TRACE METAL PARTITIONING IN ACID SULFATE SOILS, MAYES SWAMP, KEMPSEY, NSW

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INTRODUCTION

Draining of lowlands in the Kempsey area since the 1950s (Walker 1963) has exposed sulfidic sediments to the atmosphere and the subsequent oxidation of pyrite has led to low pH leachates periodically acidifying local drains and rivers (NCAI 1989). In association with the acidic conditions, high concentrations of Fe and Al as well as elevated trace metals such as Zn have been recorded within Mayes Swamp (Kehoe 2004). In high concentrations, trace metals have been shown to be a significant hazard for aquatic life, particularly when combined with low pH (Sammut & Lines-Kelly 1996, Corfield 2000).

If the soil buffering capacity is exceeded, the release of acid upon oxidation of sulfidic materials can lower soil water pH to < 3 (Dent 1986). Low pH increases weathering and the mobility of trace metals in solution which also increases the leaching of these elements (Astrom & Bjorklund 1995). As sulfides may act as a sink for trace metals their oxidation can also release these elements directly into soil water, contributing to trace metal loads (Sternbeck *et al.* 2000, Huerta-Diaz & Morse 1992). The formation of Fe oxides during oxidation, however, may act as an additional sink, effectively immobilising trace metals (Skwarnecki *et al.* 2002). Understanding where trace metals reside in Acid Sulfate Soils (ASS) and the chemical processes that can mobilise and immobilise them is essential to predicting the conditions that lead to their release.

Currently little is known about the partitioning of trace metals in ASS and their redistribution upon oxidation. Studies from Finland and Sweden have shown that pyrite in ASS can scavenge As, Cd, Co, Cu, Mn, Mo and Ni efficiently (Sternbeck *et al.* 2000) or contain only minor trace metals (Sohlenius & Oborn 2004), making pyrite a variable sink for these elements. Sohlenius & Oborn (2004) found that trace metal leaching from ASS was greatly enhanced due to low pH, but that pyrite oxidation may also contribute trace metals directly through dissolution. The current investigation aims to determine the partitioning and redistribution of trace metals in ASS at the Mayes Swamp under both oxidised and reduced conditions.

METHODS

Three one-metre cores were sampled through the profile of oxidised and reduced sediments. Two cores were taken from within similar pasture sediments 100 m apart and one core was taken from a scalded site. From each core pH and conductivity (EC) profiles were measured and three samples collected representing the oxidised zone (10-15 cm), transition zone (75-80 cm) and reduced zone (95-100 cm). Samples were dried at 40ºC and homogenised with parallel samples used for total and sequential extractions.

Total extractions using 25 ml of concentrated aqua regia were performed on all samples. Samples of ca. 1g were left for 24 hours to dissolve extractable phases. The supernatant was filtered, diluted and analysed for major (Al, Ca, Fe, K, Mg and Na) and trace metals (Ba, Be, Bi, Ca, Cd, Ce, Cr, Cs, Cu, La, Mn, Mo, Nb, Nd, Pb, Pr, Rb, Sb, Se, Sr, Th, Tl, U, V, Y, Zn and Zr) by ICP-MS and ICP-AES.

Six sequential extractions were conducted on 5 g of each sample. Increasingly stronger reagents were used to extract trace metals from fractions with increasing bond strength. The phases targeted in this study are: (1) water soluble; (2) exchangeable and sorbed; (3) organically bound; (4) bound in amorphous Mn and Fe oxides; (5) crystalline Fe oxides; and, (6) pyrite. The reagents used and tumbling times for each extraction are given in Table 1 and are discussed in detail by Chao (1984), Hall *et al.* (1998), Hall *et al.* (1996), Huerta-Diaz & Morse (1990), Sohlenius & Oborn (in press), Sahuquillo *et al.* (2003) and Xueqiu (1998). The complete separation of element concentrations associated with just one phase cannot be demonstrated in sequential extractions due to the complexity of natural sediments and experimental sensitivity (Chao 1984). However, the dissolution techniques used here have been designed to be selective and are suitably phase specific (Chao 1984). After each extraction samples were centrifuged at 4000 rpm for 30 minutes. Supernatant was filtered, acidified and analysed for trace metals (Ba, Be, Bi, Ca, Cd, Ce, Cr, Cs, La, Mn, Mo, Nb, Nd, Pb, Pr, Rb, Sb, Se, Sr, Th, Tl, U, V, Y and Zr) by ICP-MS. Unfortunately As, Cu and Zn could not be analysed in the sequential extractions for this study.

Table 1 Summary of sequential extractions used for 5g of sample

Extraction	Reagent	Target Trace Metal Binding Phases	Time (h)
# 1	50 ml MilliQ-H2O	Water soluble	6
# 2	50 ml Ammonium Acetate	Exchangeable and sorbed	6
# 3	50 ml Sodium Pyrophosphate	Organic Materials	6
# 4	50 ml Hydroxylamine Hydrochloride	Amorphous Mn and Fe oxides	6
# 5	50 ml Hydrochloric Acid (0.5M)	Crystalline Fe oxides	6
# 6	50 ml Nitric Acid (70%)	Pyrite	24

RESULTS

Soil Characteristics

The reduced lower sulfidic sediments (80-100 cm) of the pasture sites are composed predominantly of saturated blue-grey glauconitic clays with minor Fe mottles and organic constituents. The oxidised upper sediments (5-80 cm) are characterised by prominent yellow jarosite and Fe oxide mottling associated with plant roots. The oxidised and reduced zones are separated in the pasture sites by a ca. 10 cm thick shell layer at ca. 80 cm. Pasture sites have black organic-rich surface sediments (0-5 cm) supporting vegetation and, at times, salt efflorescence. The scalded site is oxidised to 100 cm with the shell layer absent and pronounced jarosite and Fe oxide mottling. The reduced zone contains ca. 0.1% pyrite with oxidised zones containing << 0.1% pyrite (Kehoe 2004).

Surface pH of the three sites ranges from 4.0 to 4.4, increasing below 80 cm in the pasture sites to between pH 6 and 7 and to pH 4.8 in the scalded site (Figure 1). The carbonate-rich shell layer that occurs around 80 cm depth in the pasture samples locally increases pH by 0.5-1.0 pH units. Surface EC varies from 744 to 1,759 μS/cm^{-1} between the three sites, and peaks at around 2,800 μS/cm^{-1} at 80 cm for the pasture sites and at 100 cm in the scald (Figure 1). Pasture sites have a bulged EC profile between 30 and 90 cm and a near-surface increase (240-250 μS/cm^{-1}). The scalded site has a monotonic profile increasing from surface to a peak at 100 cm (Figure 1).
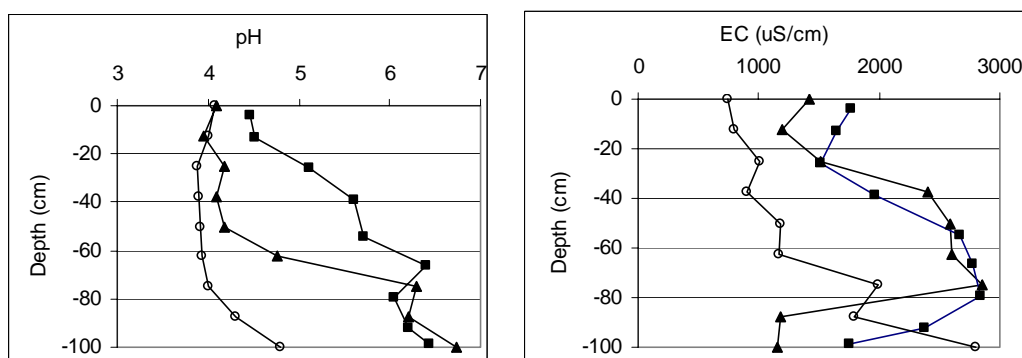

Figure 1: pH and EC profiles for pasture sites 3 (▲) and 4 (■) and scalded site (○).

Total Extractions

The three sites have similar Al, Fe and K concentrations in reduced sediments but tend to vary significantly between sites, by increasing and decreasing, in oxidised sediments (Figure 2). Iron and K show comparable trends in the oxidised zone with greater concentrations in the pasture site 3 than the scalded site which in turn has greater concentrations than pasture site 4, although, Fe has a large increase in pasture site 3. Calcium concentrations in pasture sites are strongly affected by the shell layer with high values in the transition zone (Figure 2). Sodium decreases down-profile in all three samples, whereas Mg increases significantly (Figures 2). Concentrations of trace metals Be, Ce, Cu, La, Li, Mn, Nd, Pb, Pr, Sc, Th and Zn follow the same trend as Mg increasing in concentration from oxidised surface sediments to the reduced lower sediments (Figure 2). Trace metals Cr, Cd, Sb, Sr and V show varied trends between the three cores with concentrations both increasing and decreasing with depth (Figure 2).

Sequential Extractions

The majority of trace metals were removed by extraction #6 which leached 43.3% (573 mg/kg, Figure3) of the trace metals recovered. The #5 and #3 extractions removed 16.5% (204 mg/kg) and 21.2% (262 mg/kg) respectively whilst extractions #4, #2 and #1 removed relatively minor fractions of 5.1% (63 mg/kg), 7.4% (92 mg/kg) and 3.3% (41 mg/kg, Figure3).
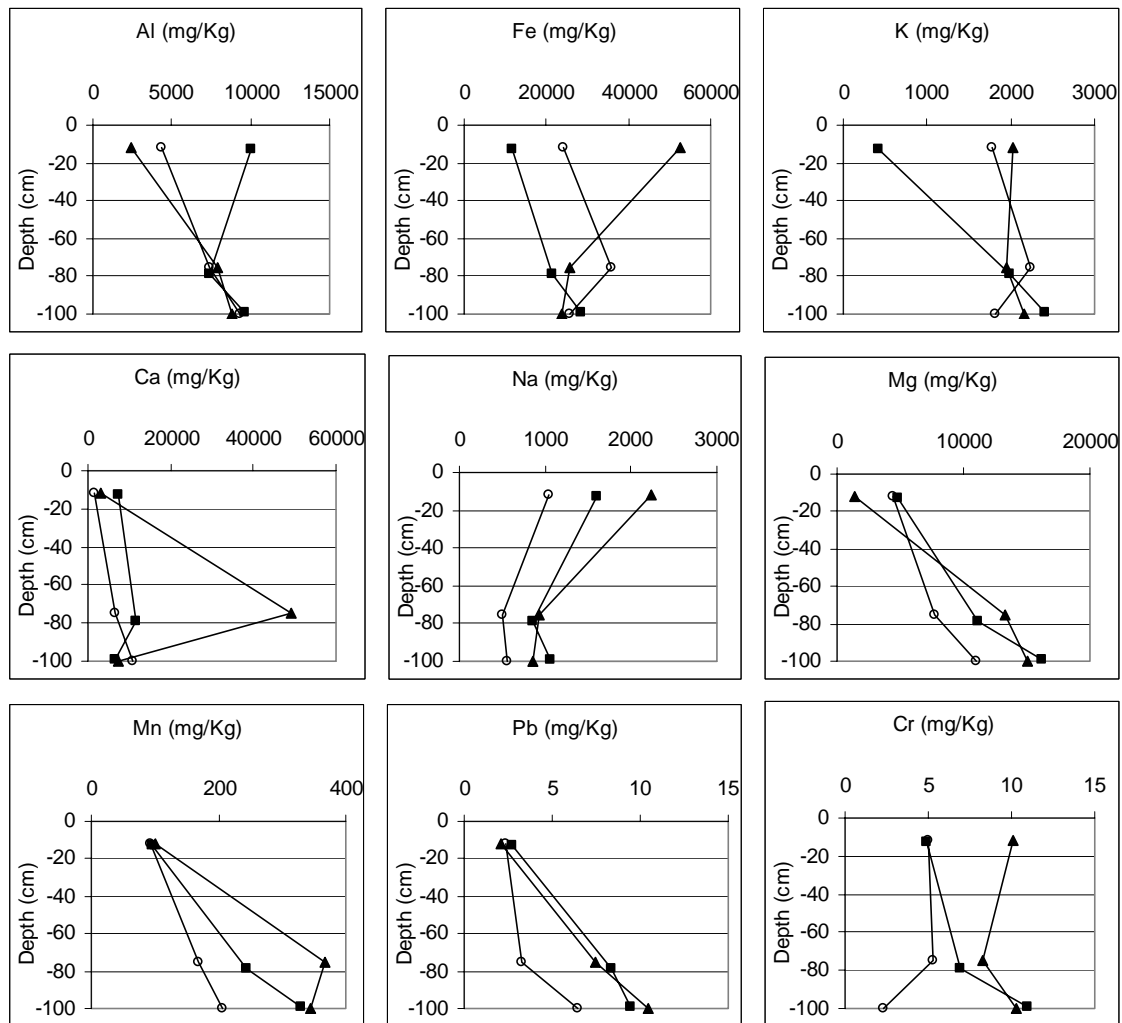
Figure 2: Total extractions from pasture sites 3 (▲) and 4 (■) and scalded site (○)

A summary of the distribution of individual trace metals between the six extractions, is given in Table 2 which shows five main groupings. Group A (Cs, Rb and Tl) is strongly associated with extraction #6 and to a lesser extent extraction #2. Group B (Ba, Bi and Pb) is dominantly found in the #6 and #5 extractions with Ba also shown in extraction #2. Group C (Nb, Zr, Mo, Th and U) is predominantly associated with extractions #6 and #3, although, extraction #4 is important for Nb and Zr. Group D (Be, Se, LREE (La, Ce, Pr and Nd) and Y) are present in #6, #5 and #3 with Be and Se also in #4. Group E (Cd, Cr, Sb, Sr and V) shows a lower distinction between extractions with varied distributions within and between cores. All trace metals analysed in this study were present in extraction #6.
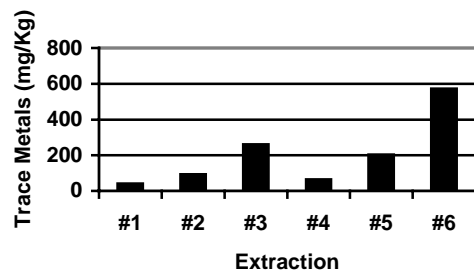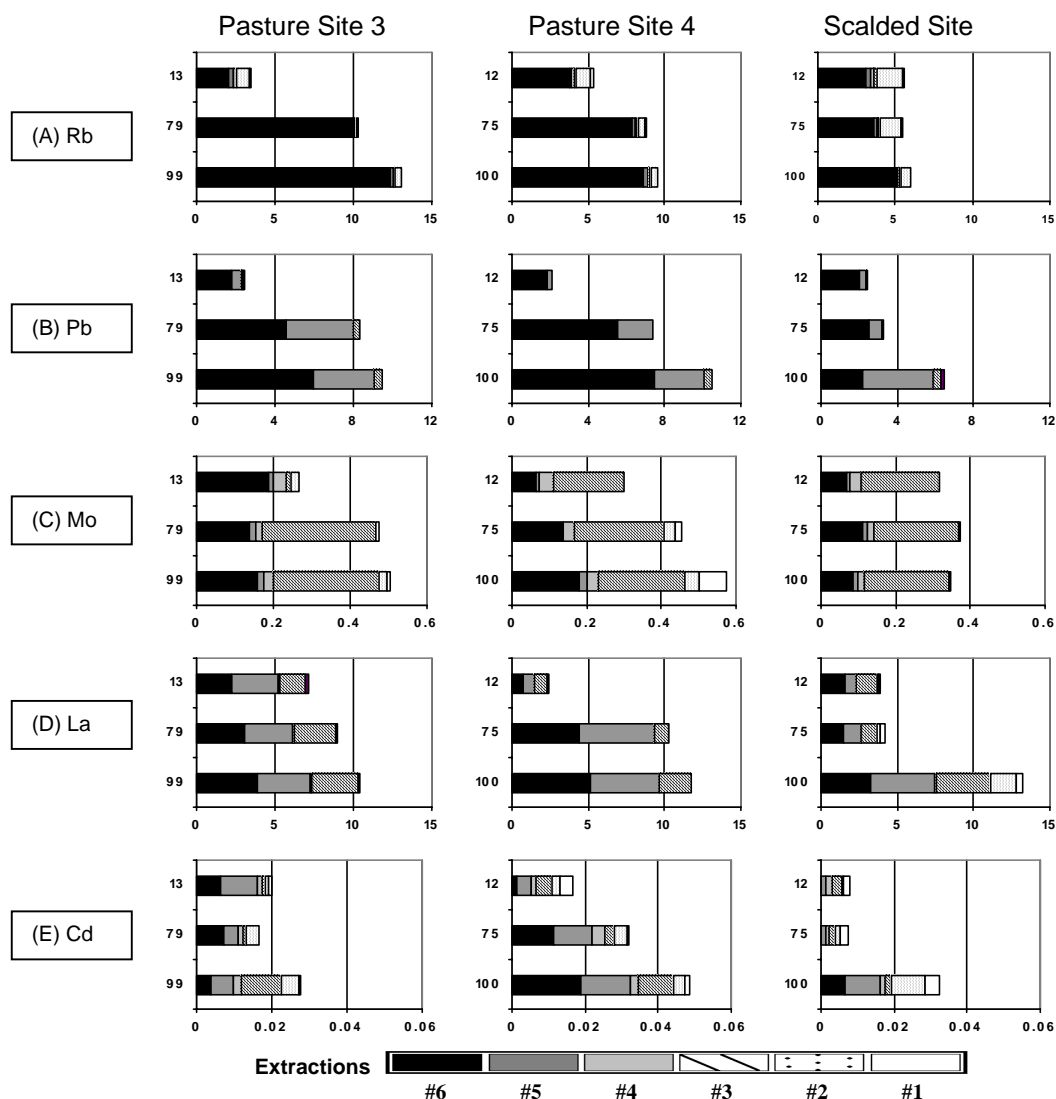

Figure 3: Sum of trace metals leached from each selective extraction

Examples of trace metals from the five groupings, according to depth and sample sites, are given in Figure 4. The partitioning of individual trace metals into particular mineral phases are shown to be consistent between sites and with depth. Few changes in the partitioning of trace metals are demonstrated, with the main difference being the total quantity of each element. The two pasture sites behave similarly sharing comparable trace metal concentrations throughout their profiles. The amount of each trace metal tends to decrease in oxidised areas of the pasture surface samples and in the scalded site.

Table 2: Summary of trace metal distribution between the six sequential extractions (X-major phase, x-minor phase).

Group	#1 Extraction	#2 Extraction	#3 Extraction	#4 Extraction	#5 Extraction	#6 Extraction
(A) Cs, Rb and Tl		x				X
(B) Bi and Pb					X	X
Ba		x			X	X
(C) Nb and Zr			X	x		X
Mo, Th and U			X			X
(D) La, Ce, Pr, Nd and Y			X		X	X
Be and Se			X	x	X	X
(E) Cd, Cr, Sb, Sr and V	x	x	x	x	x	x

Examples of trace metals from the five groupings, according to depth and sample sites, are given in Figure 4. The partitioning of individual trace metals into particular mineral phases are shown to be consistent between sites and with depth. Few changes in the partitioning of trace metals are demonstrated, with the main difference being the total quantity of each element. The two pasture sites behave similarly sharing comparable trace metal concentrations throughout their profiles. The amount of each trace metal tends to decrease in oxidised areas of the pasture surface samples and in the scalded site.

Figure 4: Trace metal partitioning between extractions according to depth and sample site. X-axis = mg/Kg; y-axis = depth (cm).

DISCUSSION

The strong variations of Al, Fe and K concentrations in the oxidised sediments indicate that these elements

may be leached or accumulated upon oxidation. The similar depth profiles of Fe and K within each core reflect the dominance of jarosite as an important mineral phase, particularly in the scald and site 4, which can act as a store for these elements. The higher Fe values, compared to K, are most likely due to the presence of Fe oxides as mottles (particularly at site 3). Concentrations of Al do not follow the Fe and K trends and alunite is not a dominant phase. The Ca profile clearly shows the dominance of the shell layer in the pasture sites, although this is not evident in the scald. Calcium carbonate is predicted to be a major contributor to the bulged conductivity profiles and localised increased pH of pasture sites. The increase of Na shows that soluble salts are concentrated near-surface as a consequence of evaporation and transpiration. Evaporation as a mode of concentration is clearly evident from the formation of salt efflorescence on the sunward side of surface soil features as noted by Kehoe (2004) and explains the increase in the conductivity profiles for pasture sites above 10 cm.

The concentrations of trace metals Cd, Cr, Cu, Pb and Zn in the Mayes Swamp ASS sediments are not above ANZECC and ARMCANZ (2000) soil guidelines, and do not represent an environmental risk in this form. However, the consistently lower concentrations of trace metals in oxidised surface sediments (apart from group E) imply leaching of these elements. Once leached from the sediments, concentration of trace metals in waterways may be high enough to be deemed environmentally significant. Although the oxidised trace-metal deficient areas also have the lowest pH values (4.0-4.5) the mobility of trace metals was found to be low in the water extractable fraction (3.3%). More acid conditions (pH < 3) are thought to be necessary for trace metal mobilisation and leaching (Dent, 1986). The removal of trace metals by episodic leaching in extreme acid conditions is considered to be an important process at this site.

Large fractions of trace metals were retrieved from the #5 (16.5%) and #3 (21.2%) extractions which represent the Fe oxide and organic phases. These phases are known to readily incorporate trace metals, which may be released in low pH conditions. The dominant extraction of trace metals is from #6 (43.3%) indicating that pyrite may be an important sink for these elements. The low percentage of pyrite in the sediment suggests the pyrite present would need to incorporate a substantial amount of trace metals to accommodate the 573 mg/kg of this extraction. In addition to the production of acid, the oxidation of pyrite could thus be an important mechanism for the direct release of trace metals. However, it is important to note that other materials may contribute to the #6 extraction (e.g., sphalerite, galena and silicates) and it is unlikely that pyrite is the sole source of all the trace metals retrieved.

Despite variations in concentration, trace metals are consistently partitioned into the same phases at all depths and sites (apart from group E). Depth profiles show that leaching of trace metals removes them from all phases examined during this study, and that little accumulation in surface sediments is evident. This indicates that trace metals are removed from the oxidised zone rather than redistributed between phases such as pyrite and Fe oxides. Once mobilised, trace metals may be incorporated into the higher pH reduced zone or flushed into receiving waters. The similarities between the two pasture sites show that under comparable conditions trace metal distributions are predictable. For the most part the scalded site is similar with the oxidised zones of the pasture sites with a distinct difference between the amounts of trace metals in reduced and oxidised sediments being evident.

CONCLUSION
The concentrations and distributions of extractable major elements (Al, Ca, Fe, K, Mg and Na) correlate well with known variations in mineralogy and EC, whilst trace metals (Be, Ce, Cu, La, Li, Mn, Nd, Pb, Pr, Sc, Th and Zn) are strongly related to pH and pyrite content. The amount of trace metals (Cd, Cr, Cu, Pb and Zn) in the ASS sampled are not classed as being environmentally hazardous by the ANZECC and ARMCANZ (2000) guidelines. However, increased weathering of these sediments during oxidising acidic conditions has been shown to periodically leach trace metals that could become environmentally hazardous if displaced into waterways. The dominant trace metal-binding phases are predicted by selective sequential extractions to be Fe oxides (16.5%), organics (21.2%) and pyrite (43.3%). If pyrite is a major sink for trace metals, oxidation of this mineral will be an important contributor to trace metal mobility. However, other phases are expected to add to the pyrite extraction. Furthermore, oxidation of the small amount of pyrite present could not account for the extent of trace metals measured. Low pH is thus predicted to be the major process of leaching. The consistency of phases that particular trace metals are partitioned into, under both oxidised and reduced conditions (apart from group E), demonstrates that transformation of trace metals into different phases within the oxidised zone is not a major process but that translocation may be important. Trace metals are leached from the oxidised sediments, possibly enriching reduced sediments, with the principal distinction between oxidised and reduced sediments being the amount of trace metals that are present.

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