumm and Morgan (1996). The difficulties in correctly measuring soil redox potentials are well documented (Bartlett 1999; Bohn 1971), and while measuring soil solution potentials overcomes many of these difficulties (Ponnamperuma 1972), such measurements should be taken as estimates only. This limitation is inherent in any presentation of results, discussions, or chemical modelling that follows. Solution samples were preserved in 10 % (v/v) nitric acid, and analysed for total dissolved As and Sb by ICP-MS at ALS Environmental, Brisbane, Australia. Commercial recoveries for dissolved As and Sb were between 93 and 105 %, with no recovery adjustments being made to sample values.

At trial completion all above-ground plant material was harvested, triple washed in distilled water, dried for 48 hours at 80 °C, weighed and ground to 1 mm. Plant samples were analysed for As and Sb by ICP-MS at ALS, following digestion using US EPA method 200.2. Commercial recoveries for plant As and Sb were between 102 and 113 %, and no recovery adjustments were made to sample values.

At harvest a surface soil sample (< 5 g) was collected from each pot. Samples were dried and ground to < 2 mm using a mortar and pestle. Samples subsequently underwent sequential extraction as detailed in Chapter 5 to determine elemental phase associations. The drying of flooded soils before extraction was justified as the effect of periodic flooding was being investigated (ie. changes to solid phase distributions of metals when the soil was oxidised following a period of wetting), and to make comparisons with field-collected soils viable. Spiked extract sample recoveries and duplicate sample precisions were commensurate with those given in Chapter 5. The summation of the extract concentrations of Al, As, Fe, P and Sb were compared to the aqua regia digestable concentrations for a subset of soils (n = 18), with the results presented in Chapter 5. The summation of extracts were deemed to be acceptably close to 100 % recovery as compared to the single aqua regia digest (Chapter 5). For Al and Fe, total soil values were taken as the aqua regia single digest concentration. The HCl extract values were excluded from the results and discussion, due to all values falling below detection limits.

7.2.2. Field sampling

Field sampling of soil and pastures was undertaken to allow comparisons with soil extract and pasture metalloid concentrations determined under the controlled conditions of the glasshouse trial. Quadrats were placed in the 2 field locations of soils L and M, as shown in Figure 7.2.
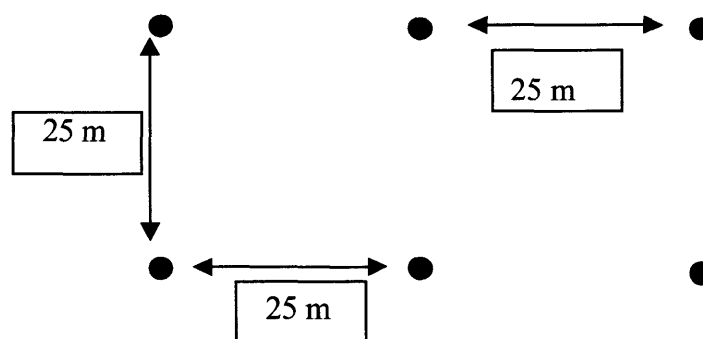

Figure 7.2. Rectangular quadrat sample point layout.

Points were sampled in March 2003 (flooded) and August 2003 and January 2004 (non-flooded). The soil L locality in March and August is depicted in Figure 7.3. Soil samples were taken across two adjacent points giving three composited samples at each locality at each sampling time. Swamp couch (*P. distichum*) formed a grazing monoculture in these localities in both flooded and non-flooded periods (Figure 7.3). Swamp couch was sampled and pooled following the soil sampling method, resulting in three samples at each site on each sampling occasion.
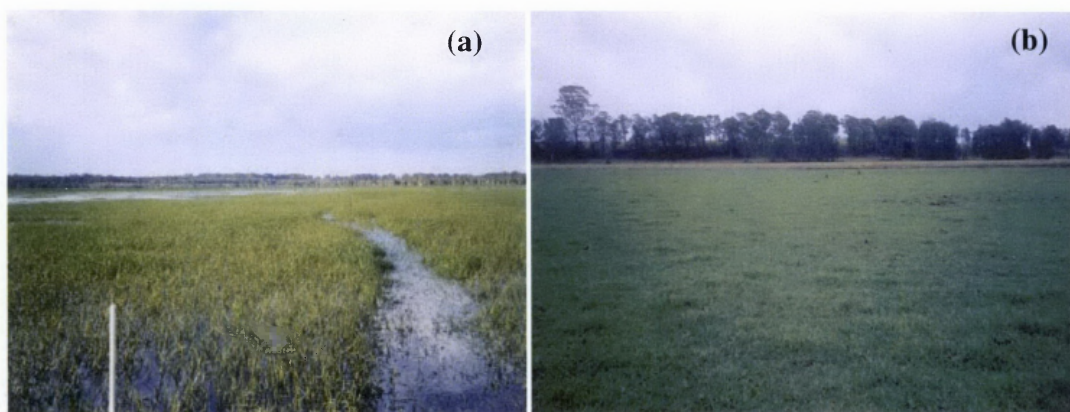

Figure 7.3a, b. Soil L field locality, March (a) and August (b) 2003.

1.1.1. Data and statistical analysis

Elemental data are presented as either concentrations (i.e. mg L^{-1} or mg kg^{-1}) or as the concentration within a phase (e.g. solution, pasture content) relative to the soil total concentration as determined by the sum of the sequential extract fractions:

$$\% = (E_i / \Sigma^5_{i=1} E_i) \times 100$$

Where % = elemental concentration in phase i as a percent of the total soil concentration.

E = elemental concentration in phase i (i.e. mg L^{-1} or mg kg^{-1})

i = phase of interest (e.g. soil extract, pasture concentration).

This was justified as the sum of the extract values gave good agreement with the aqua regia digest values (see section 7.2.1 and Chapter 5).

All statistical analysis was carried out using R version 1.6.2 (Ihaka and Gentleman 1996). Comparisons between soil solution concentrations, extract % values, and pasture concentrations of metalloids at glasshouse trial completion were made between treatments within each soil only. Differences were tested using linear and general linear modelling. General models were of the gamma or quasi gamma form, with variance proportional to the mean.

The relationships between single variables and pasture metalloid uptake were measured using Spearman rank correlations, due to non-normality of data. Correlations were also performed using the derived % values to indicate any relative changes in phytoavailability. Using the single value decomposition method of Belsley *et al.* (1980) and exploratory analysis based on the findings of Otte and Ernst (1994) and Doyle and Otte (1997), Sb (%) in soil was found to be related to the oxalate extractable Fe (%) and the wetting regime. A similar relationship was found with oxalate extractable Al, but was ambiguous. A generalised additive model was used to regress Sb (%) by oxalate extractable Fe (%) within each level of the flooding treatment. Splines were used to model the systematic effect and the random component was represented by a Gamma distribution with a log(link) function. The gam () function in R version 1.6.2 was used to compute the model. The same predictive relationship and modelling process was attempted for As, based on the findings of Otte and Ernst (1994) and for comparison with Sb. The observed data and fitted models are shown in Figures 7.4 and 7.5.

Field data were overlain on the above predictive figures, to compare findings under controlled conditions with those in the field (Figure 7.9). Due to the smaller number of data points, no independent modelling of field-based relationships were attempted.

Time series analysis was performed on the soil solution pe and pH values across the 20 weeks of the trial. Following the statistical and interpretation approach of this chapter, comparisons were limited to those within each soil, and between (+W) and (-W) treatments in the presence or absence of the sulfidic subsoil only. The time series was modelled as a mixed linear model within each soil. The random component included the influence of pot (experimental unit) and the random interaction of pot across time, modelled as a spline function. The systematic effect of time was

modelled as spline functions of the flooding and subsoil treatments. The appropriate interpretation of non-parametric models of time series data is visual (as the data itself is used to model existing trends), via high level plotting functions (Venables and Ripley 1999). The observed and modelled values were plotted using R version 1.6.2, with 95 % confidence intervals of the predicted values also plotted. Visually, areas where confidence intervals do not overlap between treatments can be interpreted as being significantly different, and this approach was used in the interpretation of the time series analysis in Figures 7.6, 7.7 and 7.8.

Speciation and chemical modelling

While there are several methods for determining the proportions of dissolved As and Sb in the 2 inorganic oxidation states (as reviewed by Nash *et al.* 2000), none of these were available during the glasshouse trial and subsequent analyses. Due to the importance of the oxidation state in As and Sb chemistry (see Chapter 2) an attempt was made to estimate the inorganic speciation using measured soil solution pe, pH and total dissolved metalloid levels (Table 7.1). Chemical modelling was performed using MINEQL+ Version 4.5 (Schecher and McAvoy 2003).

When orpiment (As_2S_3) was included in the model, dissolved As concentrations were reduced to below the actual measured concentrations by the solubility product of the solid. Orpiment was subsequently excluded from the model. The ionic strength was estimated (at 0.016 M) from average EC (μS cm^{-1}) using the equation of Griffin and Jurinak (1973). The final model (Table 7.1) was alternately run with goethite, ferrihydrite, pyrite, jarosite and $Fe_2(SO_4)_3$ controlling Fe and S solubility. Resulting variations in total Fe and S ranged from 10^{-18} to 1 M and from 10^{-20} to 10^3 M respectively, but this had no impact on modelled As and Sb speciation. This appeared to be due to the lack of thermodynamic data on soluble complex formation between metalloids and either Fe or S. Thus the speciation of As and Sb were governed only by the AsO_3^{3-}/AsO_4^{3-} and $Sb(OH)_3/Sb(OH)_6^-$ ratios as determined by inputted pe and pH. In particular, Filella *et al.* (2002b) discuss the dearth of data on soluble Sb-S complexes, and how their existence may affect the stability of the oxidation states of Sb in natural systems. This is a limitation of the modelling above. The modelled speciation of As and Sb are given As(III) and (V) states in Tables 7.3 and 7.5, as well

as the total dissolved concentrations measured experimentally and used as modelling inputs.

Table 7.1. Experimental inputs and model specifications for thermodynamic speciation of total dissolved soil solution As and Sb concentrations.

Model components	Measured inputs	Fixed entities	Fixed entities governed by	Solids not considered [†]	Dissolved solids
AsO_3^{3-} AsO_4^{3-}	As soil solution concentration	AsO_3^{3-}/AsO_4^{3-}	e-, H+	orpiment (As_2S_3) arsenolite (As_4O_6) claudetite (As_4O_6)	As_2O_5 $FeAsO_4{:}2H_2O$ realgar (AsS)
$Sb(OH)_3$ $Sb(OH)_6^-$	Sb soil solution concentration	$Sb(OH)_3/Sb(OH)_6^-$	e-, H+	Sb_4O_6 (ortho) Sb_4O_6 (cubic) Sb_2O_4 stibnite (Sb_2S_3) Sb_2O_5 senarmontite (Sb_2O_3) valentinite (Sb_2O_3) Sb metal SbO_2	$Sb(OH)_3$
Fe^{2+} Fe^{3+}	Determined by solid phase solubility	Fe^{2+}/Fe^{3+}	e-, H+	magnetite (Fe_3O) pyrite (FeS_2) sulfur melanterite ($FeSO_4{:}7H_2O$)	hematite (Fe_2O_3) goethite (FeOOH) lepidocrocite (FeOOH) ferrihydrite ($Fe(OH)_3$)
HS^- SO_4^{2-}	Determined by solid phase solubility	HS^-/SO_4^{2-}	e-, H+		$Fe_2(SO_4)_3$ greigite (Fe_3S_4) mackinawite (FeS)
e-	Soil solution pe				
H+	soil solution pH				

[†] All solids not considered were modelled as dissolved solids before removal to ensure there was no effect on final As and Sb speciation.

7.3. RESULTS

7.3.1. Soil properties

The experimental surface soils possess high S, high EC and low pH, reflecting their ASS classification, as well as high proportions of clay and organic matter (Table 7.2).

Table 7.2. Initial properties of experimental soils (n = 3).

	Soil L	Soil M	Sulfidic subsoil
pH $_{1:5\ water}$	3.49	2.78	2.57
EC $_{1:5\ water}$ ($\mu S\ cm^{-1}$)	2890	2677	3297
LOI (400) (%)	33.6	26.2	7.43
% Sand	68.4	63.5	55.3
% Silt	13.2	16.3	24.0
% Clay	18.4	20.2	20.7
Texture (International Classification (McDonald *et al.* 1990))	Loam	Loam	Loam
Australian Soil Classification (Isbell 1996)	Sulfuric, redoxic hydrosol	Sulfuric/sulfidic, redoxic hydrosol	Sulfuric, redoxic hydrosol
Soil mineralogy – Major	quartz, smectite	quartz, albite, montmorillonite	quartz, jarosite, natrojarosite
Minor	nontronite, aluminium sulfate hydroxide	Vermiculite	albite, aluminium sulfate hydroxide
Clay minerals	montmorillonite	muscovite, illite, montmorillonite	natrojarosite, albite, montmorillonite
As (mg kg^{-1})	27.9	26.8	15.0
Sb (mg kg^{-1})	10.7	22.5	3.75
Mn (mg kg^{-1})	112	133	180
Mn $_{ox}$ (%)	62.3	57.9	-
Fe (mg kg^{-1})	95800	93900	86900
Fe $_{ox}$ (%)	37.8	62.2	-
Al (mg kg^{-1})	48700	28200	28100
Al $_{ox}$ (%)	27.2	10.5	-
S (mg kg^{-1})	11300	15600	32700

Both soils have high percentages of their total Mn and Fe as 'oxalate extractable', but while soil M possesses the highest oxalate extractable Fe, it also contains a lower proportion of oxalate extractable Al than the less acidic soil L. As would be expected

of a ripe acid sulfate substrate, the subsoil had extremely low pH, high EC, 3 % S on average and detectable levels of jarosite and natrojarosite.

7.3.2. The effects of flooding, soil type and sulfidic subsoil on soil solution variables, pasture uptake and soil fractionation at trial completion (20 weeks)

The uptake of As or Sb was not significantly different between the pasture species *C. dactylon* and *P. distichum* (F = 1.08, P = 0.31) in each soil, and are presented as the pooled effect of pastures hereafter. This was necessary due to the confounded design of the glasshouse trial. The pasture biomass did not differ between pasture species within soil L treatments (F = 0.43, P = 0.56), but did differ in soil M treatments (F = 10.4, P = 0.02). Pasture biomass is also presented as the pooled effect of species hereafter (due to the confounded design of the experiment), with illustration of the species effect on biomass given in reference to soil M.

Soil L

In soil L there was a decrease in soil solution pe after 20 weeks when the soil was flooded in the absence of the subsoil. There were no other changes in soil solution pe, pH, or oxalate extractable fractions of Al, Mn or Fe (Table 7.3). Soil solution EC was quite variable but did not differ significantly between the flooding treatments. There was a large increase in pasture biomass under the non-flooded conditions in the absence of the sulfidic subsoil.

There were no changes in dissolved As or Sb across flooding treatments in either of the subsoil treatments (Table 7.4). There were changes in residual fractions of As (specifically an increase in residual As with flooding in the presence of the subsoil, but a decrease in residual As with flooding without the subsoil), but no significant changes in more reactive fractions. There were no significant changes in Sb fractionation with flooding in either the presence or absence of the subsoil (Table 7.4).

Table 7.3. Soil solution pe, pH, EC (μS cm^{-1}), oxalate extractable Al, Mn and Fe (%), and pasture biomass (g pot^{-1} dry weight) of soil L treatments at trial completion.

	+S		-S	
	+W	-W	+W	-W
pe	8.97[a]	10.47[a]	7.17[a]	9.81[b]
pH	3.88[a]	4.02[a]	4.33[a]	4.58[a]
EC	1315[a]	629[a]	1609[a]	1060[a]
Al	23.8[a]	24.4[a]	24.8[a]	24.8[a]
Mn	21.9[a]	19.7[a]	25.0[a]	31.7[a]
Fe	30.4[a]	34.3[a]	35.7[a]	30.0[a]
Pasture biomass (g pot^{-1} dry weight)	2.32[a]	2.99[a]	4.40[a]	16.2[b]

Single effect comparisons are limited to ±W in the presence or absence of the sulfidic subsoil. Differences in superscript letters denote a significant pairwise difference (P < 0.05). Other comparisons are stated with significance levels in the text.

Table 7.4. Pasture content (mg kg^{-1}), dissolved levels (mg L^{-1}), modelled inorganic speciation (mg L^{-1}), and extracted fractions (%) of As and Sb under flooded and non-flooded conditions in the presence and absence of the sulfidic subsoil at trial completion (20 weeks) in soil L.

		As				Sb			
		+S		-S		+S		-S	
		+W	-W	+W	-W	+W	-W	+W	-W
Pasture content (mg kg^{-1})		0.33[b]	0.16[a]	0.38[b]	0.10[a]	0.13[b]	0.06[a]	0.15[b]	0.03[a]
Soil solution (mg L^{-1})		0.01[a]	0.01[a]	0.02[a]	0.007[a]	0.001[a]	0.002[a]	0.001[a]	0.001[a]
Soil solution (mg L^{-1}) (III)		0	0	0	0	0	0	0	0
Soil solution (mg L^{-1}) (V)		0.01	0.01	0.02	0.007	0.001	0.002	0.001	0.001
Sequential	NaHCO$_3$	4.38[a]	3.87[a]	3.82[a]	4.18[a]	2.42[a]	2.50[a]	3.21[a]	2.54[a]
extraction	Oxalate	29.7[a]	33.1[a]	35.1[a]	29.1[a]	30.1[a]	32.9[a]	37.6[a]	30.7[a]
proportion	NaOH	18.7[a]	22.5[a]	21.9[a]	17.9[a]	0.00[a]	0.00[a]	0.00[a]	0.00[a]
(%)	Aqua Regia	47.2[b]	40.5[a]	29.1[a]	48.9[b]	67.4[a]	64.6[a]	59.2[a]	77.0[a]

Single effect comparisons are limited to ±W in the presence or absence of the sulfidic subsoil. Differences in superscript letters denote a significant pairwise difference (P < 0.05). Other contrasts made are stated with significance levels in the text.

Despite the lack of differences in fractionation (%), and dissolved metalloid concentrations between treatments, there was a general increase in pasture As and Sb content with flooding (Table 7.4). According to thermodynamic modelling, all of the

soil solution As and Sb would be present in the (V) oxidation state (assuming equilibrium between metalloid species), with the reduction potential in flooded treatments at the acidic soil solution pH of soil L not being great enough to induce As or Sb reduction to the (III) state. The flooded treatment without the sulfidic subsoil (with the significant decrease in pe (Table 7.3)) resulted in an average level of dissolved As (modelled As(V)) greater than the freshwater guideline value of 0.013 mg L^{-1} (ANZECC and ARMCANZ 2000a). There is no Sb(V) freshwater guideline value for comparison with the soil solution Sb concentrations, but all Sb concentrations (modelled As(V)) were below the freshwater quality guideline value for Sb(III) of 0.009 mg L^{-1} (ANZECC and ARMCANZ 2000a). The increases in pasture content of both As and Sb with flooding did not correspond to increased biomass (Table 7.3).

Soil M

Soil M buffered changes in pH with flooding, similar to soil L. There was a small yet significant rise (0.35 units) in pH with flooding in the absence of the sulfidic subsoil (Table 7.5). Contrasting with soil L, there was a general decrease in pe with flooding, with the decrease being more pronounced in the absence of the subsoil (t = 2.33, P = 0.038). This pe decrease also corresponded to a significant decrease in the proportion of oxalate extractable Mn (t = -3.34, P = 0.02). Despite the changes in pe and pH (and Mn $_{ox}$), there were no changes in the proportions of oxalate extractable Fe or Al in soil M treatments at trial completion (Table 7.5). As with soil L, soil solution EC was quite variable and did not differ significantly between treatments. There were no differences between pasture biomass (pooled across species) between flooded and non-flooded treatments in the presence or absence of the subsoil. The large differences in values (Table 7.5) illustrate the pasture species effect on biomass. Biomass was greater for *P. distichum* than for *C. dactylon* (t = 4.05, P = 0.0099). Coupled with the large variation between samples, this explains the lack of significant differences between flooding treatments as depicted in Table 7.5.

The pe decline with flooding (or the pe decline and pH increase with flooding in the absence of the subsoil) did not result in changes in the total concentrations of soil solution As or Sb. However, these changes did induce a small shift in the modelled

equilibrium As and Sb species from the (V) to the (III) state with flooding in the presence of the subsoil.

Table 7.5. Soil solution pe, pH, EC (μS cm^{-1}) and oxalate extractable Al, Mn and Fe (%) of soil M treatments at trial completion.

	+S		-S	
	+W	-W	+W	-W
pe	5.38[a]	9.90[b]	4.94[a]	10.6[b]
pH	4.39[a]	4.23[a]	5.09[b]	4.74[a]
EC	1030[a]	653[a]	1107[a]	661[a]
Al	5.18[a]	7.71[a]	6.30[a]	6.54[a]
Mn	10.9[a]	11.5[a]	5.28[a]	18.6[b]
Fe	67.1[a]	60.0[a]	67.6[a]	64.5[a]
Pasture biomass (g pot^{-1} dry weight)	19.4[a]	7.23[a]	54.8[a]	9.75[a]

Single effect comparisons are limited to ±W in the presence or absence of the sulfidic subsoil. Differences in superscript letters denote a significant pairwise difference (P < 0.05). Other comparisons are stated with significance levels in the text.

Table 7.6. Pasture content (mg kg^{-1}), dissolved levels (mg L^{-1}), modelled inorganic speciation (mg L^{-1}), and extracted fractions (%) of As and Sb under flooded and non-flooded conditions in the presence and absence of the sulfidic subsoil at trial completion (20 weeks) in soil M.

		As				Sb			
		+S		-S		+S		-S	
		+W	-W	+W	-W	+W	-W	+W	-W
Pasture content (mg kg^{-1})		0.32[b]	0.13[a]	0.48[b]	0.10[a]	0.12[a]	0.08[a]	0.13[a]	0.18[a]
Soil solution (mg L^{-1})		0.02[a]	0.008[a]	0.03[a]	0.02[a]	0.006[a]	0.002[a]	0.01[a]	0.002[a]
Soil solution (mg L^{-1}) (III)		0.001	0	0	0	0.0006	0	0	0
Soil solution (mg L^{-1}) (V)		0.019	0.008	0.03	0.02	0.005	0.002	0.01	0.002
Sequential	NaHCO$_3$	6.49[a]	7.68[a]	5.23[a]	7.35[b]	6.65[a]	6.40[a]	6.98[a]	6.32[a]
extraction	Oxalate	64.6[a]	62.6[a]	61.3[a]	60.5[a]	39.5[a]	39.0[a]	45.2[a]	43.2[a]
proportion	NaOH	8.82[a]	8.22[a]	16.0[b]	6.52[a]	11.5[a]	8.23[a]	3.52[a]	0.00[a]
(%)	Aqua Regia	20.1[a]	21.5[a]	17.4[a]	25.7[b]	42.3[a]	46.4[a]	44.3[a]	50.5[a]

Single effect comparisons are limited to ±W in the presence or absence of the sulfidic subsoil within each soil treatment. Differences in superscript letters denote a significant pairwise difference (P < 0.05). Other comparisons made are stated with significance levels in the text.

Modelled As(V) was greater than the freshwater quality guideline (0.013 mg L^{-1} (ANZECC and ARMCANZ 2000a)) in all treatments except the non-flooded, subsoil present treatment (Table 7.6). Plant uptake of As increased under flooding regimes, but in contrast to soil L, Sb pasture content did not change with flooding. As with soil L, there was no discernable relationship between pasture content of As or Sb and pasture biomass, although this may have been confounded by the pasture species effect and the large variation in the biomass measures within each treatment. Flooding in the absence of the subsoil produced a decline in residual As compared to the non-flooded treatment, similar to soil L. There was also a corresponding decrease in the NaHCO$_3$ As fraction, and an increase in NaOH-As. There were no changes to Sb fractionation between treatments (Table 7.6).

In general, As pasture content increased in both soils with flooding, but Sb pasture content only increased with flooding in soil L. Large variations in pe and pH were not observed in the floodplain soils, reflecting their redox and acid buffering capacities. The changes in pH and pe in soil M treatments indicated that it was less buffered. In both soils, increased pasture uptake was not reflected in differences in speciation, total dissolved metalloid levels, or the more reactive soil metalloid fractions, only the general effect of flooding. There was a significant difference in plant biomass (pooled across species) between soils (F = 9.11, P = 0.008). Specifically, there was an increase in biomass in soil M when it was flooded that was not evident in soil L (t = 2.57, P = 0.02).

7.3.3. Single variable relationships with phytoavailability

The associations of single variables with pasture As and Sb contents were measured using Spearman rank correlations, and are tabulated below. No single variable in Table 7.7 gave a strong correlation with pasture metalloid uptake. For As, pe showed the only significant relationship, indicating an increase in pasture uptake (both in absolute values and as a proportion of the total As in the soil) as redox potential decreased. There was a similar relationship with Sb and pe, but only in absolute terms. This indicated the association was due to the differences in total soil Sb (10.7 versus 22.5 mg kg^{-1}, Table 7.2) as reflected in the general pasture content of Sb, and

the higher poise (redox buffering capacity) of soil L than soil M, rather than any relationship with availability.

Table 7.7. Spearman rank correlations of plant uptake (in mg kg^{-1} and % values) with measured variables after 20 weeks (the NaOH extract values were excluded due to majority of values being below detection). Significance values are given in parentheses.

	As		Sb	
	mg kg^{-1}	%	mg kg^{-1}	%
pH	0.13 (0.56)	0.18 (0.43)	0.007 (0.98)	-0.07 (0.76)
pe	-0.47 (0.02)	-0.57 (0.007)	-0.44 (0.04)	0.23 (0.30)
EC	0.30 (0.19)	0.28 (0.22)	-0.005 (0.98)	-0.05 (0.83)
Dissolved metalloid	0.34 (0.13)	0.39 (0.08)	0.07 (0.75)	0.19 (0.41)
NaHCO$_3$	-0.06 (0.78)	0.04 (0.87)	0.27 (0.23)	-0.18 (0.43)
Oxalate	0.10 (0.65)	0.10 (0.67)	0.20 (0.37)	-0.10 (0.68)
Residual	-0.13 (0.55)	-0.14 (0.52)	0.11 (0.64)	0.13 (0.55)

7.3.4. The relationship between flooding, oxalate extractable Fe and phytoavailability

Following the exploratory data analysis and collinearity investigations (section 7.2.3), the combination of the flooding effect and the proportion of oxalate extractable Fe was found to give the strongest relationship of any variable with relative pasture availability of Sb (%) (Figure 7.5). The combinations of pasture As content (%) with flooding or co-occurring elements did not show any linear trends beyond those of the single predictors of pe and dissolved As (Table 7.7). The lack of trend is depicted for comparison in Figure 7.4 for the same variables (flooding treatment and proportion of oxalate extractable Fe) that gave the strongest relationship for Sb.

The general increase in pasture As was evident under flooded treatments regardless of the As or co-occuring element concentrations in any extract, as exemplified using oxalate extractable Fe in Figure 7.4.

Contrasting with Figure 7.4, Figure 7.5 shows a strong relationship between flooding under the controlled conditions, the phytoavailability of Sb to the pastures grown, and

the proportion of Fe present in the soil as oxalate extractable Fe. This was the most pronounced relationship derived using any of the co-occurring elements or Sb in any of the extracts, and reflects the differences in soil characteristics. All lower values of oxalate extractable Fe as plotted in Figure 7.5 were found in soil L and corresponded with higher pasture uptake of Sb (Tables 7.2 – 7.5). Thus, increased Sb uptake in pastures (%) occurred under flooded conditions and was correlated with lower levels of non-crystalline Fe in the soil.
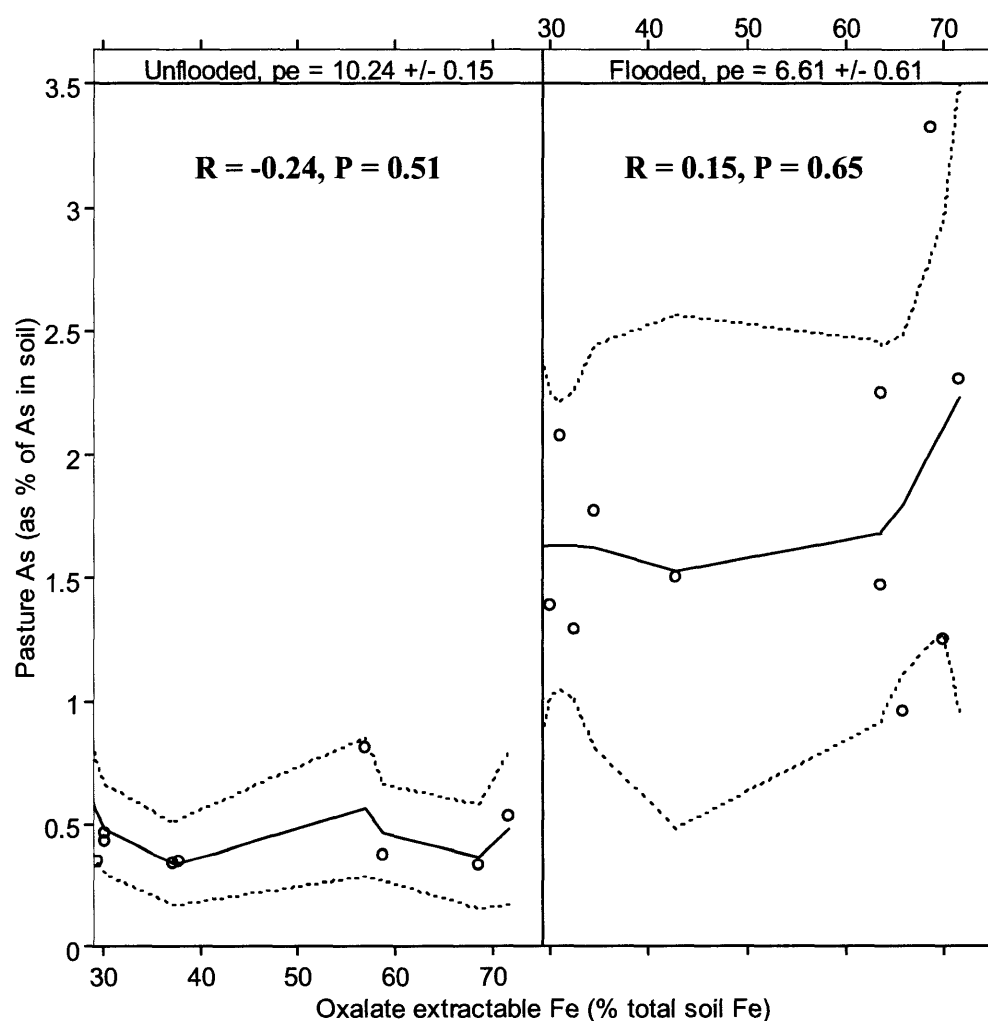

Figure 7.4. Changes in phytoavailability of As (%) as related to flooding and oxalate extractable Fe (%). Plotted lines are predicted values (solid) ± 95 % confidence intervals (broken). R values are Spearman rank correlations of the oxalate extractable Fe with pasture As values within the flooded and unflooded treatments. Significance values are as given. Total deviance explained = 84.4%.
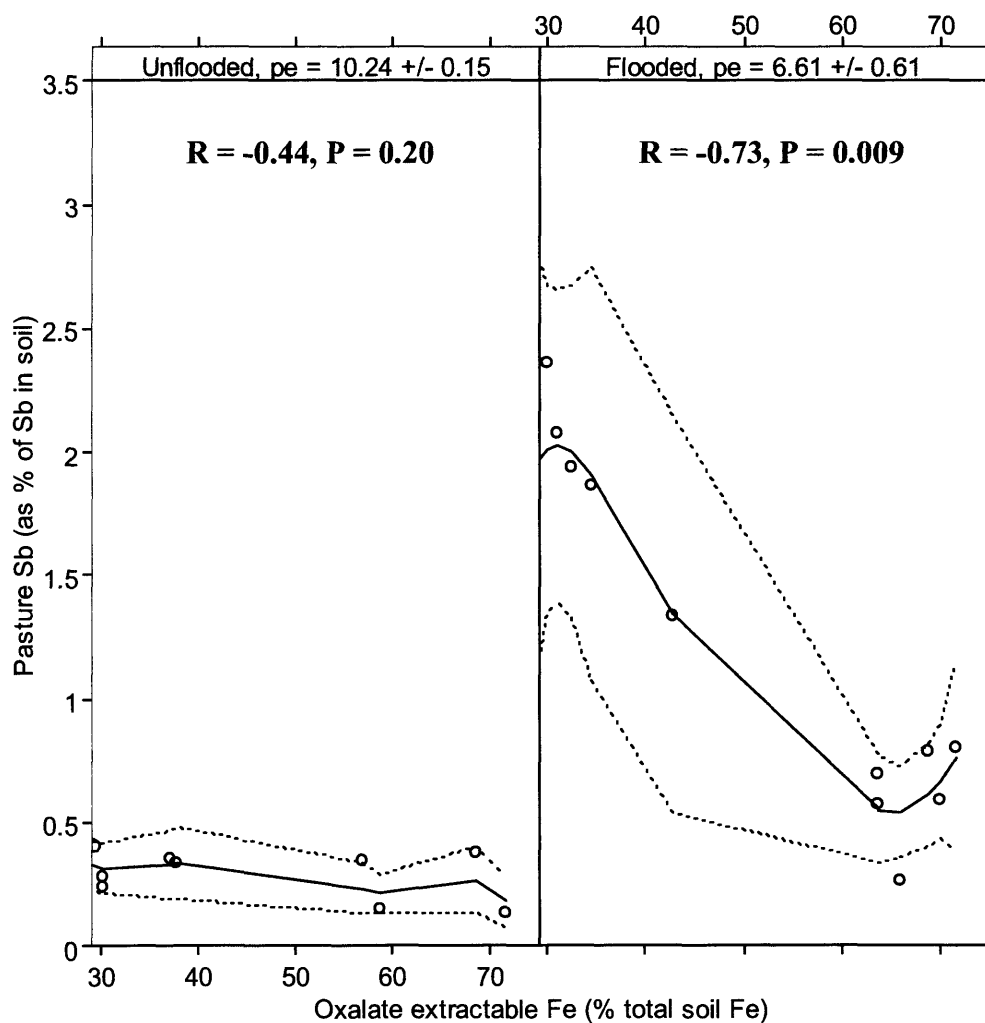
Figure 7.5. Changes in phytoavailability of Sb (%) as related to flooding and oxalate extractable Fe (%). Plotted lines are predicted values (solid) $\pm$ 95 % confidence intervals (broken). R values are Spearman rank correlations of the oxalate extractable Fe with pasture Sb values within the flooded and unflooded treatments. Significance values are as given. Total deviance explained = 91.8 %.

7.3.5. Responses of soil solution variables to flooding over time

Non-parametric modelling as described in section 7.2.3 was used to determine significant changes over time for pH, pe, total dissolved soil solution As and Sb concentrations (Figures 7.6 and 7.7), and EC (Figure 7.8) in soils L and M. Areas where confidence intervals do not overlap between treatment combinations were interpreted as being significantly different (see section 7.2.3).

Soil L

Figure 7.6a reflects the lack of pH change shown at trial completion for soil L (Table 7.3). There were no significant changes in pH across time with flooding, in either of the subsoil treatments (+S or –S), shown by the overlapping confidence intervals between flooded and non-flooded treatments. Figure 7.6b shows that the 20 week difference in pe between the –S-W and –S+W treatments followed a steady decline from 8 weeks after the trial started. A similar trend was evident in the +S+W treatment, but the decline was not significant. There was a short initial period (4 – 8 weeks from the trial start) where there was an increase in pe in the flooded treatments.

Soil solution As and Sb concentrations (mg L^{-1}) were highly variable. There was no significant difference in the concentrations of either element over the 20 weeks of the trial.

Soil M

In contrast to soil L, soil solution pH in soil M showed a significant increase over time (Figure 7.7a) in all treatment combinations except (+S+W) after 16-20 weeks by ~0.5 – 1.5 units. The greatest increase was in the (-S+W) treatment combination, which was reflected in the significant 20-week pH increase in Table 7.5. Similarly, the temporal trends in soil solution pe in soil M reflected the significant decrease in pe with flooding shown in Table 7.5. As indicated by the confidence intervals in Figure 7.7b, this decrease was significant after 14 - 16 weeks. Similar to soil L, soil solution As and Sb concentrations (mg L^{-1}) were highly variable. There was a general increase in dissolved As over 20 weeks in the absence of the subsoil, while there was also a significant increase in dissolved Sb over time (after 16 weeks) in the (-S+W) treatment. This corresponded to an increase in pH and decrease in pe.

Figure 7.6a-d. The effects of flooding in the presence and absence of the sulfidic subsoil across 20 weeks on soil solution pH (a), pe (b), As (mg L^{-1}) (c) and Sb (mg L^{-1}) (d) for soil L. Experimental values are plotted as open circles. Predicted values are given as solid lines, while ± 95 % confidence intervals of prediction are plotted as broken lines.
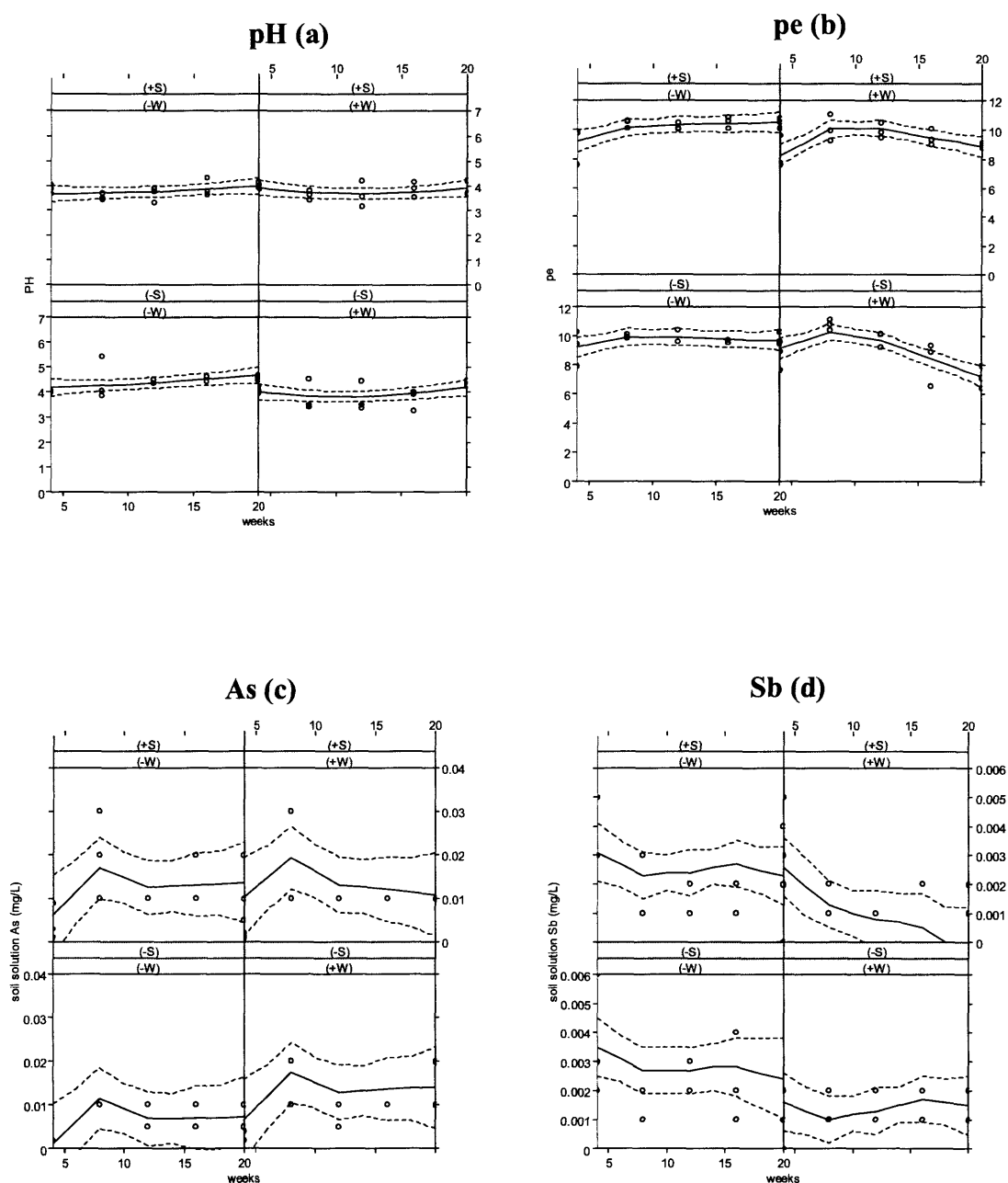
pH (a)

pe (b)

As (c)

Sb (d)
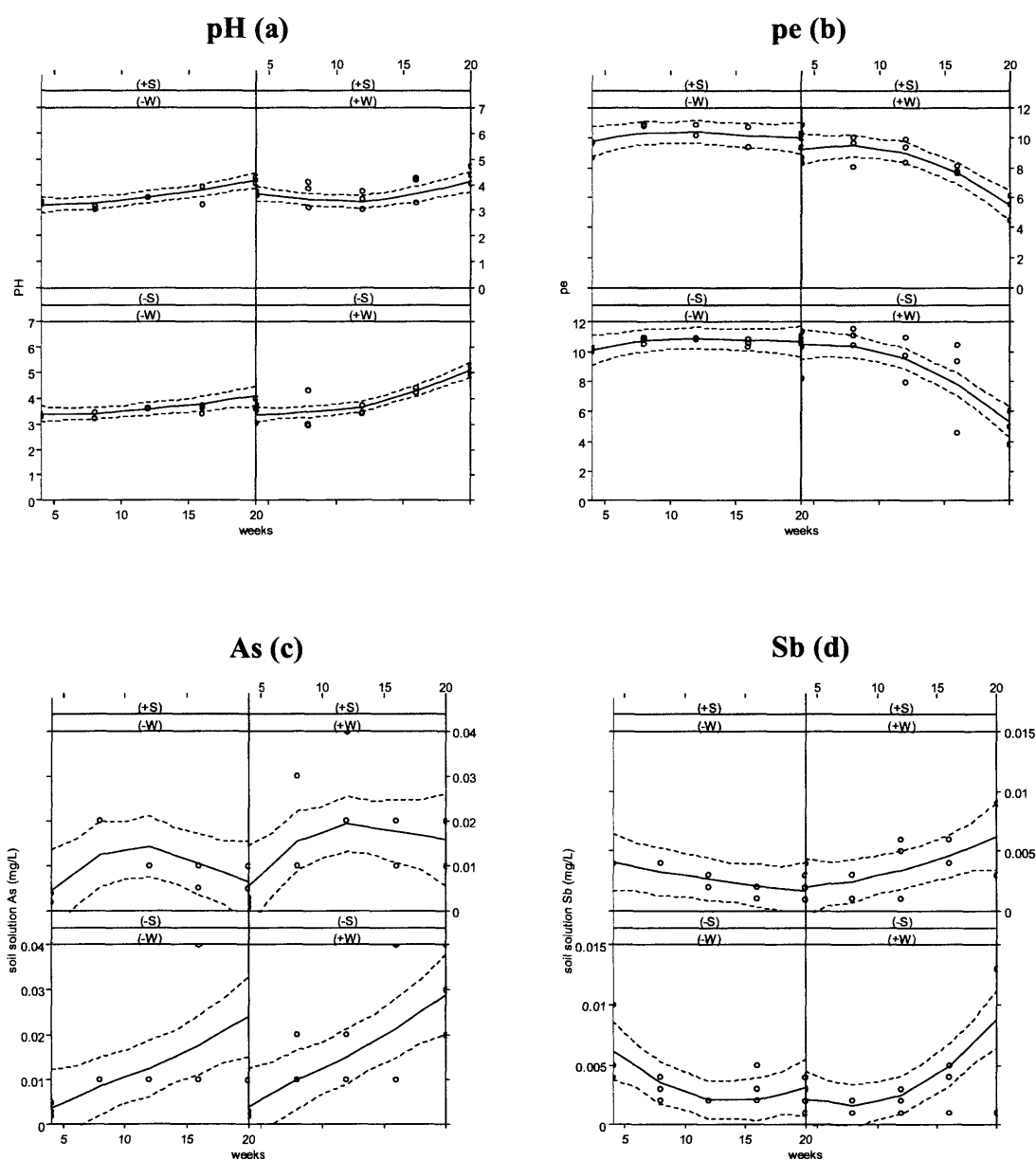
Figure 7.7a-d. The effects of flooding in the presence and absence of the sulfidic subsoil across 20 weeks on soil solution pH (a), pe (b), As (mg L^{-1}) (c) and Sb (mg L^{-1}) (d) for soil M. Experimental values are plotted as open circles. Predicted values are given as solid lines, while ± 95 % confidence intervals of prediction are plotted as broken lines.

Electrical conductivity

In both soils EC decreased significantly over the duration of the trial in non-flooded treatments, to values commensurate with the flooded treatment, which did not change throughout the trial period.

Figure 7.8a-b. The effect of flooding in the presence and absence of the subsoil across the 20 weeks of the trial on soil solution EC (μS cm^{-1}) for soil L (a) and soil M (b). Experimental values are plotted as open circles. Predicted values are given as solid lines, while ± 95 % confidence intervals of prediction are plotted as broken lines.
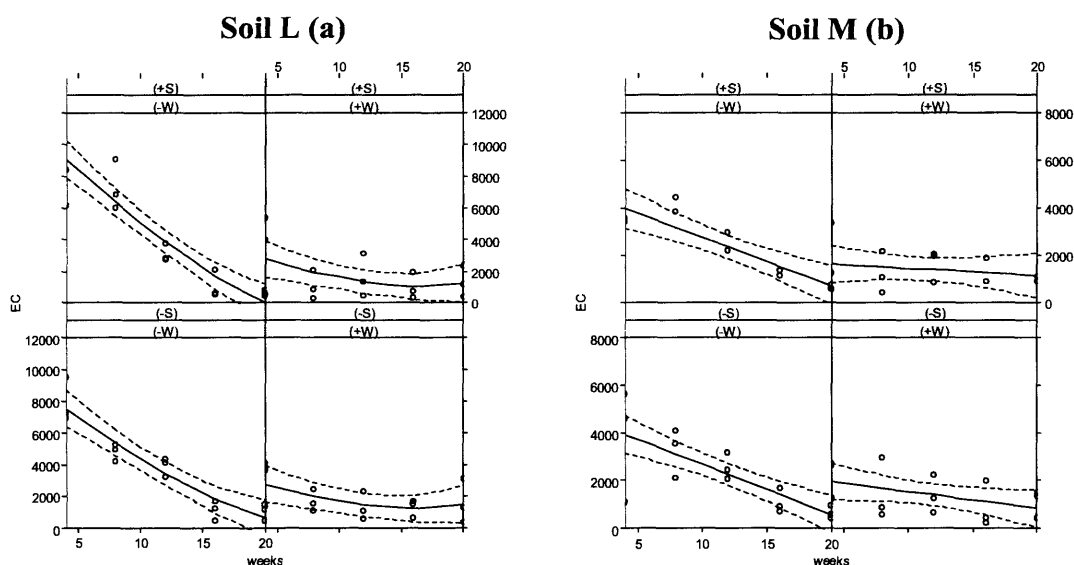
7.3.6. Comparisons with field data

To make comparisons with the findings of the glasshouse trial, field data was collected as detailed in section 7.2.2. The results are detailed in Tables 7.8 and 7.9.

Table 7.8. Pasture content (mg kg^{-1} and %) and total soil concentrations (mg kg^{-1}) of metalloids in field locations of soils L and M averaged across the 3 sampling periods (n = 9).

	As		Sb	
	Soil M	Soil L	Soil M	Soil L
Pasture content (mg kg^{-1})	2.20[a]	2.35[a]	0.67[a]	0.26[a]
Pasture content (%)	10.4[a]	12.6[a]	1.87[a]	1.54[a]
Soil total (mg kg^{-1})	20.8[a]	20.1[a]	22.0[b]	9.70[a]

Single effect comparisons are made between soils for each variable. Differences in superscript letters denote a significant pairwise difference (P < 0.05).

The pasture concentrations of As under field conditions were on average at least 10 times greater than the As pasture values measured under controlled conditions in the

glasshouse trial, regardless of the flooding state of the site during sampling. Conversely, the Sb pasture content was similar (although still higher on average) to the values measured during the glasshouse trial (compare Tables 7.3, 7.5 and 7.7).

Table 7.9. Spearman rank correlations of plant uptake (mg kg^{-1} and %) with metalloid extract values (mg kg^{-1} and %) in field locations of soils L and M averaged across the 3 sampling periods (n = 9). (NaOH extract values were excluded due to the majority of values being below detection.) Significance values in parentheses.

	As		Sb	
Extract	mg kg^{-1}	%	mg kg^{-1}	%
NaHCO$_3$	-0.40 (0.16)	-0.24 (0.42)	0.49 (0.08)	0.25 (0.38)
Oxalate	-0.26 (0.37)	-0.14 (0.64)	0.18 (0.53)	-0.40 (0.16)
Aqua regia	0.28 (0.33)	0.29 (0.32)	0.49 (0.07)	0.23 (0.43)

Similar to the glasshouse trial, single extracts from the field soils were poorly correlated with plant uptake of As and Sb, both in concentration terms and as proportions of the total metalloid present in the soil.

The relationship of pasture metalloid uptake (%) to oxalate extractable Fe was compared to that derived from the glasshouse trial results. The As concentrations in the field pasture samples was much higher than any values found in the glasshouse trial. These are plotted with the relationship derived in Figure 7.4 for flooded treatments (Figure 7.9a), to emphasise the higher As pasture contents (%) in field samples. Similarly, the field Sb pasture contents (%) are plotted with the relationship derived in Figure 7.5 for flooded treatments, to illustrate the similarities in values under the field and glasshouse conditions.

The higher pasture As content under field conditions is evident in Figure 7.9a. The relative phytoavailability of As (using % values) was higher under both flooded and non-flooded field conditions than under the flooded treatments in the glasshouse trial. Conversely, Sb phytoavailability was similar under field and controlled conditions, with 75 % of those field values plotted falling within the predicted range of values derived from the glasshouse trial results.
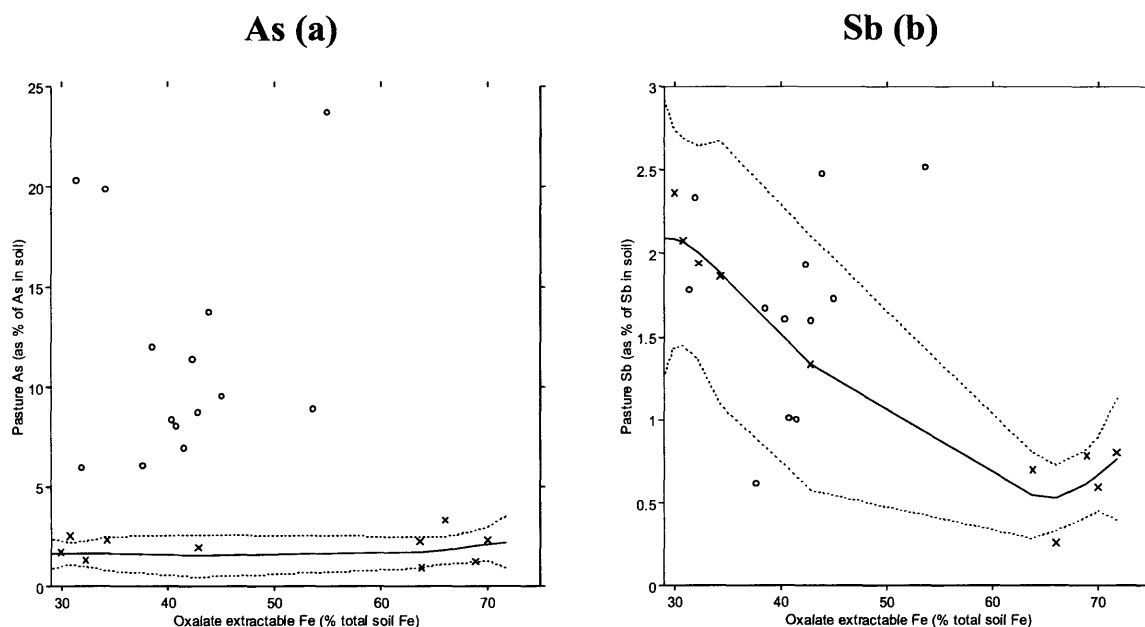
As (a)   Sb (b)

Figure 7.9a, b. Field As (a) and Sb (b) pasture content (%) overlaying flooded treatment relationships taken from Figures 7.4 and 7.5 respectively. o = field samples. × = glasshouse samples from Figures 7.4 and 7.5. Plotted lines are glasshouse trial based predicted values ± 95 % confidence intervals.

These field values corresponded well to the relationship of Sb pasture content to oxalate extractable Fe in the flooded treatment of the glasshouse trial (Figures 7.5 and 7.9b) regardless of the flooding status of the field sites during sampling. Oxalate extractable Fe in soil M in the glasshouse trial was much higher than in field samples (> 60 % compared to < 45 %). The field oxalate extractable Fe values for soil M were more similar to soil L values, and also showed higher relative pasture uptake of Sb, which was characteristic of soil L in the glasshouse trial.

7.4. DISCUSSION

7.4.1. Soil properties

The flood-related depositional nature of soils L and M is shown in their relatively high clay content compared to the floodplain soil closer to the Macleay (Table 7.2), as discussed in Chapter 6. The high levels of organic matter are a result of seasonal flooding and high water tables coupled with pasture and swamp vegetation growth.

Both soils contain concentrations of As and Sb commensurate with the findings of Chapter 6, and are a general amalgamation of the catchment weathering and sediment transport processes. They are also affected by ASS processes, which is reflected in their low pH, high EC, high S concentrations, the presence of aluminium sulfate hydroxide in soil L, and high proportions of oxalate extractable Al and Fe (Table 7.2).

Soil L has an active acid generating history, and possesses a ripe acid sulfate subsoil. Both soils are submerged for some time each year, with soil L being actively managed to retain surface water for extended periods when possible. While both soils contain high proportions of total Mn as oxalate extractable Mn (Table 7.2), the total concentration of Mn in both soils is low (112 and 130 mg kg^{-1}). If the reasonable assumption is made that the oxalate extractable Mn, Fe and Al are measures of the non-crystalline or amorphous forms of their hydroxides (Chao and Zhou 1983; Gleyzes *et al.* 2002; Wenzel *et al.* 2001), the relative amounts of each in the floodplain soils can be related to their management and acidic nature. Firstly, it may be assumed that while changes in the non-crystalline fraction of Mn (as measured by the oxalate extract) may indicate the relative redox state of the soil, the low total amounts of this phase in both soils (69.8 and 77.0 mg kg^{-1}) preclude Mn from governing soil poise. Conversely, both Al and Fe possess large proportions and large total amounts of their concentrations in the oxalate extractable phase, indicating their importance in pH buffering and poise. Omitting the effects of complexing agents, the solubility of amorphous Al(OH)$_3$ is governed by pH. A series of hydrolysis species exist in solution, but at acidic pH, Al^{3+} dominates via the following equation (equilibrium constants taken from Lindsay (1979):

$$Al(OH)_{3\ (am)} + 3H^+ = Al^{3+} + 3H_2O \qquad\qquad \log K = 9.66 \quad (7.1)$$
With:
$$Log\ [Al^{3+}] = 9.66 - 3pH$$

Reductive dissolution of amorphous Fe (III) hydroxide, on the other hand, is governed by both pH and redox potential:
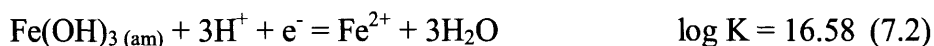
$$Fe(OH)_{3\ (am)} + 3H^+ + e^- = Fe^{2+} + 3H_2O \qquad\qquad \log K = 16.58 \quad (7.2)$$
With:

Log $[Fe^{2+}] = 16.58 - 3pH - pe$

At a given pH, a one-unit decrease in pe will increase the activity of Fe^{2+} by a factor of 10. At low pH, the predominance of other phases such as jarosite or alunite slightly decreases the solubility of Fe and Al, respectively (Lindsay 1979).

Initially, soil M had 10.5 % Al and 62.2 % Fe in the oxalate extractable fraction, with a pH of 2.78 (Table 7.2). The seasonal flooding that this soil undergoes should produce a fluctuation between high dissolved Fe^{2+} concentrations under waterlogged conditions, and reoxidation and precipitation of an amorphous (or non-crystalline) Fe^{3+} phase as the soil drains (equation 7.2). The low pH of this soil will also result in relatively high solubility of Al, which may be lost from the soil by leaching, depleting this phase in an open system, as mentioned in Chapter 3 (hence the lower fraction of oxalate extractable Al in this soil compared to soil L). Although dissolution of aluminosilicates at low pH may partially buffer such leaching, at a pH of 2.8, Al^{3+} activity controlled by montmorillonite (see Table 7.2) is still 370 times lower than Al^{3+} activity governed by $Al(OH)_3$ (assuming Mg^{2+} activity = 1mM and H_4SiO_4 activity is governed by $SiO_{2(soil)}$ (Lindsay 1979)). Therefore, depletion of the amorphous Al phase by leaching is likely, as has been found to occur in ASS areas (van Breeman 1976). Similarly, in soil L, the higher oxalate extractable Al may be attributed to the higher (although still quite acidic) pH of this soil. Furthermore, this soil locality is managed to retain surface water coverage for longer periods than other floodplain areas when possible (Smith and Yerbury 1996), which would result in longer periods of lower redox potential, increasing the solubility of Fe (compare 37.8 % oxalate extractable Fe in soil L with 62.2 % in soil M, Table 7.2).

7.4.2. A note on EC, ionic strength and competitive species

The soil solution EC at trial completion was highly variable in both soils (629-1609 μS cm^{-1}) and did not show significant changes with flooding at the 20-week measurement (Tables 7.2 and 7.4). There was an EC decline in both soils over time under non-flooded conditions (Figure 7.8). This was probably due to a combination of leaching and precipitation of salts in the non-flooded treatments. As indicated earlier, EC can be used to estimate ionic strength (Griffin and Jurinak 1973; Lindsay 1979)

which ranged from 0.008 – 0.02 M at trial completion, but was as high as 0.05 - 0.1 M at the start of the trial in non-flooded treatments. The effect of ionic strength on adsorption of anions has been well documented. For specific adsorption, below the point of zero charge (PZC) an increase in ionic strength will reduce electrostatic potential a small distance from the surface, increasing repulsion and decreasing adsorption (van Olphen 1963). This has been demonstrated for P and As (Bolan et al. 1986; Bowden et al. 1980; Smith et al. 1999). The combined effect of an increase in ionic strength on specific and non-specific adsorption may be minimal, or it may increase or decrease adsorption depending on PZC (Sparks 2003). Regardless of the potential effects of ionic strength, the PZC for the experimental soils was not determined, and any changes in binding capacities (at least at trial completion) may not be justifiably related to estimates of ionic strength and PZC interactions, because measured EC (and hence ionic strength) did not differ significantly between flooding applications at trial completion. The effect of changing ionic strength with time needs to be determined in conjunction with measurements of the soil's PZC and detailed adsorption investigations (e.g. Naidu et al. 1994). Similarly, any competitive effects on metalloid retention of other anionic species such as phosphate and sulfate (Bolan et al. 1986; Wauchope 1975) cannot be determined, as these species were not measured. The high EC in these acid sulfate affected soils suggests a high mobile sulfate concentration. The following interpretation and discussion of results is presented in the context of unknown ionic strength and competitive anionic binding effects.

7.4.3. Total dissolved soil solution As and Sb

Soil solution concentrations of As in both soils in the glasshouse trial were higher than those observed by other researchers in soils with similar total soil As concentrations. Across a pH of 5 - 6 Tyler and Olsson (2001) found that around 3 μg L^{-1} of As was in soil solution with 66 mg kg^{-1} total soil As, while Doyle and Otte (1997) found < 37 ng L^{-1} dissolved As in wetland soils with total soil As < 35 mg kg^{-1}. Soil L contained on average 7 - 10 μg L^{-1} dissolved As (Table 7.4) with only 27.9 mg kg^{-1} total soil As, while soil M contained on average 8 - 30 μg L^{-1} dissolved As (Table 7.6) with only 26.8 mg kg^{-1} total soil As. While this is no doubt a function of soil type and binding characteristics, the mobility of As in the floodplain soils (as determined by soil solution As) is comparatively high.

There are less data available on Sb concentrations in soil solution. Tyler and Olsson (2001) also measured soil solution Sb, and found concentrations at a pH of 5 - 6 of around 1 µg L^{-1}, with a total soil Sb of only 0.40 mg kg^{-1} in a cambisol with 10 % clay and 8 % organic matter. With lower pH, higher clay and higher organic matter, soil L had only 1 - 2 µg L^{-1} soil solution Sb, while soil M contained 2 – 10 µg L^{-1} (Tables 7.4 and 7.6), with 10.7 and 22.5 mg kg^{-1} total soil Sb, respectively. However, Flynn *et al.* (2003) found that the majority of their samples had no detectable soluble Sb in soils with pH < 4.5 and total soil Sb ranging from 11.9 to 336 mg kg^{-1}, although other soil characteristics were not specified. This low mobility was attributed to the unavailability of Sb sourced from mining and smelting activities. Thus, soil solution Sb in the floodplain soils seems to more closely mimic concentrations in areas of naturally occurring, low level soil Sb (which is apparently proportionally more reactive) rather than soluble Sb in areas contaminated by mining and smelting. This supports the earlier hypothesis (Chapter 6) that transport of Sb to the floodplain through the catchment increases the proportion of reactive forms.

7.4.4. Soil solution pe, pH and metalloid speciation at trial completion

Soil L

While the issues with measuring thermodynamically pertinent redox potential in soils are well known, the measurement of soil solution redox values overcomes many of these difficulties (Bartlett 1999; Bohn 1971; Ponnamperuma 1972). Soil solution pe values have been used in this study as an indication of the redox environment of the soils and treatments. Soil L resisted changes to both pH and pe after 20 weeks of flooding, particularly in the presence of the sulfidic subsoil. The following discussion outlines possible reasons and mechanisms for this buffering.

Poise, acid buffering and soil phases

Ponnamperuma (1972) stated that soils low in active Fe and with more than 3 % organic matter attain very low redox potential (e.g. pe = -3.4) within 2 weeks of submergence. This is due to the phenomenon of sequential reduction (see Chapter 2, section 2.4.1 and Table 2.2). While soil L contained a high proportion of organic matter (34 %), it also contained a high percentage of active or non-crystalline Fe (as

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indicated by the oxalate extractable Fe). Table 2.2 shows that in a waterlogged soil, oxygen and nitrate are initially reduced, followed by Mn and Fe. As already stated, the low total concentration of Mn in soil L probably limits its ability to affect redox potential. Similarly, Ponnamperuma (1972) stated that if the proportion of active Fe is low, the redox potential will decrease rapidly, but as most soils contain more Fe (III) hydrates than any other oxidant, the decrease in redox and increase in pH of acid soils following submergence is largely due to Fe reduction. This has been known to take several months for acid sulfate affected soils (Ponnamperuma 1972). The reduction of phases such as non-crystalline Fe (III) consumes H^+ as well as electrons, but is usually dependent upon a source of oxidisable organic C (as a reductant), and biological activity in both the aerobic and anaerobic stages. In the case of the experimental soils, the high LOI values (Table 7.2) also indicate a large pool of possibly reducible organic matter.

While flooding of the acid soil L may have induced a small amount of Fe reduction, the soil was obviously buffered by the large pool of reducible Fe (H^+ and e^-) (36200 mg kg^{-1} Fe$_{ox}$), and the amorphous or non-crystalline Al – Al^{3+} system (H^+) (13200 mg kg^{-1} Al$_{ox}$). Little change to redox was reflected in the Mn$_{ox}$ (%) values (Table 7.3), which did not differ significantly between treatment combinations. In the absence of the sulfidic subsoil, flooding after 20 weeks had begun to overcome the poise of the soil as indicated by pe, although this was not reflected in the Mn$_{ox}$ or Fe$_{ox}$ values (Table 7.3). The pe of the soil would be expected to decrease before the pH increased, due to the acidic buffering effect of Al (Ponnamperuma 1972). Conversely, the slight decrease in pe when the soil was flooded in the absence of the subsoil suggests the oxidised acid sulfate associated soil minerals and phases in the subsoil increase the poise of the soil. A possible mechanism follows.

Jarosite and the subsoil effect

If the relative proportions of Fe^{3+} and Fe^{2+} in the soil solution are taken as an indicator of the soil's state, the presence of jarosite in the soil can add to the poise of the soil. Jarosite is present in the sulfidic subsoil (Table 7.2), but is more soluble than non-crystalline Fe(OH)$_3$ at pH values greater than approximately 4 (Lindsay 1979). The pH of the soil solution of soil L at trial completion ranged from 3.88 – 4.02 (Table

7.3) when the sulfidic subsoil was present. Dissolution of jarosite from the subsoil would increase soil solution Fe^{3+} in the short term and further buffer the soil via the Fe^{3+}/Fe^{2+} equilibrium in the surface soil.

Soil M

After 20 weeks, soil M showed a significant decrease in pe with flooding (in both subsoil treatments), and a rise in pH under flooded conditions when the subsoil was absent. The pe decrease in the flooded, subsoil absent treatment was reflected in a decrease in Mn_{ox} (%) in this treatment at trial completion. Soil M was taken from an acid sulfate locality lacking the active acid history of soil L, and consequently, this soil had the lower acid buffering capacity.

Poise, acid buffering and soil phases

The lower buffering capacity of soil M was indicated by the difference in the amount of non-crystalline Al between the soils. Soil L contained 13200 mg kg^{-1} Al_{ox}, while the less buffered soil M only contained 2960 $mgkg^{-1}$ Al_{ox}. This phase serves to buffer changes in acidity, but may be less effective in soil M, if it is leached more heavily as previously hypothesised (section 7.4.1). Conversely, soil M contained much more non-crystalline $Fe(OH)_3$, with 58400 mg kg^{-1} Fe_{ox} compared to soil L with 36200 mg kg^{-1} Fe_{ox}. If this phase was governing soil pe, then soil M should have displayed higher poise than soil L, not lower.

A possible explanation may be differences in biological activity and respiration rates between the soils. While there was no difference in plant biomass produced in non-flooded treatments, the biomass produced in flooded soil M treatments was significantly greater than that produced in flooded soil L treatments (section 7.3.2). This may imply higher fertility of soil M, and higher biological activity and respiration rates in the rhizosphere (Kludze and Delaune 1996), increasing the reduction rate over time. Alternatively, the dissolved Al may be present at a higher concentration in soil L (i.e. in quasi-equilibrium with Al_{ox}), and thus have a toxic effect on micro-organism and plant respiration, which could result in the observed pe differences. Any influences of biomass and biological activity on aerobic or anaerobic respiration remains to be tested in these soils, and may be confounded by the

experimental design in this trial. Nevertheless, the decrease in pe with flooding was more pronounced in the absence of the sulfidic subsoil (Table 7.6), again reflecting the effect the ASS material had on poise, as for soil L.

The rise in pH may be attributed to the partially successful reduction of the $Fe(OH)_3$ phase (or similar reductants consuming protons), but is probably due more to the lower content of oxalate extractable Al in this soil (Table 7.1). Assuming the oxalate extractable phase is in quasi-equilibrium with Al^{3+}, any conversion of Al^{3+} to amorphous Al would be relatively less and would result in less acid production in soil M than in soil L.

Metalloid speciation

Soil L

Most changes in pH and pe in soil L treatments were not significant at trial completion, and the combination of pe and pH used for modelling the speciation of As and Sb indicated that no reduction occurred for either metalloid. The assumptions of chemical equilibrium may not always be justified, however, because of kinetic limitations of metalloid conversions considered when discussing the modelled speciation (see Chapter 2). For example, the presence of organic substances (such as low molecular weight organic acids) can stabilise Sb(III) (Sun *et al.* 1982), while Belzile *et al.* (2001) found that Sb(III) can be rapidly oxidised by amorphous Fe hydroxides. These are processes that need elucidation in natural systems, and relate specifically to the characteristics of soils L and M. Such kinetic effects must be assumed to be minimal in the use of the modelled speciation values.

There is a dearth of metalloid speciation data in soil solution, as outlined in Chapter 2, section 2.5.3. There appears to be a higher proportion of As and Sb(V) than (III) in the soil solutions that have been measured, and even under redox influences the thermodynamically unfavourable species appears to persist (Hamon *et al.* 2004; Johnson *et al.* 2005; Wenzel *et al.* 2002). Furthermore, the uncharged (III) species are generally more mobile than the (V) species (Matera and Le Hecho 2001). No apparent metalloid reduction in this glasshouse trial is therefore consistent with the observed lack of change in total dissolved levels of Sb and As. Because of the high degree of pe

and pH buffering in this acid soil, decline in pe was insufficient to indicate conversion of the dissolved metalloids from the less toxic (V) to the more toxic (III) state. When soil L was flooded in the absence of the subsoil, however, the average soil solution As value was greater than the As(V) freshwater guideline value (Table 7.4). This was not observed in the treatments containing the sulfidic subsoil indicating that the addition of the ripe ASS subsoil may have reduced the mobility of As found in this soil, via the effects on pH and poise, and the lack of As reduction.

Soil M

As with soil L, the combination of pH and pe determined the inorganic speciation of the metalloids in the modelling calculations for soil M. The increase in pH and decrease in pe in soil M with flooding saw a small shift in the dissolved Sb and As from the (V) to (III) state, with the Sb shift being slightly greater (Table 7.6). Again, there is little actual speciation data in similar circumstances to compare this with. 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 was the stable form. Mok and Wai (1990) found that on average up to 0.816 μg L^{-1} of dissolved As in an Idaho river occurred as As(III), out of a total dissolved As concentration of 0.902 μg L^{-1} (90 % of the total As concentration as As(III)). Conversely, only 1.2 % of the 4.085 μg L^{-1} Sb occurred as Sb(III) in the same samples. They did not measure redox, but attributed the differences in dissolved speciation to the relative release of the (III) and (V) species from sediments. Other studies, mentioned above, have found the majority of soluble As or Sb in contaminated soils occurring as the (V) species (see earlier comparisons (Johnson *et al.* 2005; Wenzel *et al.* 2002)). Nevertheless, the lower pe in soil M under flooded conditions at trial completion resulted in a larger conversion of Sb(V) to Sb(III) (when pH did not change but pe was lowered (Table 7.5)). The non-flooded treatment with the sulfidic subsoil was the only soil M treatment that gave As(V) soil solution levels lower than the guideline value (Table 7.6). This is the treatment that would most closely resemble active acid sulfate processes in this soil, and as with soil L, implies that the ASS subsoil decreased the relative mobility of As. Although the observed average Sb concentration (modelled as Sb(III)) in the -S+W treatment was

lower than the freshwater guideline value (Table 7.6), generally the levels of Sb as Sb(V) have no freshwater guideline value for comparison.

7.4.5. pe, pH and soil solution metalloid concentration changes with time

pe and pH

The high acid buffering capacity and poise of soils L and M is again evident in Figures 7.6 and 7.7a and b. The decline in the soil solution pe of soil L in the flooded, subsoil absent (-S+W) treatment was significant only after 16 weeks, and only resulted in a pe drop of 2.64 units (Table 7.3). Similarly, the larger decline in the pe of flooded soil M treatments (5.7 and 5.9 units, Table 7.5) only began after approximately 16 weeks. Changes in pH followed a similar, if less pronounced pattern. Ponnamperuma (1972) stated that the Eh of an aerobic soil will reach a minimum after 8-12 weeks of submergence. Both soils used in this study only started to decline in redox potential after 12 weeks of submergence (treatments were only flooded after 4 weeks) and were still decreasing at the 20-week measurement. The potential buffering components of soil L have been discussed in section 7.4.4. It follows from this that the high pe buffering capacity is coupled with the acidic buffering capacity of soil L, again emphasising the role of the large pool of non-crystalline Fe in the system, and the relatively small effect of the high amount of organic matter in these soils for inducing pe changes. The lower poise and acid buffering capacity of soil M as hypothesised from the pe and pH measurements at trial completion (Table 7.6) are supported by the significant decreases in pe and increases in pH in this soil near trial completion (again, after 12 weeks of flooding). A further mechanism that may have altered the pe response to flooding was the concentration of dissolved Al. If the concentration of dissolved Al was lowest in soil M (i.e. if Al^{3+} was in quasi-equilibrium with Al_{ox}) then any toxic effect on biological activity would have been less, and the higher respiration rate could increase reduction in this soil.

Metalloid concentrations

The increase in the soil solution concentration of Sb in the flooded, subsoil absent (-S+W) treatment in soil M after 16 - 18 weeks did correspond to both a decline in pe and increase in pH in this treatment, but this metalloid increase was not significantly different to the non-flooded, subsoil absent (-S-W) treatment, due to high variability

(Table 7.5). While As soil solution concentrations generally increased over time in the treatments containing the subsoil, and in the (-S+W) treatment for Sb, these did not differ significantly to the soil solution metalloid concentrations in the other treatments at trial completion. Nor did they reflect any obvious trends in the pasture metalloid concentrations at trial completion. The lack of any marked differences in soil solution As and Sb may be due to the lack of change in pH and pe in these soils. The lack of pe-responsive speciation change after 20 weeks (Tables 7.4 and 7.6), and the acid pH of both soils imply that soil retention of the negatively charged species of both As and Sb (ie. as $H_2AsO_4^-$ and $Sb(OH)_6^-$) would be high over the duration of the trial.

7.4.6. Soil extract concentrations at trial completion

The proportions of the total soil As and Sb in each extract of the sequential scheme did not change significantly for most fractions regardless of flooding for the duration of the trial. This was irrespective of the presence or absence of the sulfidic subsoil (Tables 7.4 and 7.6).

NaHCO₃

The $NaHCO_3$ extract has been suggested as a measure of labile, or plant available As (Walsh and Keeney 1975; Woolson *et al.* 1971), following the plethora of work on P in this context (Coventry *et al.* 2001). The proportions extracted (< 8 % of soil total) were similar to $NaHCO_3$-As (1.2 – 7.4 % total soil As) extracted in loam soils with pH values of 3.73 – 6.75 and total soil As of 5.2 – 51 mg kg^{-1} (Johnston and Barnard 1979), and also commensurate with radiolabile As proportions measured by an $NH_4H_2PO_4$ based extraction in soils with high total levels of As (725 – 4770 mg kg^{-1}) (Hamon *et al.* 2004). However, the proportions of $NaHCO_3$-Sb (2.4-7.0 % of soil total) were much higher than estimates of the 'mobile' fraction measured by NH_4NO_3 extraction in soils with up to 500 mg kg^{-1} Sb (Hammel *et al.* 2000), but were similar to proportions of Sb extracted with acetic acid (< 8.6 %) in highly contaminated soils (up to 15113 mg kg^{-1} Sb) (Baroni *et al.* 2000). This disparity may be due to the inefficiency of NO_3^- when added as NH_4NO_3 in removing anions loosely bound to the soil (Johnston and Barnard 1979). This is presumably a pH-based difference between NO_3^- and HCO_3^-. The proportions of both metalloids extracted by $NaHCO_3$ in both soils of this study (with their moderate total As and Sb concentrations), are similar to

proportions extracted from highly contaminated soils mentioned above. This indicates that a relatively high proportion of both metalloids are weakly bound in the floodplain soils.

There was a slight decrease in the proportion of $NaHCO_3$-As extracted when soil M was flooded in the absence of the subsoil. This corresponded to an increase in NaOH-As, a decrease in residual-As, and an increase in pasture As. This did not correspond to a pH-pe dependent dissolved species change (as modelled), but may relate to a decrease in weakly binding positively charged sites with the increase in pH (Pierce and Moore 1982). There was no corresponding change in soil solution As concentrations. If pH dependent desorption did occur, it could not be separated from plant uptake or co-occurring specific adsorption to other solid phases.

Ammonium oxalate/oxalic acid

The function of the oxalate extract, as stated previously, is its high reducing (pe = -6.4) and complexing capacity for Fe (Gleyzes *et al.* 2002). A high proportion of total Fe is extracted in the oxalate step at both soil characterisation (Table 7.2) and trial completion (30 - 36 % in soil L; 60 - 68 % in soil M), as well as As and Sb (29 - 65 % As; 30 – 45 % Sb). While the treatments did not induce changes in the proportions of metalloids associated with this fraction, the strong retention of As and Sb by this phase was ubiquitous to, and correlates well with previous findings, such as those of Wenzel *et al.* (2001) and Lintschinger *et al.* (1998) (see Chapter 2, section 2.5.3). Both soil L and M have high proportions of non-crystalline hydroxide phases (as shown by their Fe_{ox} proportions, Tables 7.3 and 7.5). The high surface area of non-crystalline hydroxides such as ferrihydrite (Grafe *et al.* 2002), their positive charge at acidic pH (Matera and Le Hecho 2001; van Olphen 1963), and the known affinity of both As and Sb for these phases explains the high proportions of both metalloids associated with this fraction under both non-flooded and flooded conditions (Tables 7.4 and 7.6).

Kashem and Singh (2004) found that flooding over 24 weeks released Fe from the oxide fraction in mildly acidic metal contaminated soils. They hypothesised that this was due to reductive dissolution, which caused an increase in retention sites as the

surface of the oxide fraction became more poorly ordered. Dissolved Fe concentrations were not measured. They theorised that this increase in poorly ordered surfaces increased the retention of metals in their study. In the current glasshouse trial, an increase in soluble Fe (or metalloids) was not observed via a depletion of the proportion of Fe_{ox} extracted in flooded compared to non-flooded treatments in either soil in the glasshouse trial. However, a relatively high proportion of the Fe_{ox} phase would have to be reduced and mobilised for this to be detected as a significant change of the Fe phase concentrations. Additionally, the drying prior to extraction may have masked any such effect via re-oxidation of any mobilised Fe^{2+}. The justification for this drying has been given earlier (section 7.2.1). Root induced oxidation in the rhizosphere may also have counteracted dissolution of this phase, making any changes due to flooding undetectable (see the discussion below on plant metalloid uptake mechanisms, section 7.4.6).

NaOH

Relatively small proportions of both As and Sb were extracted in both soils with NaOH. As discussed in Chapter 5, following the increase in pH with the hydroxide addition, metalloids that are sorbed to or bound within organics such as humic acids should be released. It is not appropriate to compare the proportions of metalloids extracted with NaOH in this sequence with previous work, as most studies that have used NaOH as an extract have not used a preceding hydroxide specific (i.e. oxalate) step. Therefore, the NaOH extract has been assumed to extract As bound to the surfaces of oxyhydroxides and has been interpreted as such (e.g. McLaren *et al.* 1998). It is feasible to say that the NaOH step extracted As and Sb strongly associated with organics, which may act as a buffering phase during flooding when detrital or strongly bound As is released (see discussion below).

Aqua regia

In both soils, the proportion of residual As decreased with flooding in the absence of the subsoil. This corresponded to a significant decrease in pe in both soils, as well as an increase in pH in soil M (Table 7.5), and corresponds well to pH dependent and reductive dissolution of scorodite ($FeAsO_4.2H_2O$) (Zhu and Merkel 2001), goethite, hematite, jarosite, or alunite (Brookins 1988; Gault *et al.* 2005; Lindsay 1979), which

may contain occluded As (although significant substitution of As(V) in jarosite or natrojarosite is questionable (Dudas 1987)). While the re-oxidation of samples on drying may have reversed dissolution occurring from other phases (as discussed above), changes to the residual phase should be more irreversible. In soil L, the decline in residual As did not correspond to a significant increase in any other fraction except pasture content, but this increase was not large enough to account for the large (19.8 %) change in residual As. It is more likely that the As released from the residual phase was distributed across the oxalate and NaOH phases, producing a non-significant increase in these fractions. Such a change was evident in soil M, where the residual As decrease was accompanied by a significant increase in NaOH-As (Table 7.6). There were no significant changes in residual Sb in either soil.

7.4.7. Pasture metalloid levels and uptake mechanisms

Pasture As levels in the glasshouse trial were much lower than the floodplain pasture metalloid levels measured and reported in Chapter 6. Pitten *et al.* (1999) found the highest median value of As across 9 plant species was 1.0 mg kg^{-1}, with total soil As of 71 - 2915 mg kg^{-1}, while Bhumbla and Keefer (1994) state that for plant levels to reach 1 mg As kg^{-1} (fresh weight) soil levels must exceed 200 - 300 mg As kg^{-1}. Additionally, Kabata-Pendias (2000) stated that As in plants growing in uncontaminated soils range from 0.009 to 1.5 mg kg^{-1} (dry weight), and Thoresby and Thornton (1979) cited in Kabata-Pendias (2000) showed that pasture As did not exceed 0.5 mg kg^{-1} until total soil As was > 250 mg kg^{-1}. Tables 7.4 and 7.6 shows that the pastures in the glasshouse trial accumulated 0.10 - 0.38 mg kg^{-1} As in soil L, and 0.10 - 0.48 mg kg^{-1} As in soil M. While these values fall within the expected range of background concentrations for terrestrial plants (Bowen 1979), the above comparisons to plant uptake in soils with several hundred mg kg^{-1} of total As indicate that the pastures grown in soils L and M displayed slightly elevated As concentrations for soils with total As < 30 mg kg^{-1} (i.e. almost 50 % of what was expected in soils with 6 - 10 times the total soil As).

Antimony pasture concentrations were generally lower than As concentrations, and were similar to the field pasture measurements made in Chapter 6. These data are commensurate with herbage and crop levels in soils that contained up to several

hundred mg kg^{-1} Sb, as described in Chapter 2, although pasture uptake of Sb can be dramatically higher (> 1000 mg kg^{-1}) in contaminated soils if the extractable fraction (in this case determined by an acetic acid extract) is high (Baroni *et al.* 2000). Thus, while the availability of Sb is lower than As, uptake similar to soils that contained much higher total Sb concentrations was exhibited in the floodplain soils in the glasshouse trial.

Uptake mechanisms

Flooding both soils increased the uptake of As (by 2 – 4.8 times). Otte and Ernst (1994) proposed a possible mechanism for this, following on from the observation that As bound to iron oxyhydroxides in the rhizosphere appeared to remain available to plants during flooding in wetland soils. They suggested that reduction outside the root zone would be accompanied by increased dissolved concentrations of Fe (II) and As previously bound to Fe (III) phases. Oxidation of Fe (II) by roots in the rhizosphere would result in an increase in As bound to Fe (III) plaques formed in the rhizosphere, which would be accompanied by a larger diffusion gradient for As towards the root zone (Doyle and Otte 1997). The plant may access the bound As via uptake mechanisms, such as plant induced reduction of Fe (III) to Fe (II) before uptake. This would increase the availability of As in the rhizosphere. However, the availability of As bound in this way in the rhizosphere appears to be variable. Blute *et al.* (2004) found that while Fe (III) plaques did adsorb large amounts of As in the rhizosphere, this As was relatively unavailable to *Typha latifolia*. They attributed this to interspecies differences in uptake mechanisms. Alternatively, Kabata-Pendias (2000) suggested that As may be taken up passively with water flow. The increase in As pasture content in both soils when they were flooded could be due to increased evapo-transpiration. This may occur even without an increase in metalloid soil solution concentrations (such as in this trial), simply due to the total amount of metalloid taken up with increased water flow. These uptake mechanisms may both be operating depending upon the attributes of pasture species.

Flooding also increased the pasture content of Sb in soil L (but not soil M). The Fe$_{ox}$:Sb$_{ox}$ ratio was similar in both soils, so if the proposed As-Fe uptake mechanism also operated for Sb, either the reducible phase in soil L contained a higher proportion

of surface bound or reactive Sb than soil M, or other properties (e.g. the lower poise of soil M affecting the preferential oxidation and accumulation of Sb close to roots) reduced the phytoavailability of Sb under flooded conditions in soil M, even though the total soil Sb was higher. The lack of change in the pasture content of Sb with flooding in soil M argues against the passive uptake of Sb via a mechanism analogous to the water dependent mechanism postulated for As uptake, although both mechanisms may be operating concurrently to some extent.

7.4.8. Relationships of variables to phytoavailability

The $NaHCO_3$ extract has been used for decades to predict available P in agronomic practices (e.g. Williams and Cooke 1962), and was suggested as early as the 1970s as a potential estimator for As phytotoxicity. Woolson *et al.* (1971) found a strong correlation (R = 0.82) between plant weight decrease and $NaHCO_3$ extractable soil As. For P, such relationships have been extended into predicting actual plant element concentrations, as opposed to plant responses such as weight changes (e.g. Schoenau and Huang 1991). There appears to have been little work attempting to relate actual plant As or Sb content with extract levels of these metalloids.

In general, dissolved or extracted metalloid levels, pe or pH were poor single predictors of As or Sb in pastures measured as either concentrations ($mg\ kg^{-1}$) or relative to the total soil metalloid concentrations (%) (Table 7.7). The significant increase in pasture As (both in $mg\ kg^{-1}$ and % values) with decreased pe reflected the general effect of flooding. The lack of a significant correlation does not mean one or more of these variables was not controlling pasture metalloid uptake, but such a relationship may have been masked by a concurrent buffering effect from one or more of the other phases or variables. This is an issue that has been eliminated in agronomic glasshouse trials and trace element studies with isotopic doping and tracing techniques (e.g. Hamon *et al.* 2004). This would be an invaluable aid in predicting phase relations to mobility and availability such as in this study (if a source of isotopic Sb could be found).

Uptake mechanisms and measures of availability

The possible pasture uptake mechanism that is dependent upon flooding and the precipitation of non-crystalline hydroxides in the rhizosphere, as discussed in section 7.4.7, was used in constructing the combined variable phytoavailability relationships for As and Sb. The general increase in pasture As under flooded conditions (Figure 7.4) was consistent with the relationship of pasture As with pe (Table 7.7), but there was no relationship of relative availability of As (as indicated by % values) with Fe_{ox} (%) (or Al_{ox} (%)). This is consistent with a passive uptake mechanism dependent primarily upon the movement of water into the plant. However, both mechanisms may be operating to some extent, and the effect of one may partially mask the effect of the other. Figure 7.6, conversely, shows a strong relationship between the pasture available Sb (as a % of the total soil Sb), flooding, and the proportion of Fe_{ox} in the soil. This relationship was confounded by soil type and needs to be regarded cautiously. As noted in section 7.3.4 all of the samples with lower Fe_{ox} (%) values came from soil L.

7.4.9. Field verification

The higher As pasture concentrations in the field samples were very similar to the values in the pasture investigations reported in Chapter 6. This suggests that the uptake of As into these perennial pastures is time dependent, with much higher accumulation occurring (> 10 % of soil total As, Table 7.8) over the longer periods of growth experienced in the field, as opposed to the shorter glasshouse trial period. This provides further support for the passive uptake mechanism. Field-based soil solution data may have indicated if this increase in availability was related to increased As in the soil solution, but these measurements were not available. The relative plant availability of As was also much higher than in soils contaminated with high levels of As derived from anthropogenic activities (see section 7.4.7).

Field pasture Sb concentrations, conversely, were much lower and more commensurate with both the glasshouse trial uptake and the pasture content of Sb found in Chapter 6. This indicates that the availability of Sb was lower than As (both under controlled and field conditions) and less directly dependent upon time (and perhaps more dependent upon the accumulation of Fe (III) plaques and Sb in the

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rhizosphere). Despite this, Sb availability in the floodplain appears to be high in comparison to accepted background ranges (e.g. Bowen 1979), and some studies on plant uptake in highly contaminated (mining and smelting affected) soils (e.g. Hammel *et al.* 2000; section 7.4.7).

Similar to the glasshouse findings, the metalloid levels in the single extracts were not good indicators of phytoavailability (Table 7.9). Soil solution redox measurements were not available, so it is unclear whether there was a relationship between pasture As uptake and pe in the field situation.

Field evidence of uptake mechanisms

The comparison of field values with the data in Figure 7.4 (using the combined predictor of As availability in the flooded treatments only - Figure 7.9a) did not indicate any trend in availability except that the field As pasture concentrations were generally higher than the glasshouse trial values. This occurred in both the flooded and non-flooded field conditions, implying that if passive uptake occurred during flooding, then the As pasture concentrations may only depend upon a history of flooding, not the time of sampling (at least for a perennial like swamp couch). For Sb, both non-flooded and flooded field samples were commensurate with the combined predictor data for Sb under flooded conditions (Figure 7.9b), indicating that like As, Sb pasture levels in the field were not dependent upon the redox state during sampling, but a history of site-submergence. Compared to the As values, the concentrations of Sb in the field samples were not distinctly elevated above glasshouse values. This reflects the lower availability of the metalloid, and supports the proposed mechanism of availability mediated by the non-crystalline oxyhydroxide fraction, as opposed to passive uptake related to water flow.

7.5. CONCLUSIONS

The glasshouse trial and field validation indicated that the mobility and phytoavailability of As and Sb is relatively higher in the floodplain than would be expected in other soils with comparable total As and Sb concentrations. Also, the data show that soil properties alter the effect of flooding on pH, pe and modelled metalloid speciation. Specifically;

The floodplain soils have both high acid buffering capacity and poise. Both of these are increased by the presence of ripe, sulfidic subsoil, and they limit the effect of flooding for durations of less than 12 weeks.

The dissolved and weakly bound metalloid concentrations are relatively high compared to other soils with low to moderate total As and Sb. While grossly contaminated soils with high 'exchangeable' fractions of these elements may have higher dissolved or soluble metalloid concentrations compared to the floodplain soils, soils contaminated from mining or smelting activities can produce dissolved or soluble As and Sb levels similar to the soils examined here.

Pasture metalloid uptake in these floodplain soils is relatively high compared to soils with commensurate metalloid concentrations. Again, grossly contaminated soils with high 'exchangeable' fractions of metalloids have higher plant metalloid availabilities than observed in this study, but relative uptake in the floodplain soils is commensurate with or higher than plant uptake in soils with high total As or Sb that also have low exchangeable or soluble fractions of these metalloids.

The proportions of the metalloids in each extract were a poor proxy measure of plant metalloid availability. This is due, at least in part, to a lack of generally accepted understanding of the functions of extracts and how they target metalloids.

The solid phase metalloid fractionation in this study is similar to As and Sb fractionation in other studies, and emphasises the importance of the non-crystalline hydroxide soil phase (operationally defined) in the binding of these metalloids. Possible buffering of uptake or metalloid mobility by solid phases was difficult to establish without isotopic spiking and/or tracing.

Flooding increased the pasture uptake of As (and Sb in soil L). The increased concentrations of As in pasture field samples compared to the glasshouse samples imply passive uptake of As with water. The pattern of Sb uptake under controlled and field conditions supports the hypothesis of an uptake mechanism dependent upon the non-crystalline (Fe) hydroxide soil phase and redox conditions (both past and present). Micro-scale changes in redox across

the rhizosphere boundary and concurrent movements of Sb need to be examined to confirm this mechanism.

There is a complex and intimate relationship between pasture uptake, flooding, and the buffering capacities of the soils studied. Ponded pasture management to reduce ASS discharges will not produce large changes in redox potential or pH in soils with high buffering capacities over the short periods practical in the field. Also, the poise may be increased by the presence of a ripe ASS subsoil. While acidic conditions usually increase binding of metalloids, both of the proposed mechanisms of plant uptake detailed in this chapter appear to overcome this limitation, particularly in soils with lower proportions of Fe_{ox}. Assuming that the pH does not decrease too dramatically, an oxidised, active acid sulfate soil appears to reduce the availability of the both of the metalloids to the pastures examined. The increases in the pasture uptake of the metalloids with flooding needs to be assessed in terms of environmental risk and agricultural food chain transfer (Chapter 9).

CHAPTER 8 - ADSORPTION OF ANTIMONY (V) BY FLOODPLAIN SOILS, AMORPHOUS IRON (III) HYDROXIDE AND HUMIC ACID

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