

The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia

Paul Shand, Sonia Grocke, Jason Kirby & Andrew K Baker

November 2012

Report for: Department of Water, Environment and Natural Resources, South Australia.

Water for a Healthy Country Flagship Report series ISSN: 1835-095X

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills.

CSIRO initiated the National Research Flagships to address Australia's major research challenges and opportunities. They apply large scale, long term, multidisciplinary science and aim for widespread adoption of solutions. The Flagship Collaboration Fund supports the best and brightest researchers to address these complex challenges through partnerships between CSIRO, universities, research agencies and industry.

The Water for a Healthy Country Flagship aims to provide Australia with solutions for water resource management, creating economic gains of \$3 billion per annum by 2030, while protecting or restoring our major water ecosystems.

For more information about Water for a Healthy Country Flagship or the National Research Flagship Initiative visit www.csiro.au/org/HealthyCountry.html

Copyright and disclaimer

© 2012 CSIRO To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of CSIRO.

Important disclaimer

CSIRO advises that the information contained in this publication comprises general statements based on scientific research. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No reliance or actions must therefore be made on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, CSIRO (including its employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

Contents

Acknowledgments	v
Executive summary	vi
1 Introduction	1
2 Sampling and Analytical Techniques	3
2.1 Field Sampling	4
2.2 Acid-Base Accounting and pH results	5
2.3 Porewater Fractionation	6
2.4 Sequential Extractions	7
3 Porewater chemistry	10
3.1 Introduction	10
3.2 Porewater Concentrations	13
3.3 Summary of porewater chemistry	28
4 Sequential Extractions	29
4.1 Introduction	29
4.2 Sequential extraction data	29
4.3 Summary of sequential extraction chemistry	46
5 Discussion	47
5.1 Introduction	47
5.2 Solution phase partitioning of metals and metalloids	47
5.3 Solid phase partitioning of metals and metalloids	49
5.4 Implications for water quality and ecology	52
6 Conclusions	54
7 References	55
Appendix A Sub-aqueous soil profile descriptions for studied sites	58
Appendix B Acid-Base Accounting Data	60
Appendix C Soil porewater data	62
Appendix D Soil extraction data	63

Figures

Figure 2-1 Map of the Lower Lakes and adjacent tributaries showing the locations of study areas.....	3
Figure 2-2 Core sampling sites and core profiles from Point Sturt (left) and Dog Lake (right).	4
Figure 2-3 Acid-base accounting data for soil materials sampled in profiles from Point Sturt (LF02A&D), Dog Lake (LF 19A) and Boggy Lake (LF20A).	5
Figure 2-4 pH profiles for sites. Black line is initial pH (pH_{KCl} except for samples LF02D, LF19 A4-5 where there was insufficient sample and pH_{w} was used), and red line is incubation pH measured after 16 weeks in a chip tray. pH 4 shown as vertical dotted line.	6
Figure 2-5 Soil porewater profile for sample LF02A showing manganese (Mn) in the < 0.45-3 kDa μm and < 3 kDa filter fractions. Note the log scale for Mn concentration.....	7
Figure 2-6 Sequential extraction data showing arsenic (As) concentrations (top) and percentages (bottom) in the sequential extractions of profile LF19A (Dog Lake).	9
Figure 3-1 Porewater concentrations of sodium (Na) in subaqueous soil profiles.	13
Figure 3-2 Porewater concentrations of sulfate (SO_4) in subaqueous soil profiles.....	14
Figure 3-3 Porewater concentrations of aluminium (Al) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Al is 0.055 mg l^{-1}	15
Figure 3-4 Porewater concentrations of iron (Fe) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Fe is 0.3 mg l^{-1}	16
Figure 3-5 Porewater concentrations of manganese (Mn) in subaqueous soil profiles. Note the log scale for Mn concentration in LF02 profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Mn is 1.7 mg l^{-1}	17
Figure 3-6 Porewater concentrations of beryllium (Be) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Be is $0.13 \mu\text{g l}^{-1}$	18
Figure 3-7 Porewater concentrations of vanadium (V) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) V is $6 \mu\text{g l}^{-1}$	20
Figure 3-8 Porewater concentrations of chromium (Cr) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Cr (Cr III) is $3.3 \mu\text{g l}^{-1}$	21
Figure 3-9 Porewater concentrations of nickel (Ni) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Ni is $11 \mu\text{g l}^{-1}$	23
Figure 3-10 Porewater concentrations of zinc (Zn) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Zn is $8 \mu\text{g l}^{-1}$	24
Figure 3-11 Porewater concentrations of arsenic (As) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) As (As V) is $13 \mu\text{g l}^{-1}$	25
Figure 3-12 Porewater concentrations of lead (Pb) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Pb (hardness dependent, see ANZECC Guidelines) is $3.4 \mu\text{g l}^{-1}$...	26
Figure 3-13 Porewater concentrations of uranium (U) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) U is $0.5 \mu\text{g l}^{-1}$	27
Figure 4-1 Sequential extraction data for Al in the subaqueous soil samples. Note the difference in scale for LF2A.....	30

Figure 4-2 Sequential extraction data for Al in the subaqueous soil samples showing the data plotted as percentages of the total.	31
Figure 4-3 Sequential extraction data for Fe in the subaqueous soil samples. Note the differences in scale.	32
Figure 4-4 Sequential extraction data for Fe in the subaqueous soil samples showing the data plotted as percentages of the total.	32
Figure 4-5 Sequential extraction data for Mn in the subaqueous soil samples. Note the differences in scale.	33
Figure 4-6 Sequential extraction data for Mn in the subaqueous soil samples showing the data plotted as percentages of the total.	34
Figure 4-7 Sequential extraction data for Be in the subaqueous soil samples. Note the differences in scale.	35
Figure 4-8 Sequential extraction data for Be in the subaqueous soil samples showing the data plotted as percentages of the total.	35
Figure 4-9 Sequential extraction data for V in the subaqueous soil samples. Note the differences in scale.	36
Figure 4-10 Sequential extraction data for V in the subaqueous soil samples showing the data plotted as percentages of the total.	37
Figure 4-11 Sequential extraction data for Cr in the subaqueous soil samples. Note the differences in scale for LF02A.	38
Figure 4-12 Sequential extraction data for Cr in the subaqueous soil samples showing the data plotted as percentages of the total.	38
Figure 4-13 Sequential extraction data for Ni in the subaqueous soil samples. Note the differences in scale for LF02A.	39
Figure 4-14 Sequential extraction data for Ni in the subaqueous soil samples showing the data plotted as percentages of the total.	40
Figure 4-15 Sequential extraction data for Zn in the subaqueous soil samples. Note the differences in scale for LF2A.	41
Figure 4-16 Sequential extraction data for Zn in the subaqueous soil samples showing the data plotted as percentages of the total.	41
Figure 4-17 Sequential extraction data for As in the subaqueous soil samples. Note the differences in scale for LF02A.	42
Figure 4-18 Sequential extraction data for As in the subaqueous soil samples showing the data plotted as percentages of the total.	43
Figure 4-19 Sequential extraction data for Pb in the subaqueous soil samples. Note the differences in scale.	44
Figure 4-20 Sequential extraction data for Pb in the subaqueous soil samples showing the data plotted as percentages of the total.	45
Figure 4-21 Sequential extraction data for U in the subaqueous soil samples. Note the differences in scale.	45
Figure 4-22 Sequential extraction data for U in the subaqueous soil samples showing the data plotted as percentages of the total.	46
Figure 5-1 Solubility of gibbsite ($\text{Al}(\text{OH})_3$) in relation to pH (calculated using PHREEQC2). Total solubility is high under acidic and alkaline conditions with minimum solubility at circumneutral pH (from Shand et al. 2008).	48

Figure 5-2 Progressive changes in redox species in an oxidising water through reaction with organic carbon (from Shand et al. 2007).....49

_Toc316902187

Tables

Table 2-1 Sampling dates and location of soil sampling sites. Easting’s and Northing’s are based on the WGS84 datum, Zone 54H.4

Table 2-2 Sequential extraction procedure used in this study.....8

Table 3-1 Trigger Values (95%) for freshwater and selected metal and metalloid concentrations in porewater from profile sections from different locations. Red font indicates exceedance of trigger value (As and Cr assumed to be in oxidised form for presentation purposes).....11

Table 5-1 Typical fractionation of contaminants derived from Sequential Extraction procedure. Large tick: generally a major fraction; small tick: often a moderate fraction or a major fraction in some profiles..50

Acknowledgments

This work was co-funded with the Department of Environment, Water and Natural Resources' Lower Lakes and Coorong Recovery program. The Lower Lakes and Coorong Recovery is part of the South Australian Government's \$610 million *Murray Futures* program funded by the Australian Government's \$12.9 billion *Water for the Future* program. Our thanks go to Ann Marie Jolley and Dr Liz Barnett for support throughout this study.

We are grateful to Claire Wright, Julie Smith and the Analytical Services team at the CSIRO laboratories for their patience in dealing with difficult analytical challenges. Nilmini Jayalath is thanked for completing the soil pH data, and Josh Cowan for helping with field work. We are also grateful to Dr Stuart Simpson and Warren Hicks for constructive reviews.

Executive summary

Increased flow from the River Murray since 2010 caused a return to pre-drought water levels in the Lower Lakes that helped to mitigate hazards associated with acid sulfate soils along the previously exposed shores of the Lakes. The high rate of inflow helped to minimise impacts to surface water from acid and metal mobilisation. This was largely due to dilution and the establishment of high surface water head which induced a downward flux of acidity and contaminants.

Soil monitoring by CSIRO to date has shown that soil recovery, in terms of acid neutralisation, is taking a considerable time to return to pre-drought conditions. However, the hazards posed by trace metal and metalloid contaminants and their fate were poorly known. This study examines subaqueous soil porewater, and 'solid phase' speciation of metals from soil material at selected sites in Lake Alexandrina. Sequential extractions were also carried out on the soil cores from Point Sturt (two profiles), Dog Lake and Boggy Lake, all sites which oxidised during the drought to produce sulfuric soil materials.

The porewater chemistry data show that the soils are very variable within soil profiles as well as between different sites. In general, metal and metalloid contaminant concentrations were lowest in the upper parts of the profiles, due to infiltration from fresh surface lake water. This resulted in a downward flux of solutes and acidity. For all profiles, the concentrations of a number of contaminants exceeded ANZECC/ARMCANZ Guideline values (ANZECC/ARMCANZ 2000). The worst affected sites were Dog Lake and Boggy Lake, with one soil layer in Dog Lake having extremely high concentrations of some contaminants. A number of metal and metalloid contaminants were measured in porewaters at concentrations well above Guideline values including aluminium (up to 875 mg l⁻¹), arsenic (up to 186 µg l⁻¹), cadmium (up to 5 µg l⁻¹), chromium (up to 288 µg l⁻¹), cobalt (up to 1744 µg l⁻¹), copper (up to 82 µg l⁻¹), iron (3206 mg l⁻¹), manganese (896 mg l⁻¹), lead (up to 10 µg l⁻¹), nickel (up to 3225 µg l⁻¹), uranium (up to 35 µg l⁻¹) and zinc (up to 2072 µg l⁻¹). However, the waters had very high hardness values, and although the effect of hardness on ecotoxicity is not fully understood, the ANZECC/ARMCANZ Water Quality Guidelines for some metals (Cd, Cr (III), Cu, Pb, Ni, Zn) have algorithms for hardness dependency (ANZECC/ARMCANZ 2000; Markich et al. 2001). Taking this into consideration, Cd and Pb were below corrected Guideline values in all samples. For some samples, concentrations of metals were very high (e.g. 568 µg l⁻¹ Ni) but fell below hardness corrected Guideline values. Beryllium was also very high (up to 91 µg l⁻¹), with solute concentrations above the Environmental Concern Level (ECL, which is used as an indicative working level) of 0.13 µg l⁻¹. A comparison of different pore size filters showed that in most instances the metal and metalloids were present as dissolved species (< 3 kDa), although some deeper soil samples contained colloidal material (between 0.45 µm and 1kDa), and two samples contained colloidal manganese at shallow depth.

The sequential extraction data showed that a large number of trace metals and metalloids were present at high concentrations in different 'soil fractions'. Although the exchangeable fraction formed a small part of the total, for some metals, levels/concentrations were still high enough to be of concern in relation to water quality limits. Most metals were present in a range of fractions, but were often highest in the dilute hydrochloric acid (potentially representing poorly crystalline materials) and nitric acid extractions (potentially representing pyrite fraction). The pyrophosphate extraction (potentially representing the organic fraction) was also important for a number of metals as well as the metalloid arsenic. In contrast, zinc concentrations were generally highest in the dithionite extraction (potentially representing crystalline iron and manganese oxide phases) and uranium concentrations were typically highest in the weak hydrochloric acid extraction. The data provide a good basis for making future predictions of metal mobilisation under different geochemical scenarios, and as a basis from which to ascertain in more detail the mineralogical phases present in the soils and their metal/metalloid associations.

The implications for ecological recovery at the study sites are significant. The loss of water, as well as acid generation and contaminant release, had a severe impact on the lakes marginal subaqueous soil biodiversity, through loss of much of the soil food-web biodiversity. The presence of soil porewaters with

high contaminant concentrations may have an adverse effect on the re-establishment of soil communities, that are likely to provide linkages to other ecological functions within the Lower Lakes ecosystem. The kinetics of future oxidation at this stage, e.g. a return to low water levels, may be more rapid due to the likely presence of poorly crystalline mineral phases which are known to be more reactive than aged more crystalline forms. The data from this study present a baseline from which to monitor changes in metal and metalloid form (speciation) as the soils age or undergo imposed geochemical change, e.g. due to future drought.

1 Introduction

The development of sulfuric soil materials caused by the oxidation of sulfidic soil materials around the shores of the Lower Lakes (Lakes Alexandrina and Albert) during the recent drought (Fitzpatrick et al. 2008), led to major challenges in management options to address issues associated with low water levels. Surface water levels decreased rapidly during 2007 with the lowest levels during April 2009, when levels were around -1 m AHD. A number of management options were implemented (up to 2010 when flows increased) to minimise impacts from soil acidity development around the lakes. A further hazard was identified relating to metal and metalloid availability, these contaminants being derived either from sulfides or other soil minerals under the acidic oxidising conditions in some soils (Simpson et al. 2010; Shand et al. 2010). Management options for hazard mitigation included the construction of a bund and two regulators to lessen further effects, and pumping water from Lake Alexandrina to Lake Albert.

A rapid return to near pool levels in the Lower Murray and significant flows to the Lower Lakes helped minimise impacts from acid sulfate soils due to dilution and high surface water heads. The surface subaqueous soils have returned to circumneutral pH and, helped by high water levels, formed an effective reactive barrier to upward acid and metal fluxes. However, current monitoring by CSIRO has highlighted that the subsoil over large areas have remained acidic, buffered by hydroxysulfate minerals such as natrojarosite. Peep profiles at selected sites also indicated that slight soil recovery has occurred and some metal concentrations have decreased in soil porewaters (Creepers et al. 2012). Although the timescales of recovery for deeper soils has been shown to be considerable (months to years), there remains limited understanding of some of the chemical processes taking place and the dominant controls on hydrochemistry, particularly kinetics. This has significant implications, particularly for the reestablishment of benthic communities, biodiversity of species within communities and metal uptake.

A number of key questions pertinent to the development of a predictive reaction-transport model remain. These include:

- What is the distribution of metals and metalloids in the sub-surface soils ?
- What are the metals bound to and what is their bioavailability and toxicity ?
- What are the likely reactions and transport mechanisms of metals/metalloids ?
- What is the role of colloids in the transport of metals/metalloids as pH increases over time ?

The reactivity and toxicity of metals and metalloids is dependent on both their form (speciation) and the degree to which they exist in true solution or sorbed onto colloids or nanoparticles. Colloids are defined as particles of a diameter $< 1 \mu\text{m}$ (Ranville et al. 2005) that can play a crucial role in the movement of contaminants in the environment (Jensen et al. 1999; Denaix et al. 2001). The importance of colloids in soil/sediment science has been recognised for many years. Recently, there has been increased attention focused on colloids in soils and sediments due to their recognised role in transport of inorganic and organic contaminants, e.g. colloid-facilitated contaminant transport in groundwaters (Bin et al. 2011; DiCarlo et al. 2006).

Colloids occur naturally in aquatic and terrestrial environments and consist of clay minerals, aluminium-, iron- and manganese-oxyhydroxides, organic macromolecules, viruses and microorganisms such as bacteria (Brady and Weil 2002). They are dynamic particles; the distribution of particle sizes and their reactivity in natural systems is governed by the often changing physical and chemical environment in soils and sediments (e.g. pH, Eh, ionic strength and texture). The large surface area to volume ratio of colloids enables them to sorb large quantities of organic and inorganic pollutants (Kretzschmar et al. 1999). The mobility of different types of colloids may vary in response to physical and chemical changes in the environment, which affect colloid properties. Such properties govern their transport and deposition, and also their size and shape (Ranville et al. 1999). Therefore, both size fractionation and chemical

characterisation of soil and sediment colloids are necessary to help understand colloids in terms of their role as carriers of different pollutants in the environment (Buffle et al. 1995).

In this study, we fractionated porewater metal concentrations, using filtration techniques, into metal concentrations in the dissolved (< 3 kDa) and colloidal ($< 0.45 \mu\text{m} - 3$ kDa) fractions to assess the porewaters potential risk from colloidal mediated transport of metals in sediments.

The sequential extraction of the sub-aqueous soils was carried out following porewater collection to separate the porewater phase from the initial aqueous extraction and subsequent extractions in the sequential process. This has allowed a more refined discrimination of metal and metalloid distribution over the readily soluble aqueous extraction phases where significant levels of metals or metalloids are present in solution, as well as distribution coefficients between the solution and chemically stronger extraction fractions.

This report examines the solid and solution speciation characteristics of metals and metalloids using a range of techniques at key sites selected on the basis of previous acidic events, but where some recovery has occurred. This allows for a range of sorbent and sorbed metal characteristics to be assessed. The sites selected were Point Sturt, Dog Lake and Boggy Lake in Lake Alexandrina.

2 Sampling and Analytical Techniques

The selection of sites was based on data from an on-going monitoring program of acid sulfate soils in the Lower Lakes (Baker et al. 2010). Three sites (Figure 2-1) were selected from marginal soils in Lake Alexandrina which were known to pose a high acid sulfate soils hazard (Fitzpatrick et al. 2008; Baker et al. 2010). Two profiles were collected from Point Sturt (LF02A and D), one each from Dog Lake (LF19A) and Boggy Lake (LF20A). Under drought conditions the soils at all sites acidified strongly. During refilling of the lake, the pH of surface water in Boggy Lake decreased drastically to pH 2.8, whilst in Dog Lake, despite the presence of similarly acidic soils, the surface water became acidic only in small areas. This may be due to the better connectivity of Boggy Lake with the main part of Lake Alexandrina.



Figure 2-1 Map of the Lower Lakes and adjacent tributaries showing the locations of study areas.

The methodologies used included porewater extraction by centrifugation, use of different membrane filter sizes ($< 0.45 \mu\text{m}$ and $< 3\text{kDa}$) to assess colloidal materials, and sequential extraction and solid/solution speciation. Acid-base accounting data was completed to provide information on actual and stored acidity in the samples. This chapter presents a summary of the sampling and analytical techniques, and provides relevant background information such as peroxide testing, incubation and acid-base accounting data.

2.1 Field Sampling

Sampling sites are shown on Figure 2-1 and locations in Table 2-1. A push tube was used to collect undisturbed samples in the water saturated soils. The sampler was made from a clear plastic tube. To achieve sample collection, a wooden rod with a rubber bung attached to the end was inserted into the clear tube. The tube was then pushed into the subaqueous sediment whilst the wooden rod and bung were pulled out of the top end of the tube. This created a vacuum that allowed the sampler to slide into the sediment whilst drawing the core sample into the tube. The internal diameter of the plastic push tube was 30 mm.

Table 2-1 Sampling dates and location of soil sampling sites. Easting's and Northing's are based on the WGS84 datum, Zone 54H.

Site ID	Locality	Sampling Date	Easting	Northing
LF02-A	Point Sturt North	20/03/2012	321247	6070294
LF02-D	Point Sturt North (closest to shore)	20/03/2012	321220	6070249
LF19-A	Dog Lake	19/03/2012	332033	6086787
LF20-A	Boggy Lake	19/03/2012	335054	6089352

Approximately four soil cores were collected at each study site. Immediately after soil cores were collected, they were extruded from the push tube and sub-sampled in the field by observable horizon. Representative subsamples were transferred to nitrogen filled plastic bags and stored in ice for transportation to the laboratory.



Figure 2-2 Core sampling sites and core profiles from Point Sturt (left) and Dog Lake (right).

Sample morphology data were taken from a recent previous sampling (December 2011) which formed the basis of the sampling for this study and provided in Appendix A. At Point Sturt, the marginal sub-aqueous soils were mainly sands becoming a sandy loam at the base of the profile, whereas further from shore, heavy clays were present at a depth of 57 cm below the sediment/water interface. The Dog Lake soils also comprised sands overlying heavy clay. A black gel overlying soft clay was the dominant soil material at

Boggy Lake. A yellow coloured mineral, probably natrojarosite, was recorded in all profiles, mainly in deeper layers. These were more conspicuous in the more acidic layers, particularly in Dog Lake.

2.2 Acid-Base Accounting and pH results

Acid-base accounting data are presented in Appendix B and shown graphically on Figure 2-3. Net acidities at Point Sturt were slightly negative at the surface, and low but positive in the middle of the profiles. In the profile furthest from shore (LF02A), net acidity was high (up to 101 moles H⁺/tonne) at depth in contrast to the near shore profile (LF02D) that had negative net acidity caused by very high acid neutralisation capacity (ANC). Most of the high net acidity was associated with sulfide, with minor titratable actual acidity (TAA) present. Only the two surface layers were available for the Dog Lake profile and net acidities varied from 31-34 moles H⁺/tonne. Previous monitoring at the site indicated that these layers were directly underlain by soil material with higher net acidity. At depth, these were underlain by low net acidity material, associated with high levels of ANC. The highest net acidities were present in the Boggy Lake sub-aqueous soils, varying from 131 to 890 moles H⁺/tonne, comprising different amounts of TAA, sulfide and retained acidity (due to the presence of natrojarosite).

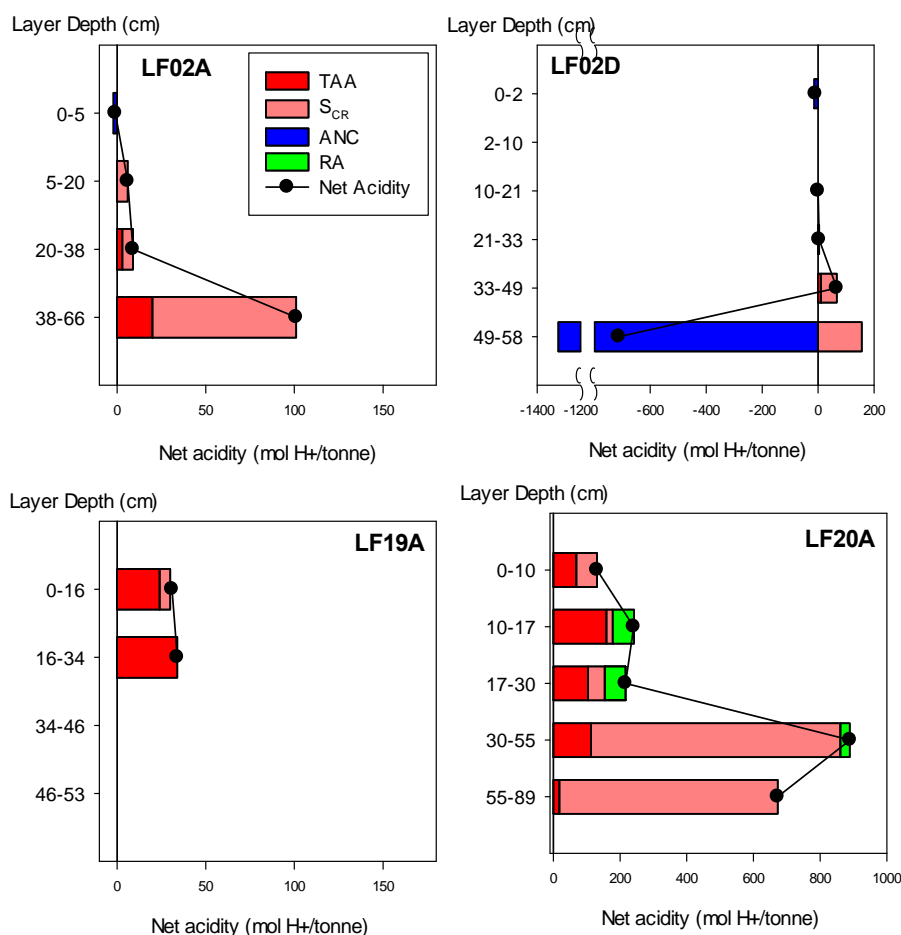


Figure 2-3 Acid-base accounting data for soil materials sampled in profiles from Point Sturt (LF02A&D), Dog Lake (LF19A) and Boggy Lake (LF20A).

The pH data for the profile samples are shown on Figure 2-4. For Point Sturt (LF02A&D), the upper soil layers of both profiles had a circumneutral pH that changed little during incubation. At LF02D, the deepest sample also showed little change in pH with incubation due to high ANC. The other samples had variable pH initially, but all incubated to form sulfuric soil materials (i.e. pH < 4).

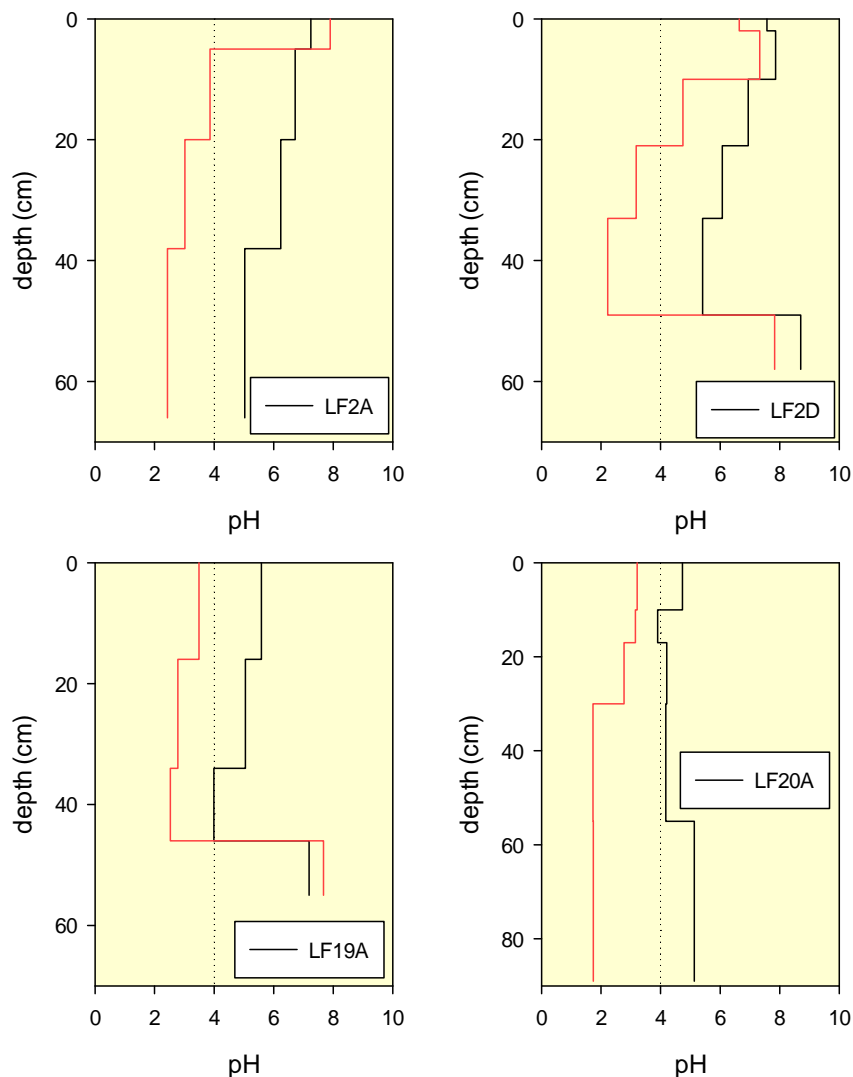


Figure 2-4 pH profiles for sites. Black line is initial pH (pH_{KCl} except for samples LF02D, LF19 A4-5 where there was insufficient sample and pH_w was used), and red line is incubation pH measured after 16 weeks in a chip tray. pH 4 shown as vertical dotted line.

2.3 Porewater Fractionation

Sediment core sections (ca. 10 g) were weighed into individual 50 ml centrifuge tubes ($n = 5-10$) in an anaerobic chamber. The centrifuge tubes were sealed, removed from the anaerobic chamber, and centrifuged at 2000 g for 20 minutes to extract porewater. Centrifuge tubes were returned to the anaerobic chamber and porewater removed from the surface of sediments using a pipette and placed into 50 ml centrifuge tubes (total porewater extracted from the samples was 10-30 ml). The solution was filtered to $< 0.45 \mu\text{m}$ using syringe filters (Sartorius Minisart CE) into 15 ml centrifuge tubes for pre water metal fractionation.

Approximately 3.5 ml of the $< 0.45 \mu\text{m}$ filtered porewater was used to examine the distribution of metals into colloidal ($< 0.45\mu\text{m}-3 \text{ kDa}$) and dissolved ($< 3 \text{ kDa}$) fractions using an ultrafiltration technique developed by Cornelis et al. (2011) to investigate the partitioning of manufactured nanomaterials in soils. Centrifugal ultrafiltration (UF) devices (Pall-Gellman) (3 kDa) were preconditioned by filtering approximately 1 ml of the $< 0.45 \mu\text{m}$ filtered porewater solutions at 2000g for 10 min. The $< 0.45 \mu\text{m}-3 \text{ kDa}$ colloidal fraction was determined by pipetting approximately 2.5 ml of the $< 0.45 \mu\text{m}$ filtered porewater into the reservoir of the 3 kDa centrifugal UF devices and centrifuging at 2000g for 40 min. Following

centrifugation, 1-2 ml of the 3 kDa filtered solution was diluted to 14 ml using 2 % HNO₃ and total metal concentrations determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro ARCOS) or inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500ce). The remaining < 0.45 μm filtered porewater was diluted to 14 ml using acidified Milli-Q water, and total metal concentrations determined by ICP-OES or ICP-MS using appropriately diluted standards.

The concentration of metals associated with the < 0.45μm-3kDa colloidal fractions can be determined using the following equation:

$$\text{< 0.45}\mu\text{m-3 kDa colloidal metal concentrations} = \text{< 0.45 }\mu\text{m filtered total metal concentration} - \text{3 kDa filtered total metal concentrations}$$

The data are plotted as concentration profiles for the different pore size membranes used, with an example shown on Figure 2-5.

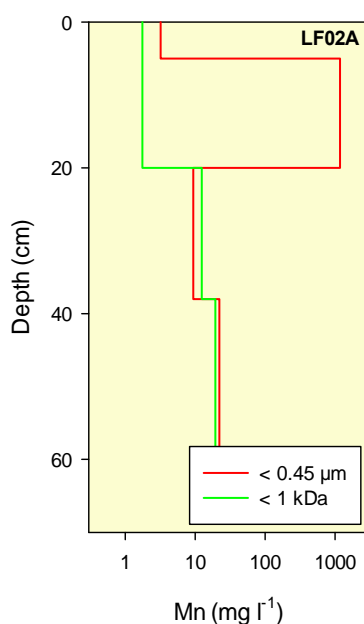


Figure 2-5 Soil porewater profile for sample LF02A showing manganese (Mn) in the < 0.45-3 kDa μm and < 3 kDa filter fractions. Note the log scale for Mn concentration.

2.4 Sequential Extractions

Sequential extraction procedures, based upon Tessier et al. (1979), for sediments and soils have been extensively used to assess operationally defined pools of trace elements, characterising their lability on the basis of the dissolution behaviour of the target binding phases in soils and sediments. This information can be used to provide a guide into the binding mechanisms and strength, and provide distribution coefficients (solution to solid ratio) for metals and other potential contaminants. In this study, we used a modified sequential extraction procedure outlined by Claff et al. (2010a, b) to assess metal fractionation and lability in sediments (Table 2-2). The extractions were carried out following the removal of porewater (section 2.2) from the soils.

Sample preparation for sequential extraction steps occurred in an anaerobic glove box to avoid changes in samples due to oxidation. Following porewater extraction, the sequential extraction procedure involved an initial extraction step using 1M magnesium chloride (MgCl₂) solution to determine the potential labile pool of metals in sediments (exchangeable metal concentrations). A second extraction using 1M hydrochloric acid (HCl) followed to estimate metals concentrations in a low pH aqueous medium as these conditions are often realised in the field following soil oxidation, e.g. easily mobilised non-exchangeable metal concentrations (including carbonates, poorly ordered oxides and hydroxides). The third sequential

extraction step used sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) (pH 10) (Rayment and Higginson 1992) to assess organically bound/complexed metals. Extraction step four used an acetic acid/citrate buffer with sodium dithionite (CBD) (pH 4.8) to assess metal concentrations associated with reducible crystalline phases (McKeague and Day 1966; Gleyzes et al. 2002; Poulton and Canfield 2005). The acetic acid/citrate and dithionite extractant reacts with secondary mineral oxides of iron as a strong reducing agent and represents the strongest phase of aqueous extraction in the sequential process.

Table 2-2 Sequential extraction procedure used in this study

Sequential Fractionation Procedure	Metal Fraction	Treatment
1	Labile: readily soluble salts and exchangeable ions	1 M magnesium chloride
2	Weak acid soluble: includes carbonates and poorly ordered sulfides and oxides	1 M hydrochloric acid
3	Organic: reactive organic components	0.1 M sodium pyrophosphate (pH 10)
4	Reducible crystalline phases e.g. Fe and Mn oxides	0.35 M acetic acid/0.2M sodium citrate buffer with 50 g/L sodium dithionite (pH 4.8)
5	Sulfides, primarily pyrite	Concentrated nitric acid
6	Residual	EPA method 3052 (reverse aqua regia. microwave assisted extraction procedure)

Step five used concentrated nitric acid (HNO_3) as an extractant to assess metals bound or associated with sulfide phases, primarily pyrite. The final extraction step uses US EPA method 3052 for microwave assisted extraction of siliceous and organic based matrices using nitric acid and hydrochloric acid to determine metal concentrations associated with the residual fraction (RevAqReg).

The supernatants from each sequential extraction step, excluding the acid digest stages, were centrifuged at 2000 g for 20 minutes, filtered to $< 0.45 \mu\text{m}$ (Sartorius PES membrane) and analysed for total metal concentrations using ICP-OES or ICP-MS using appropriately diluted standards.

The sequential fraction data for metals and metalloids are presented on stacked horizontal bar charts, with an example shown on Figure 2-6.

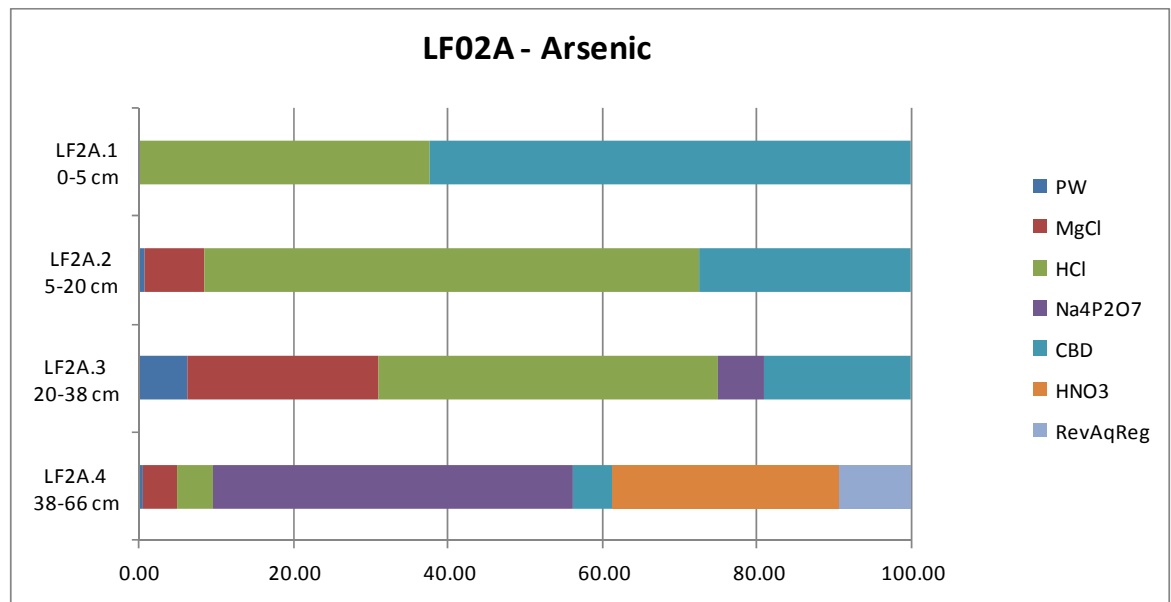
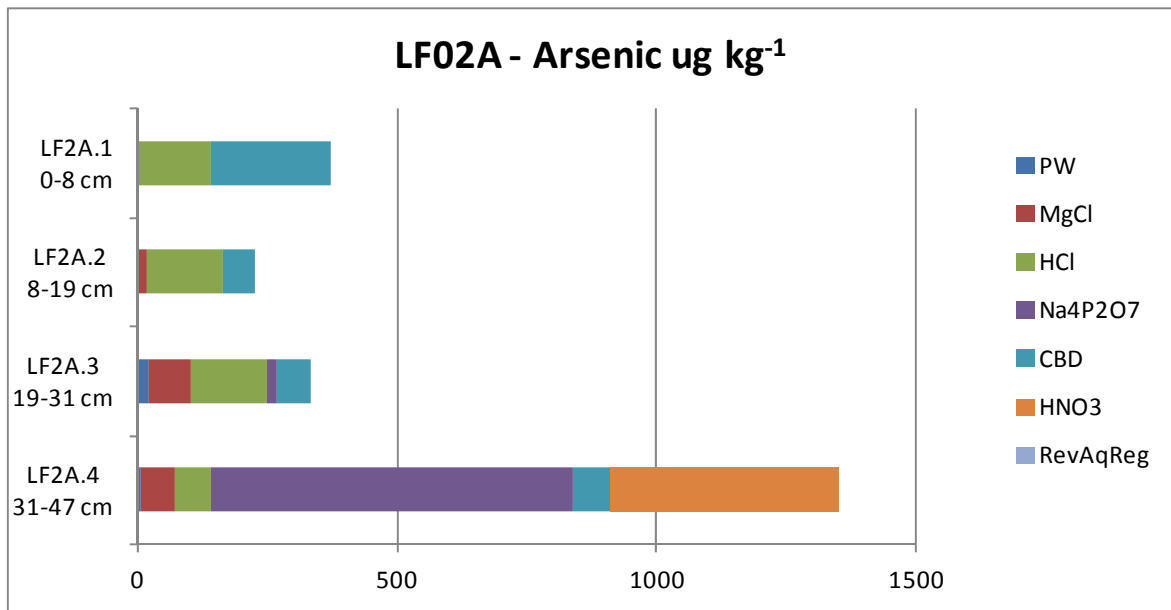


Figure 2-6 Sequential extraction data showing arsenic (As) concentrations (top) and percentages (bottom) in the sequential extractions of profile LF19A (Dog Lake).

3 Porewater chemistry

3.1 Introduction

Porewater concentrations represent the most bioavailable pool of nutrients and contaminants in soils. In this study, the Australian and New Zealand Guidelines for Freshwater and Marine Water Quality (ANZECC 2000) were used to assess porewater quality. The guideline values for selected metal contaminants are shown in Table 3-1, along with the range found in porewaters for the different profiles. The metal concentrations in porewater can be compared to the 95% protection trigger values outlined in the ANZECC water quality guidelines for freshwater. The 95% protection level was used, as this trigger value applies to ecosystems that could be classified as slightly-moderately disturbed, although a higher protection level (e.g. 99%) could be applied to slightly disturbed ecosystems where the management goal is no change in biodiversity. For some metals hardness corrected values were used for comparison.

Metal concentrations in porewater were found to exceed the 95% protection trigger values at the four selected locations, especially LF19A (Table 3-1). The bioavailability and hence potential toxicity of metals in porewaters will be dependent on the physical and chemical properties (e.g. pH, redox, and ionic strength), solution speciation (e.g. oxidation state, free ion or complexed, and/or associated with inorganic and organic colloids), and type of organism (e.g. routes of exposure and detoxification mechanisms).

For some metals, the ANZECC water quality guideline values were exceeded in profiles at all sites (Table 3-1). In some cases, the concentrations exceed these values by several orders of magnitude, especially for Dog Lake (LF19A).

The percentage of metals associated with colloidal (< 0.45 μm -1 kDa) and truly dissolved fractions in porewaters from core profiles is essential to understand their bioavailability and therefore their toxicity. It also has implications for transport processes through soil pores and in surface waterways. Previous studies of metal release from acid sulfate soils has suggested that colloidal transport may be more significant in soils which have higher pH (e.g. acidification has been reversed), as the solubility of typical colloidal materials (clays, oxides) is high at low pH (Shand et al. 2010). At higher soil pH, colloids are negatively charged and may be coated by humic acids through hydrophobic interaction, with the result being enhanced negative charge and enhanced stabilisation (Batley et al. 2012). Due to a loss of surface charge, colloids should flocculate at low pH and hence be of a minor relevance in acid environments.

Metal and metalloid contaminants (e.g. As) have previously been identified associated with colloidal materials in acid mine drainage that typically consisted of hydrous oxides of iron and aluminium (Morel and Gschwend, 1987). The mobility, reactivity and potential bioavailability of metal contaminants associated with colloidal material in porewaters will depend on the physical and chemical properties of the particles (e.g. size and charge), strength of complexation (e.g. strong or weakly sorbed, exchangeable, etc.), solubility (e.g. stability of pure or mixed sulfide phases), physical and chemical properties of the porewater (e.g. pH, ionic strength, DOC concentrations, etc.), solution and solid partitioning (e.g. sorption during transport, sieving, aggregation) and the biological route of exposure.

The recovery of porewater was variable in the soils, with the sands proving the most difficult. There was sufficient sample for cation analyses for both < 0.45 μm and < 3 kDa fractions for all samples except LF02D layer 4 (21-33 cm) where only the < 0.45 μm was analysed. There was insufficient sample for the measurement of pH and EC, and the soil pH should be used as a guide (Figure 2-4), but bearing in mind that some minor oxidation may have occurred during the process despite precautions to prevent this.

Table 3-1 Trigger Values (95%) for freshwater and selected metal and metalloid concentrations in porewater from profile sections from different locations. Red font indicates exceedance of trigger value (As and Cr assumed to be in oxidised form for presentation purposes).

Metal	Trigger value	Location ⁱ			
	95% Level of protection ^j µg l ⁻¹	LF02A µg l ⁻¹	LF02D µg l ⁻¹	LF19A µg l ⁻¹	LF20A µg l ⁻¹
Aluminium (pH < 6.5)	55, 0.8 ^a	< 200 – 34237 ⁱ	< 230 – 3963	< 700 – 875000	< 500 – 127400
Arsenic (III)	24				
Arsenic (V)	13	< 0.4 – 107	< 0.2 – 36	< 1 – 186	< 0.5 – 122
Beryllium	0.13 ^k	< 0.03 – 12	< 0.02 – 5.3	< 0.14 – 91	< 0.02 – 37
Cadmium	0.2 (1-28) ^j	< 0.07 – 1.65	< 0.04 – 0.87	< 0.3 – 5.0	< 0.06 – 0.28
Chromium (III)	3.3 ^b (16-309) ^j				
Chromium (VI)	1.0	< 0.2 – 4.13	< 0.1 – 1.62	< 0.7 – 288	< 0.23 – 21
Cobalt	2.8 ^c	0.13 – 271	0.35 – 85	804 – 1744	0.35 – 380
Copper	1.4 (7-155) ^j	< 1.5 – 3	0.9 – 40	< 0.8 – 82	< 0.4 – 15
Iron	300 ^d	< 428 – 443000	< 200 – 115962	256 – 3206250	< 2310 – 2240000
Lead	3.4 (37-3846) ^j	0.16 – 2.9	< 0.07 – 1.96	0.18–10.4	< 0.1 – 4.2
Manganese	1900	3210 – 1180000	1700 – 860300	38700 – 89600	2772 – 24220
Molybdenum	34 ^e	< 0.8	< 0.3 – 43	< 1.4	< 1.4
Nickel	11 (55-1216) ^j	1.3 – 1196	< 6 – 1049	310 – 3225	5.5 – 623
Selenium (Total)	11	< 5.6	< 5.6	0.7 – 12.4	< 0.56 – 1.6
Silver	0.05	< 0.03 – 0.09	< 0.14	< 0.14 – 0.23	< 0.14
Thallium	0.03 ^f	< 0.07 – 0.34	< 0.07 – 0.67	< 0.5 – 1.47	< 0.07 – 0.08
Uranium	0.5 ^g	0.3 – 16.9	0.5 – 27	4 – 35	< 0.7 – 3.5
Vanadium	6 ^h	< 0.3 – 10.5	< 0.3 – 9.2	< 1.4 – 1354	0.6 – 188
Zinc	8.0 (40-885) ^j	1.1 – 686	1 – 286	56 – 2072	6 – 1085

^a Indicative interim working level. A freshwater low reliability trigger value of $0.8 \mu\text{g l}^{-1}$ was derived for aluminium at $\text{pH} < 6.5$ using an AF (Assessment Factor) of 20 on the low pH brown trout (*Salmo trutta*) LC50 figure; moderate reliability trigger of 55 if $\text{pH} > 6.5$. ^b A low reliability freshwater trigger value for chromium (III) of $3.3 \mu\text{g l}^{-1}$ was derived using an AF of 20 on the lowest, *Oncorhynchus mykiss* (rainbow trout) figure, from a limited set of chronic data. This figure should only be used as an indicative interim working level. ^c Although a freshwater moderate reliability trigger value could be derived for cobalt ($90 \mu\text{g l}^{-1}$ with 95% protection) using the statistical distribution method, both the 95 % and 99 % ($30 \mu\text{g l}^{-1}$) figures were well above some experimental chronic figures, particularly for *Daphnia magna* (between NOEC of $2.8 \mu\text{g l}^{-1}$ and LC50 of $27 \mu\text{g/l}$). Hence, a low reliability fresh water trigger value was derived by dividing the lowest chronic figure ($2.8 \mu\text{g l}^{-1}$) by an AF of 2 (cobalt is an essential element). ^d There was insufficient data at this stage to derive a reliable trigger value for iron. The current Canadian guideline concentration is $300 \mu\text{g l}^{-1}$, which could be used as an interim indicative working level, but further data are required to establish a figure appropriate. ^e A freshwater low reliability trigger value of $34 \mu\text{g l}^{-1}$ was calculated for molybdenum using an AF of 20 (because the limited data were chronic) on the *D. magna* figure. ^f A freshwater low reliability trigger value of $0.03 \mu\text{g l}^{-1}$ was derived from the *Hyalella* reproduction figure with an AF of 20 (because the data were chronic). ^g A freshwater low reliability trigger value of $0.5 \mu\text{g l}^{-1}$ was calculated for uranium using an AF of 20 on limited chronic data. This should only be used as an indicative interim working level. ^h A freshwater low reliability trigger value of $6 \mu\text{g l}^{-1}$ was calculated for vanadium using an AF of 20 (applied to the lowest experimental chronic figure). This should only be used as an indicative interim working level. ⁱ The values in red represent metal concentrations that exceed the 95 % trigger value or low reliability trigger value. ^j brackets show overall range of hardness corrected guideline values for samples, note that each analysis will have a specific Guideline Value dependent on hardness. ^k Environmental Concern Level (ECL).

3.2 Porewater Concentrations

This section describes selected porewater concentrations from the four profiles sampled (Table 2-1). These are plotted as line graphs for each profile, showing the metal concentrations in the $< 0.45 \mu\text{m}$ and $< 3 \text{ kDa}$ filtered fractions. In some cases, the $< 1 \text{ kDa}$ fraction was higher than the $< 0.45 \mu\text{m}$ fraction. In some cases, the larger pore size filter displayed a reddish-brown precipitate, and it would appear that some precipitation has removed Fe (and other trace elements) during the filtration process. It is not clear why this happened in some samples (e.g. LF02A 38-66 cm) only for the $0.45 \mu\text{m}$ filter, but may be due to turbulent flow induced by a larger pore size.

3.2.1 SODIUM (Na)

Porewater sodium (Na) concentrations are shown on Figure 3-1. Sodium generally correlates with chloride (Cl) in waters in the lakes, and is therefore taken as a surrogate for salinity. Most soil waters had moderate salinity, and all profiles show a consistent increase with depth. This is most likely related to downward advective flow of lake water following refilling of the lakes at the end of the drought. The concentrations in the colloidal and dissolved fraction are very similar (within analytical error) showing that Na is present mainly in dissolved form. This provides a basis from which to interpret less conservative solutes.

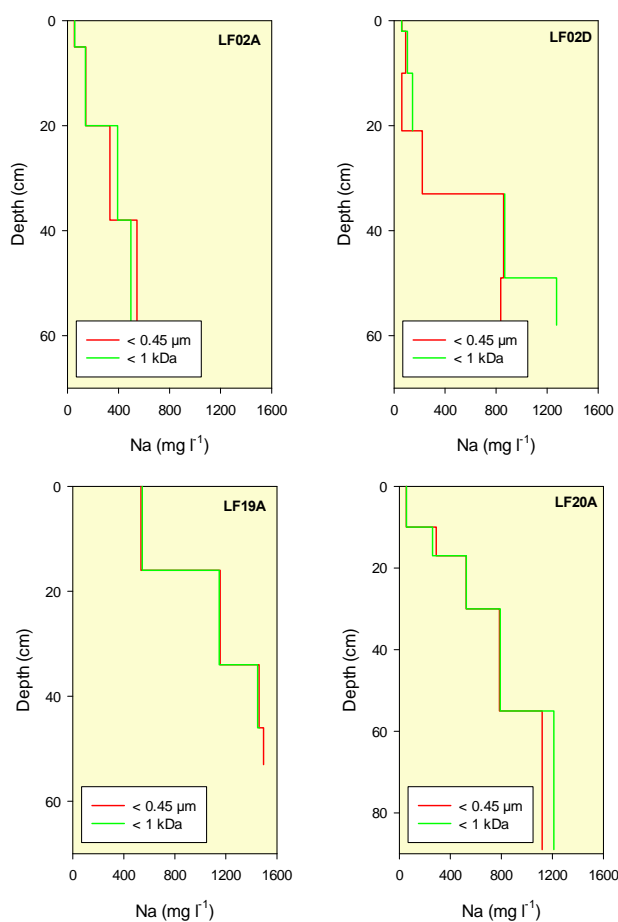


Figure 3-1 Porewater concentrations of sodium (Na) in subaqueous soil profiles.

3.2.2 SULFATE (SO₄)

Porewater sulfate (SO₄) concentrations are shown on Figure 3-2. Sulfate concentrations vary from relatively low concentrations in the upper soil layer, to much higher concentrations at depth (although SO₄ is high at the surface in Dog Lake: LF19A). The SO₄ is generally much too high to be derived solely from cyclic salts.

Although Cl was not determined, the ratio of SO₄ to Na (which typically follows Cl) varies from 0.31 to 15, with most samples being much higher than the seawater ratio of 0.26. The highest ratios were found in Dog Lake especially the top two layers of the profile which were very similar (ratios of 14.6 and 15.2) despite very different SO₄ concentrations. This suggests simple dilution of the top layer. The excess SO₄ is most likely derived from dissolution of hydroxysulfates which had formed during the drying phase of the soils in the previous drought. The similarity in concentrations for both filtered fractions shows that SO₄ was present mainly in dissolved form in all samples.

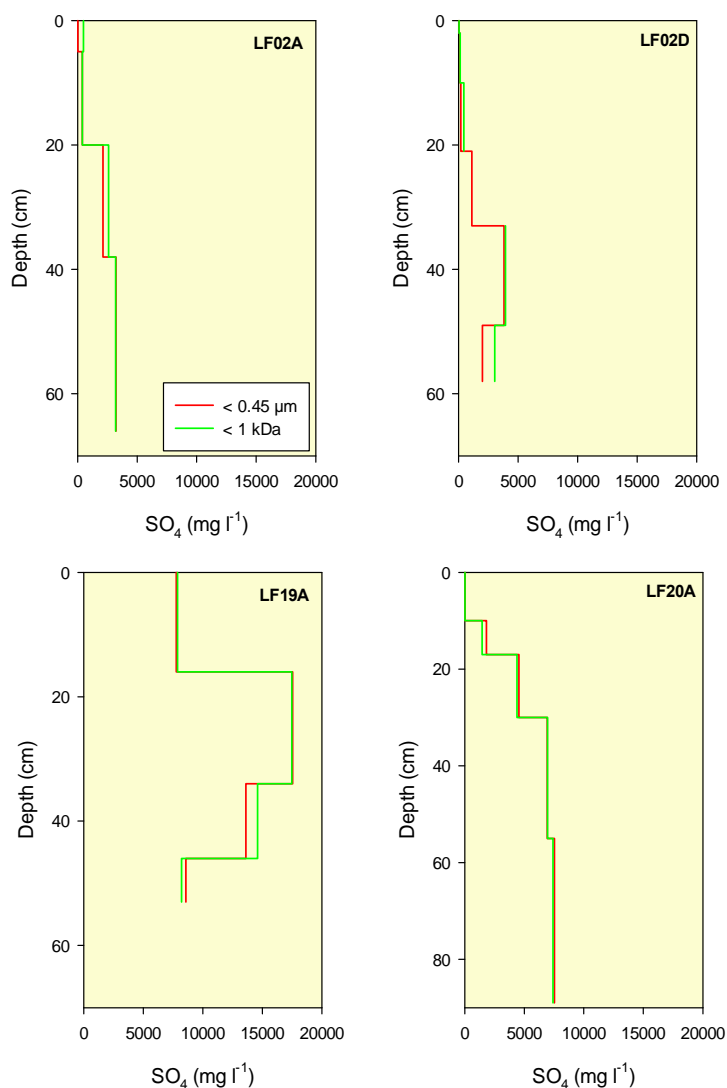


Figure 3-2 Porewater concentrations of sulfate (SO₄) in subaqueous soil profiles.

3.2.3 ALUMINIUM (Al)

Porewater aluminium (Al) concentrations are shown on Figure 3-3. The highest Al concentrations were found in Dog Lake (LF19A) in those layers where SO_4 was highest. The profiles show a similar trend in all profiles to that of SO_4 (Figure 3-2). Most samples also had concentrations much higher (up to more than 3 orders of magnitude) than the ANZECC water quality guideline value (Table 3-1).

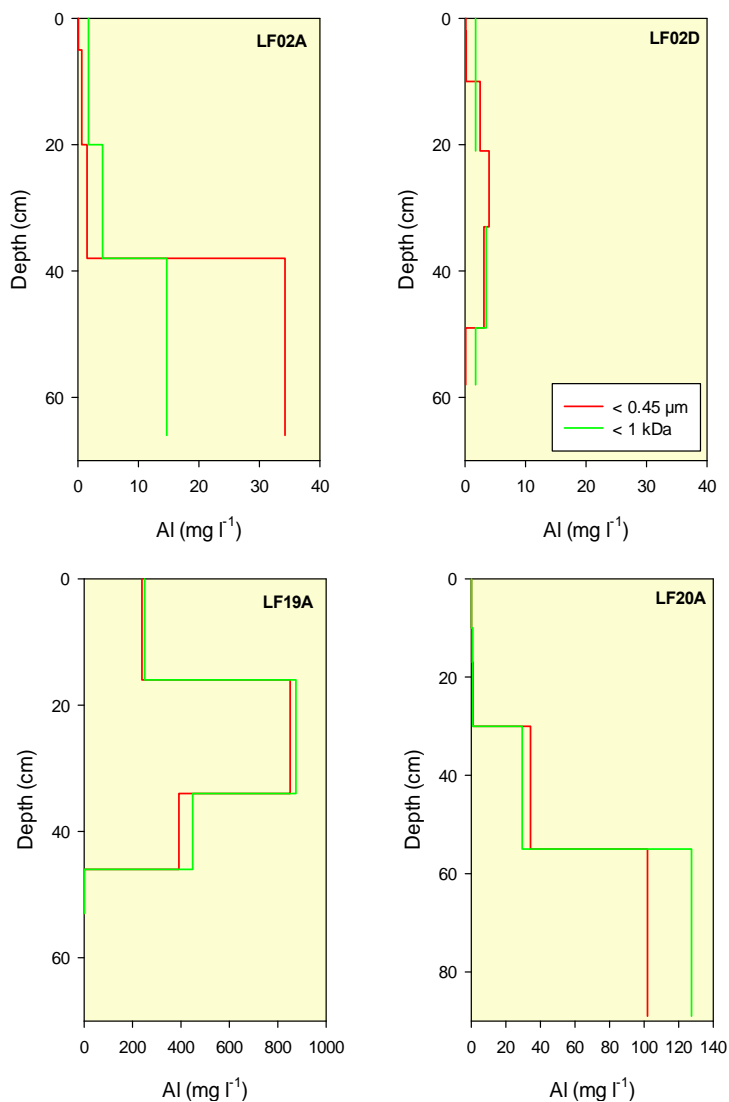


Figure 3-3 Porewater concentrations of aluminium (Al) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Al is 0.055 mg l⁻¹.

Aluminium correlates negatively with pH as expected, and displays a positive correlation with SO_4 at higher concentrations. The data also suggest that Al is mainly in the dissolved fraction, the exception being the deepest soil layer in LF02A (Figure 3-3).

3.2.4 IRON (Fe)

The distribution of redox sensitive elements such as iron (Fe) and manganese (Mn) in porewater can be used to give an indication of the redox and/or acidic conditions in sediments. Porewater Fe concentrations are shown on Figure 3-4. Iron concentrations in porewater samples were below ICP-OES detection in 3 of the 4 surface layers; being high in Dog Lake. Profile shapes were quite similar to Al, but with a peak at intermediate depths.

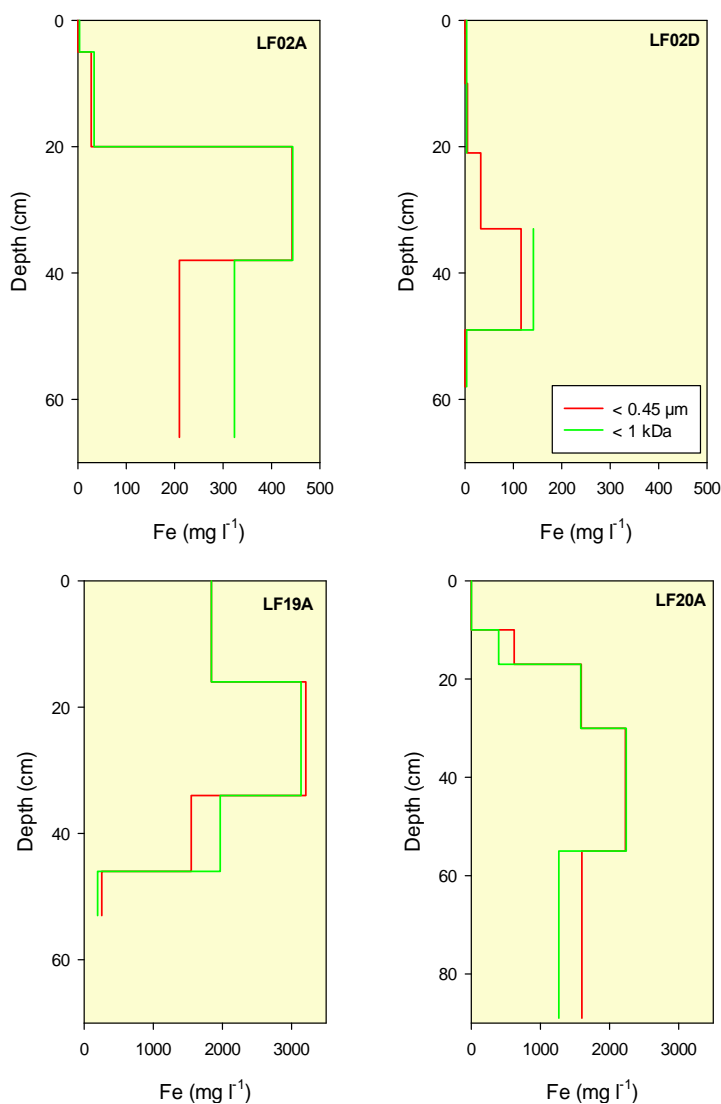


Figure 3-4 Porewater concentrations of iron (Fe) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Fe is 0.3 mg l⁻¹

There was a good negative correlation with pH and a near linear positive correlation with SO₄. Taking into account the presence of strongly oxidised sulfuric materials prior to refilling, it appears likely that the dissolution of Fe hydroxysulfate minerals has contributed to the dissolved Fe and SO₄. In most cases, Fe appears to be in the dissolved fraction rather than colloids at the pH values measured.

3.2.5 MANGANESE (Mn)

Manganese (Mn) is soluble under acidic and reducing conditions. During a change to reducing from oxidising conditions, Mn is typically reduced prior to Fe. Porewater Mn concentrations are shown on Figure 3-5. At Point Sturt, Mn was extremely high in soil layers at depths of 5 to 20 cm (LF02A) and 10 to 21 cm (LF02D). Concentrations were much lower in the < 3 kDa fraction showing that Mn was mainly in colloidal form. For the other soil layers, Mn was dominantly in dissolved form, with all but one sample being above the ANZECC water guideline value (Table 3-1).

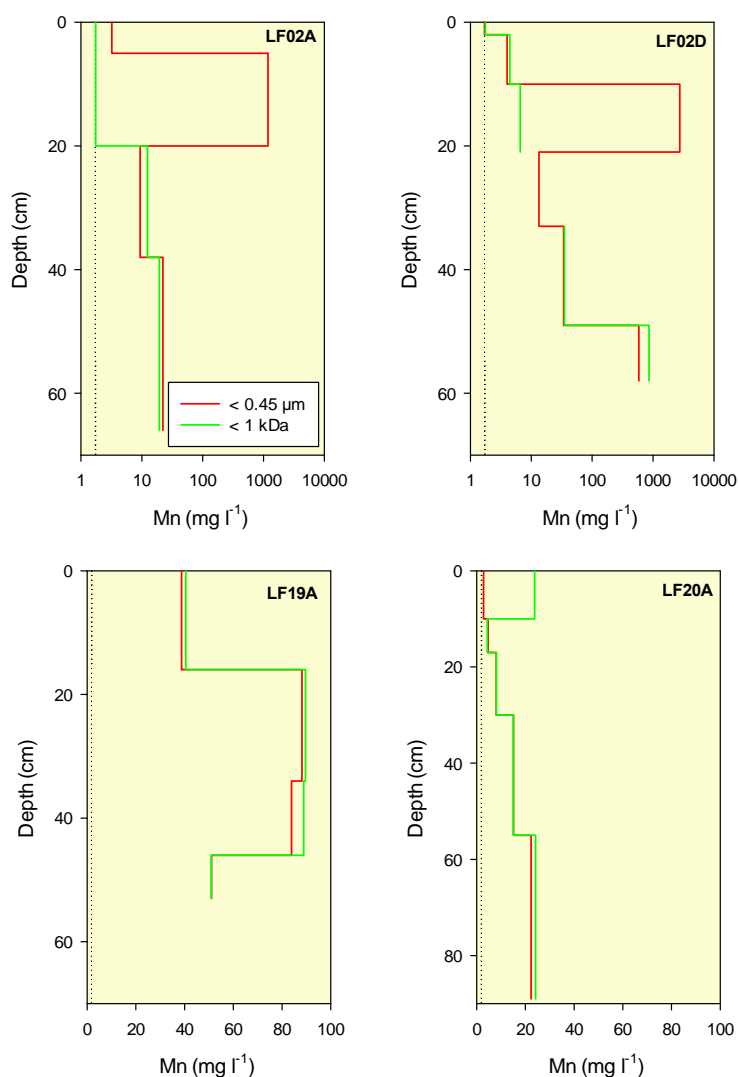


Figure 3-5 Porewater concentrations of manganese (Mn) in subaqueous soil profiles. Note the log scale for Mn concentration in LF02 profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) for Mn is 1.7 mg l⁻¹

3.2.6 BERYLLIUM (Be)

Porewater beryllium (Be) concentrations are shown on Figure 3-6. The profile shapes are similar to other metals such as Al, consistent with a dominant control by pH (both elements are not redox sensitive). Apart from LF19A, the concentration of Be was low in the surface soil layers, but at depth reached very high concentrations well above the ANZECC/ARMCANZ Environmental Concern Level of $0.13 \mu\text{g l}^{-1}$. In profile LF19A, concentrations were low at depth but high in the surface layer (Figure 3-6). There is a good negative correlation with pH for most samples, but in the shallow profile at Boggy Lake, concentrations were low in acidic samples implying low abundance. At higher concentrations, Be also correlates positively with SO_4 .

Beryllium was found to be mainly in the dissolved ($< 3\text{kDa}$) fraction in porewater samples, but the deepest sample in LF02A may contain some colloidal Be. The source of the Be is not known, but is most likely derived from clays. It is rarely analysed routinely, but this data suggests that it should be given more attention due to its potential toxicity.

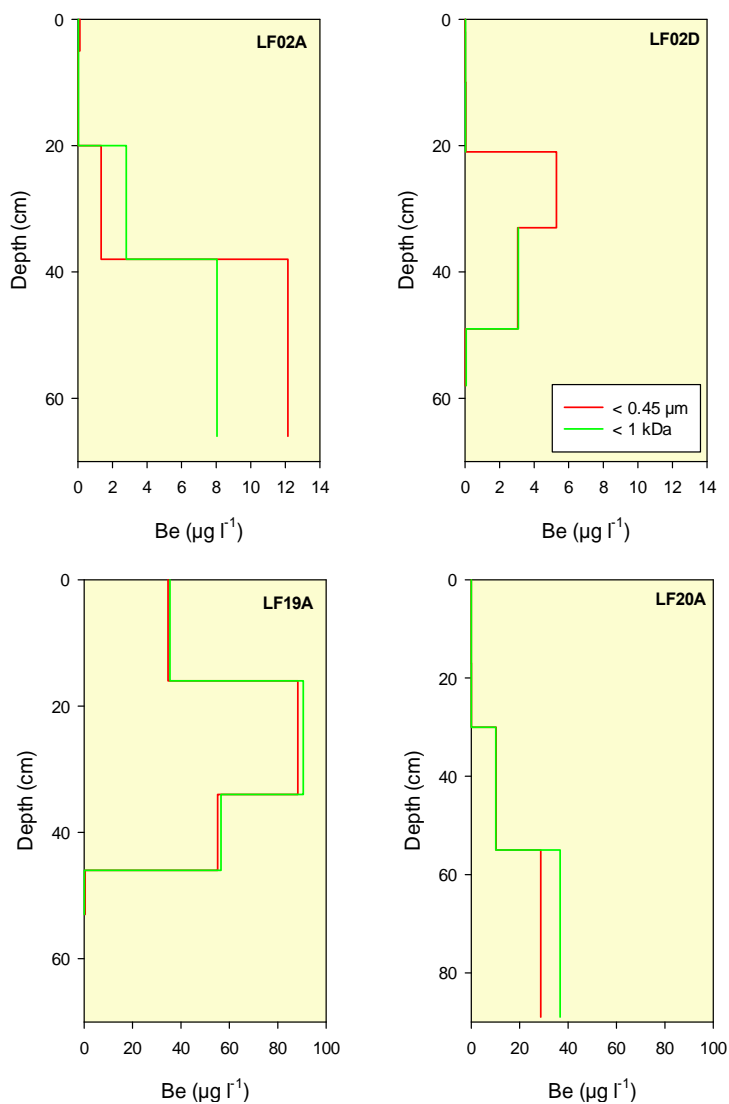


Figure 3-6 Porewater concentrations of beryllium (Be) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Be is $0.13 \mu\text{g l}^{-1}$

3.2.7 VANADIUM (V)

Porewater vanadium (V) concentrations are shown on Figure 3-7. The mobility of V is dependent on both pH and Eh, and the more reduced species, V(III) is not stable under oxidising conditions, substituting for Fe^{3+} in Fe oxides. Like As, it forms oxyanions in solution and may be mobile at both high and low pH in natural waters. In the Dog and Boggy Lake samples, V correlates well with SO_4 and Fe. The aqueous geochemistry of V is strongly controlled by both redox state and sorption onto iron oxide and clay minerals (Crans and Tracey, 1998). Adsorption of V(V) onto colloidal iron oxides produced at hydrothermal vents has been shown to control the concentration of V in seawater (Trefry and Metz, 1989) and ferric oxyhydroxides in particulate matter have been shown to control the chemistry of V in the English Channel (Auger et al. 1999). In the pH range of natural waters, V exists mainly as the vanadium (V) oxyanion, vanadate, the most common species being H_2VO_4^- . In acidic environments, especially under more reducing conditions, vanadyl oxyanion (V(IV)), becomes more abundant with the most common species being VO^{2+} . The presence of these V species in porewater samples would have a significant influence on the partitioning, mobility and bioavailability of V in sediments. Concentrations are relatively low at Point Sturt (LF02), typically below the ANZECC water quality guideline value of $6 \mu\text{g l}^{-1}$, although slightly higher in the deepest soil layers. In Boggy Lake (LF20A), and especially Dog Lake (LF19A), however, V concentrations are very high and present mainly in the dissolved fraction. Vanadium correlated well with Fe and SO_4 , especially in the more acidic samples where concentrations were high.

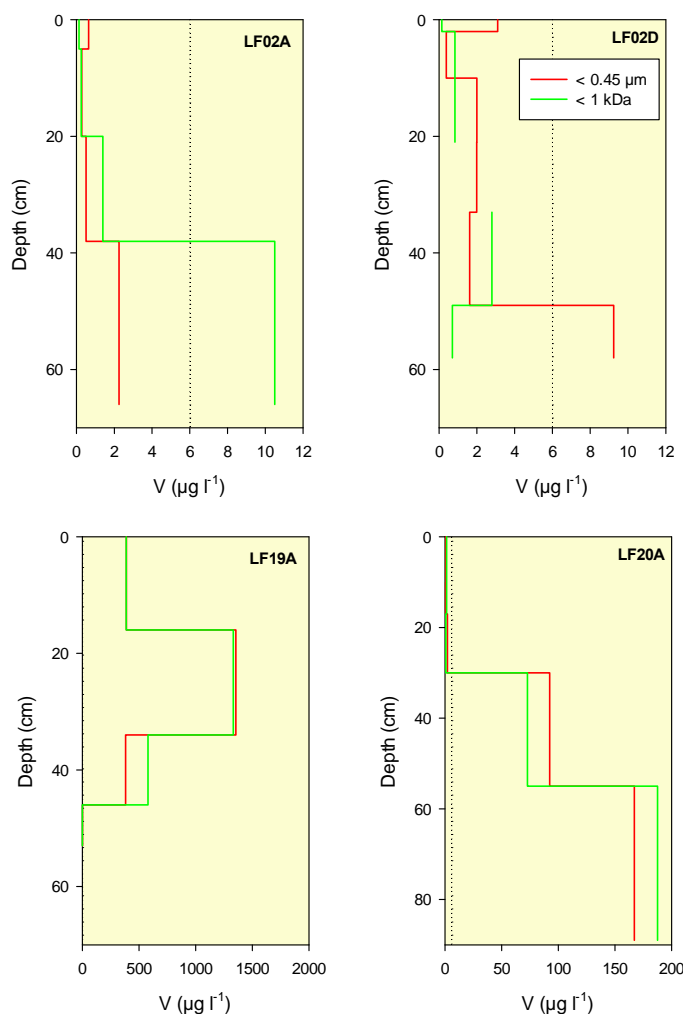


Figure 3-7 Porewater concentrations of vanadium (V) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) V is $6 \mu\text{g l}^{-1}$

3.2.8 CHROMIUM (Cr)

Porewater chromium (Cr) concentrations are shown on Figure 3-8. The shapes of the profiles are generally similar to other metal profiles, with very high concentrations in soil porewaters from Dog Lake (LF19A).

Chromium exists in a number of states in natural waters, but typically dominated by Cr (III) and the more toxic Cr (VI). Under the conditions present in the deeper soils, it is likely that Cr (III) is dominant, but possible that the hexavalent species may be present or have been present during the previous oxidation of the soils. Chromium is mainly in the dissolved fraction in the porewaters.

The porewaters display a general negative correlation of Cr with pH and a positive correlation with SO_4 , especially for the porewater samples with high metal contents.

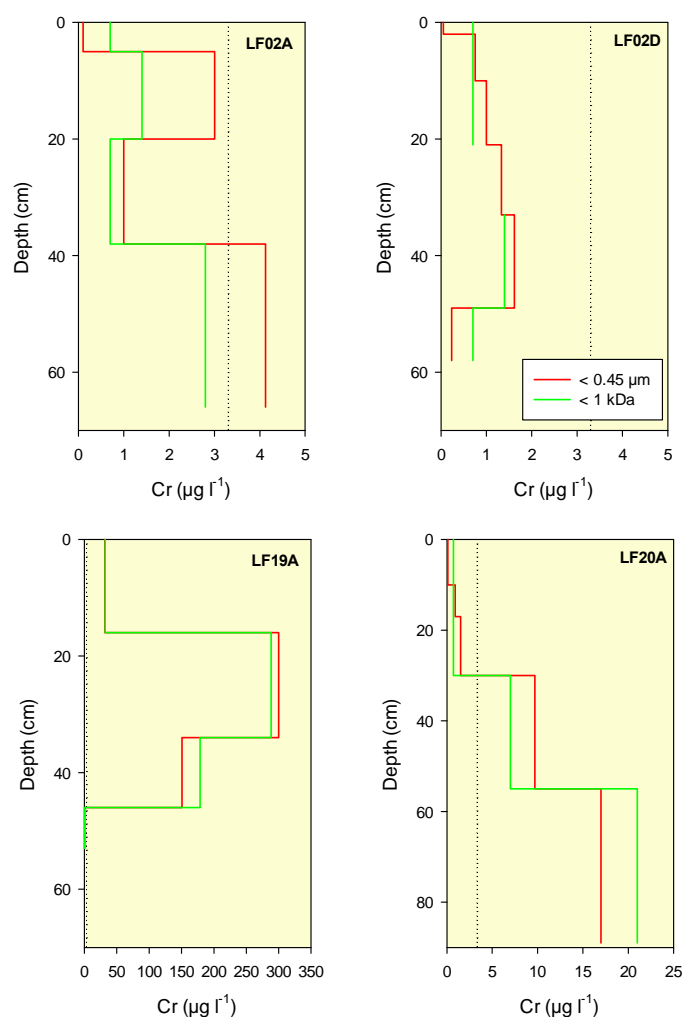


Figure 3-8 Porewater concentrations of chromium (Cr) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Cr (Cr III) is $3.3 \mu\text{g l}^{-1}$

Taking into account hardness algorithms for hardness, only the soils at LF19A were above corrected guideline values. However, the hardness values are extremely high and outside the range of parameters used to estimate such corrections.

3.2.9 NICKEL (Ni)

The concentrations of nickel (Ni) were below the ANZECC water quality guideline trigger values in the shallow soil porewater samples in three profiles, but high in the shallow soils of Dog Lake (LF19A). All profiles contained deeper layers with very high Ni concentrations (up to 3225 $\mu\text{g l}^{-1}$), well above the ANZECC water quality guideline trigger value of 11 $\mu\text{g l}^{-1}$ (Figure 3-9). Even taking into account hardness factors, many samples remained significantly higher than corrected guideline values. The profile shapes of Ni are very similar to Be (Figure 3-6).

Nickel is readily adsorbed onto Fe oxides, although typically to a lesser degree than Mn oxides. Although not a redox sensitive element, it can thus be controlled by redox processes by sorption/desorption onto oxide surfaces. For most samples Ni is present mainly in the dissolved fraction, except for the deepest sample in profile LF02A, where a large part may be present in the colloidal fraction, similar to Be and Al.

Nickel concentrations in porewater samples shows a negative correlation with pH, although the surface samples from Boggy Lake (LF20A) were low. It also displayed a general positive correlation with SO_4 .

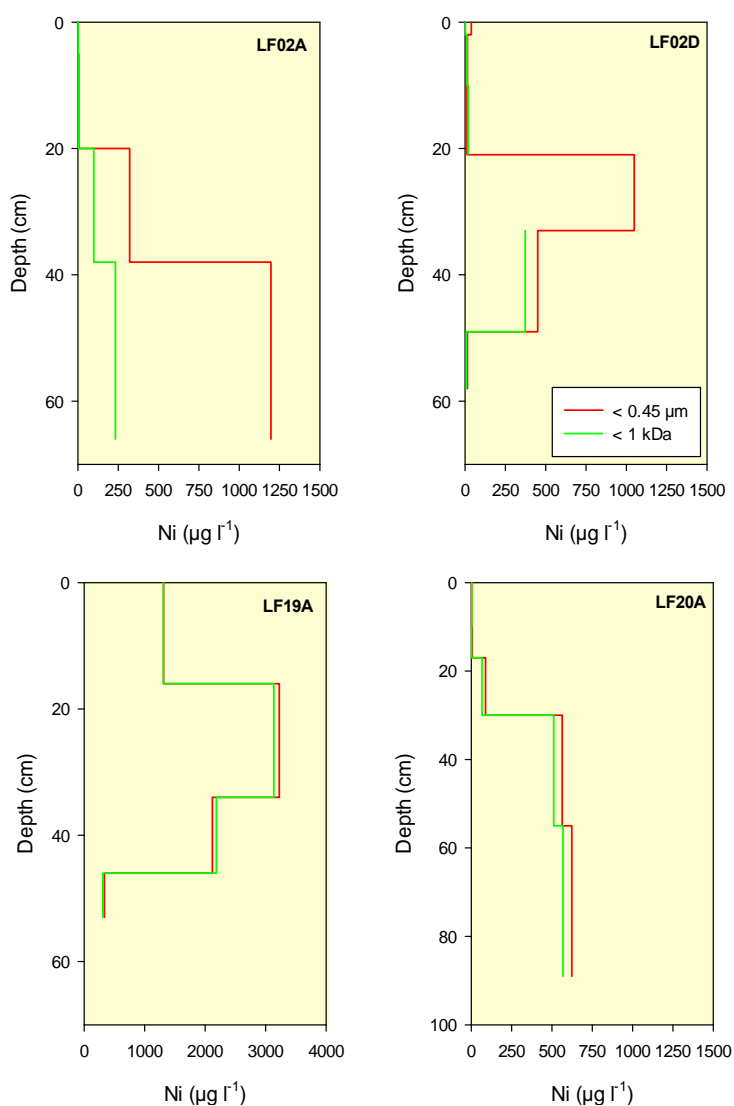


Figure 3-9 Porewater concentrations of nickel (Ni) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Ni is $11 \mu\text{g l}^{-1}$

3.2.10 ZINC (Zn)

The profile shapes for zinc (Zn) (Figure 3-10) are similar to those for Ni (Figure 3-9). It also displays similar correlations with pH and SO_4 . Like Ni, Zn is not a redox sensitive element, but its solubility and mobility may be controlled by redox processes as it may sorb to oxide surfaces. The solubilities of Zn carbonate and hydroxide are quite high, hence Zn may be soluble across a range of pH. In the porewater samples, the highest concentrations were present at low pH similar to the other metals studied.

For most samples Zn is present mainly in the dissolved fraction, except for the deepest sample in profile LF02A, where a significant part may be present in the colloidal fraction, similar to Be, Al and Ni. The concentrations of Zn were below the ANZECC water quality guideline trigger value in the shallow soil porewater in three profiles, but high in the shallow soils of Dog Lake (LF19A). All profiles contained deeper layers with very high Zn concentrations (up to $2072 \mu\text{g l}^{-1}$), well above the ANZECC water quality trigger value of $8 \mu\text{g l}^{-1}$ (Figure 3-10). Even taking into account hardness factors, many samples remained significantly higher than corrected guideline values.

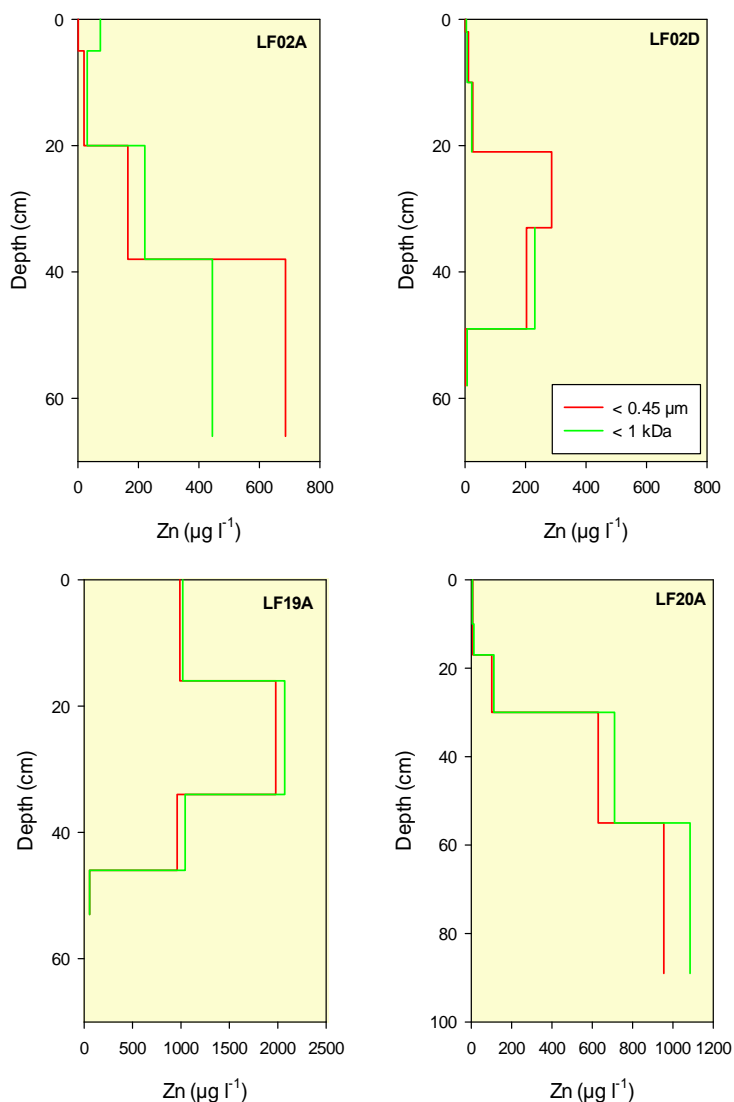


Figure 3-10 Porewater concentrations of zinc (Zn) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Zn is $8 \mu\text{g l}^{-1}$

3.2.11 ARSENIC (As)

Arsenic commonly has two main oxidation states in groundwater, As(III) and As(V). Under oxidising conditions, inorganic As occurs primarily in solutions as oxyanions, H_2AsO_4^- and HAsO_4^{2-} , in the pH range from 2–11. At low Eh values, the uncharged oxyanion H_3AsO_3 is the dominant As species present under reducing conditions. As(III) is more problematic than As(V) since As(III) is more toxic and mobile than As(V) (Viraraghaven et al. 1999; Smith et al.1998). However, disequilibrium is commonly observed because of slow kinetics of As redox reactions and microbiological effects. The capacity of iron oxides to adsorb As(V) is particularly well-documented, although the adsorption is strongly pH-dependent, being much less at high pH (greater than around 8.5). Nevertheless, As displays a negative correlation with pH and a positive correlation with SO_4 indicating similar geochemical behaviour in these soils, especially the Dog Lake and Boggy Lake samples, which display very similar porewater profiles to the metals studied.

The concentrations of arsenic (As) in soil porewater profiles are shown on Figure 3-11. Arsenic concentrations were significantly above the ANZECC water quality guideline values (Table 3-1) mainly in the deeper soils porewaters. Arsenic was found to be mainly in the dissolved fraction, although consistently higher concentrations in the $< 0.45 \mu\text{m}$ fraction above the $< 3 \text{ kDa}$ fraction suggests a significant colloidal fraction in this sample.

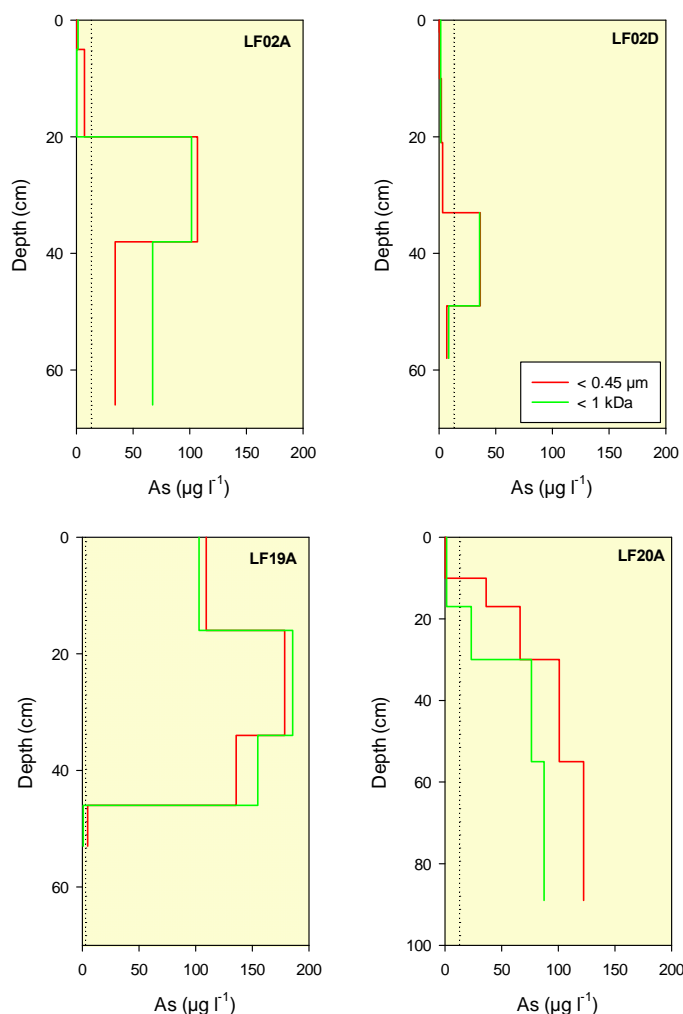


Figure 3-11 Porewater concentrations of arsenic (As) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) As (As V) is $13 \mu\text{g l}^{-1}$

3.2.12 LEAD (Pb)

The concentrations of lead (Pb) in soil porewater profiles are shown on Figure 3-12. Lead concentrations were highest in Dog Lake (LF19A) and Boggy Lake (LF20A), but were slightly higher than the ANZECC Guideline values of $3.4 \mu\text{g l}^{-1}$ in the deepest part of Point Sturt in profile LF02A. All samples were, however, less than guideline values corrected for water hardness.

In general, lead was present mainly in the dissolved fraction in porewater samples, with a maximum concentration of $10.4 \mu\text{g l}^{-1}$. It's mobility in waters is generally limited by sorption onto clays, organic matter and Fe oxyhydroxides, but it may be mobile under acidic conditions. Concentrations of Pb were highest in the porewaters at Dog Lake (LF19A) in the surface layers. Although the impacted sites are similar to the other metals, the profile shapes are slightly different. There is, however, still a negative correlation with pH for most samples and a positive correlation with SO_4 suggesting similar controls on solubility and mobility.

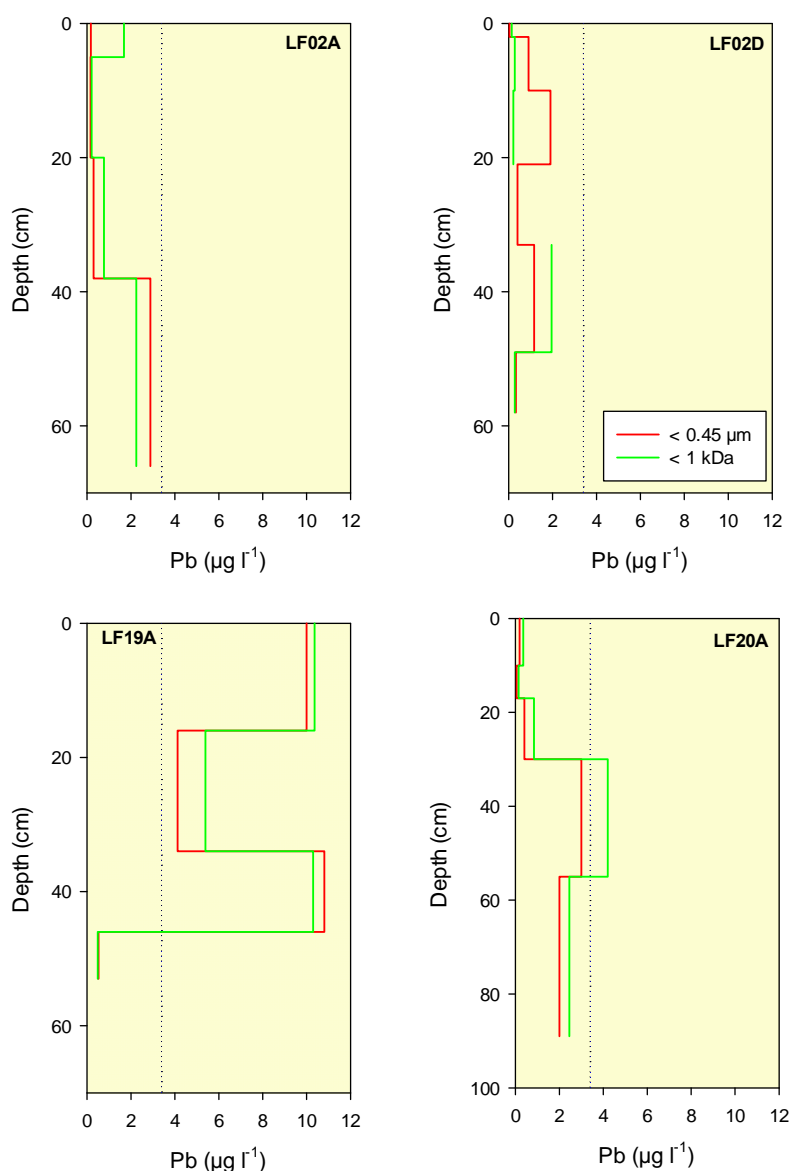


Figure 3-12 Porewater concentrations of lead (Pb) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) Pb (hardness dependent, see ANZECC Guidelines) is $3.4 \mu\text{g l}^{-1}$

3.2.13 URANIUM (U)

The porewater data for uranium (U) is shown on Figure 3-13. Concentrations were high in all profiles, reaching $35 \mu\text{g l}^{-1}$ in Dog Lake, more than an order of magnitude higher than the low reliability water quality guideline value of $0.5 \mu\text{g l}^{-1}$.

Uranium occurs dominantly as the hexavalent U (VI) species, and the quadrivalent U (IV) species is typically low because of the low solubility of the mineral uraninite. In oxidising conditions, at pH less than around 5, uranyl (UO_2^{2+}) is the dominant dissolved species. At higher pH, uranyl carbonate species become more important. Complexes with phosphate can also occur at near-neutral pH. Complexation with sulfide and fluoride can occur under acidic conditions and with Cl and SO_4 in saline conditions. As a result of this speciation behaviour, U is broadly expected to be more mobile under oxidising conditions and to have low concentrations in reducing groundwaters. Although Eh was not measured, the appearance of natrojarosite in some parts of the profile show that very oxidising conditions are present in these soil layers.

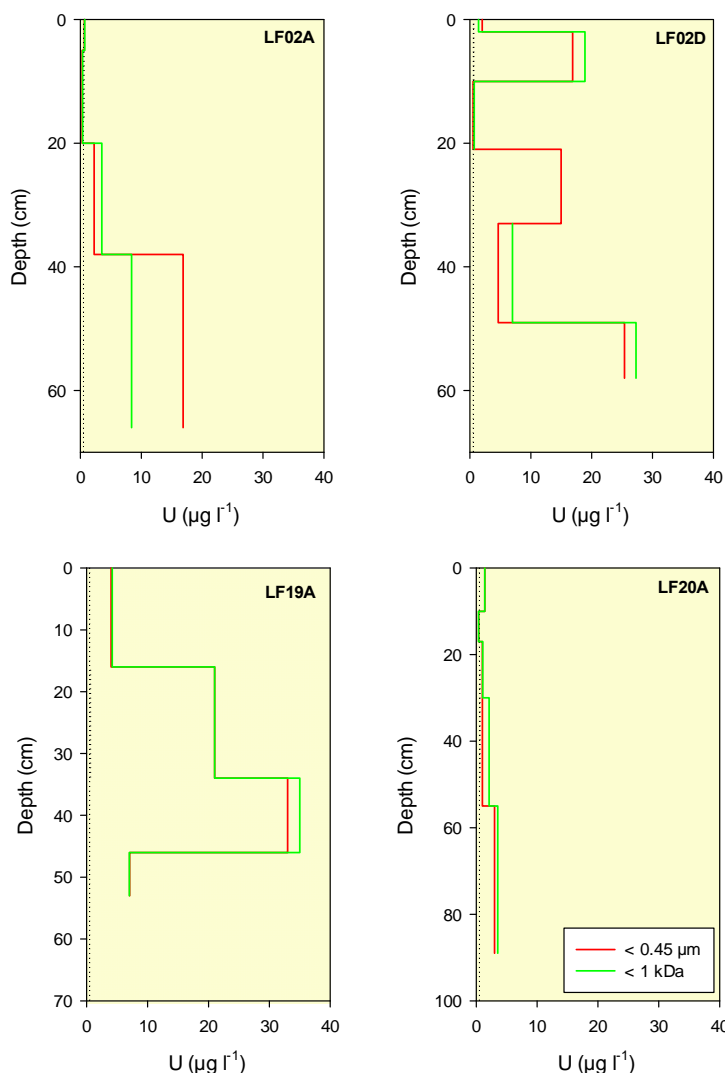


Figure 3-13 Porewater concentrations of uranium (U) in subaqueous soil profiles. ANZECC Freshwater Guideline for ecosystem protection (95%) U is $0.5 \mu\text{g l}^{-1}$

3.3 Summary of porewater chemistry

The concentrations of major and trace solutes in the subaqueous porewaters varied significantly between sites and within individual profiles. For three of the profiles (LF02A, LF02D & LF20A), the concentrations of major solutes were low in the upper soil, increasing with depth most likely as a consequence of downward flux of surface water from the Lake following increased water levels since 2010. This is also reflected in low concentrations of metals and metalloids in the upper layers of these profiles. In Dog Lake (LF19A), concentrations were relatively high in the shallow soil layer (0-10 cm) for a number of metals (as well as Na) consistent with a more loamy soil containing jarosite.

Metal and metalloid concentrations in porewaters were found to be mainly present as truly dissolved solutes. The main exception was the deepest soil layer at Point Sturt (LF02A), where the elements Al, Be, Ni, Cr, Zn and U (as well as Co, Y and the Rare Earth Elements) were present partly in the colloidal fraction. For both profiles at Point Sturt, Mn was also very high in a layer below the soil surface down to ca. 20 cm depth (Figure 3-5), where it was dominated by colloidal material.

Porewater samples from intermediate depths at Dog Lake (LF19A) were particularly high in a number of metals and metalloids, presenting the highest hazard site. Concentrations were significantly higher than Boggy Lake, despite Boggy Lake acidifying following refill. The potential effect of surface liming will be discussed in Chapter 5. At Point Sturt, contaminant concentrations tended to be highest in the deeper soil layers for the site furthest from the shore (LF02A), and at intermediate depths for the near shore profile (LF02D). Although not as high for some solutes in Dog and Boggy Lakes, the porewater concentrations at Point Sturt for some solutes were very high and well above ANZECC Guideline values (Table 3-1). Surface sediment porewater metal concentrations (actual hazard to benthic organisms) in some samples were found to exceed the 95% protection trigger values for some metals e.g. Cu, Ni, Tl, U, and Zn (Table 3-1). Porewater metal concentrations in surface sediment at LF19 were found to exceed the 95% protection trigger values for all metals examined, except Ag, Mo, Se and Sn (Table 3.-1). These findings highlight the importance in examining porewater metal concentrations in surface and sub-surface sediments as these metals represent the most mobile and bioavailable pool to organisms living in these environments.

4 Sequential Extractions

4.1 Introduction

The partitioning and lability of metal and metal contaminants can be assessed using soil extraction techniques which determine the potential availability of contaminants and distribution coefficients (e.g. Goody et al. 1995). Sequential extraction techniques have been successfully developed to remove gradually less labile contaminants with each step (Gleyzes et al. 2002). Although these are often assumed to provide information about 'solid-phase speciation', due to behaviour of individual elements and chemical composition of the sample, the technique strictly defines operational definitions (Nirel & Morel 1990). The operational definitions may include several phases, but are aimed at some of the more common mineral assemblages in soils. Therefore, care should be taken when extrapolating to specific mineral phases and the data are best assumed to represent a gradation of association with trace elements and the solid phase. These techniques have been modified by Claff et al. (2010b) to discriminate organic- and pyrite-bound iron in acid sulfate soils. As well as representing operational definitions, the sequence in reality is dependent on the redox status, hence the contaminants released in the nitric acid extraction may be more labile under oxidising conditions than earlier extractions might suggest. The association between the aqueous extract and potential sources is shown on Table 2-2. Hydroxysulfate minerals are a common feature of ASS in more arid climates, but their solubility and kinetics are very variable. Claff et al. (2010) showed that schwertmannite is likely to be dominated by the HCl extractions, whilst Jarosite was both HCl and CBD. Some hydroxysulfate minerals such as sideronatrite may belong to early extraction phases, but further work is required to test this.

The sequential porewater extraction data for trace metals and metalloids discussed in Chapter 3 are presented in this chapter to highlight the potential availability and likely mineral phases. There is very little information on the extraction range of complex hydroxysulfate minerals (e.g. natrojarosite, sideronatrite, alunite) for metals other than Fe as discussed above, which are found in oxidised acid sulfate soils, but these minerals are known to host a range of trace metals and metalloids (Hudson-Edwards & Wright 2011; Antelo 2012). Nevertheless, the data can be interpreted within a geochemical framework to provide a guide to the likelihood of contaminant hazard and impact under future changing geochemical conditions. Further work would be required to relate specific extractions to mineral phases in detail.

4.2 Sequential extraction data

This section presents selected porewater metal and metalloid concentrations data from the four profiles sampled (Table 2-1). These are plotted as horizontal bar graphs for consecutive extractions displaying both concentrations (mg kg^{-1}) and percentages for each soil layer and profile. The concentration plots highlight the total concentrations better, whilst the relative proportions of the element of interest is better shown on the percentage plots. These allow comparisons to be made of the availability of sorbed contaminants in the different soil layers. Porewater concentrations were recalculated on a dry soil weight basis and are also included on the plots.

4.2.1 ALUMINIUM (Al)

The concentrations of Al extracted in each sequential step are shown on Figure 4-1. All profiles showed an increase at depth. The dominant source of Al is present in the residual fraction, but significant concentrations are present in more labile forms, particularly the sodium pyrophosphate ‘organic’ fraction (purple); aluminium is known to form strong complexes with organic matter. Aluminium was also present in the exchangeable ($MgCl_2$) and poorly ordered oxide/sulfide acid soluble phases (red and green) at concentrations (up to 334 and 771 $mg\ kg^{-1}$ in the $MgCl_2$ and HCl extractions respectively) that could pose a risk if mobilised. The high dissolved Al concentrations (Figure 3-3) in porewaters already show that it is currently a hazard in these soils.

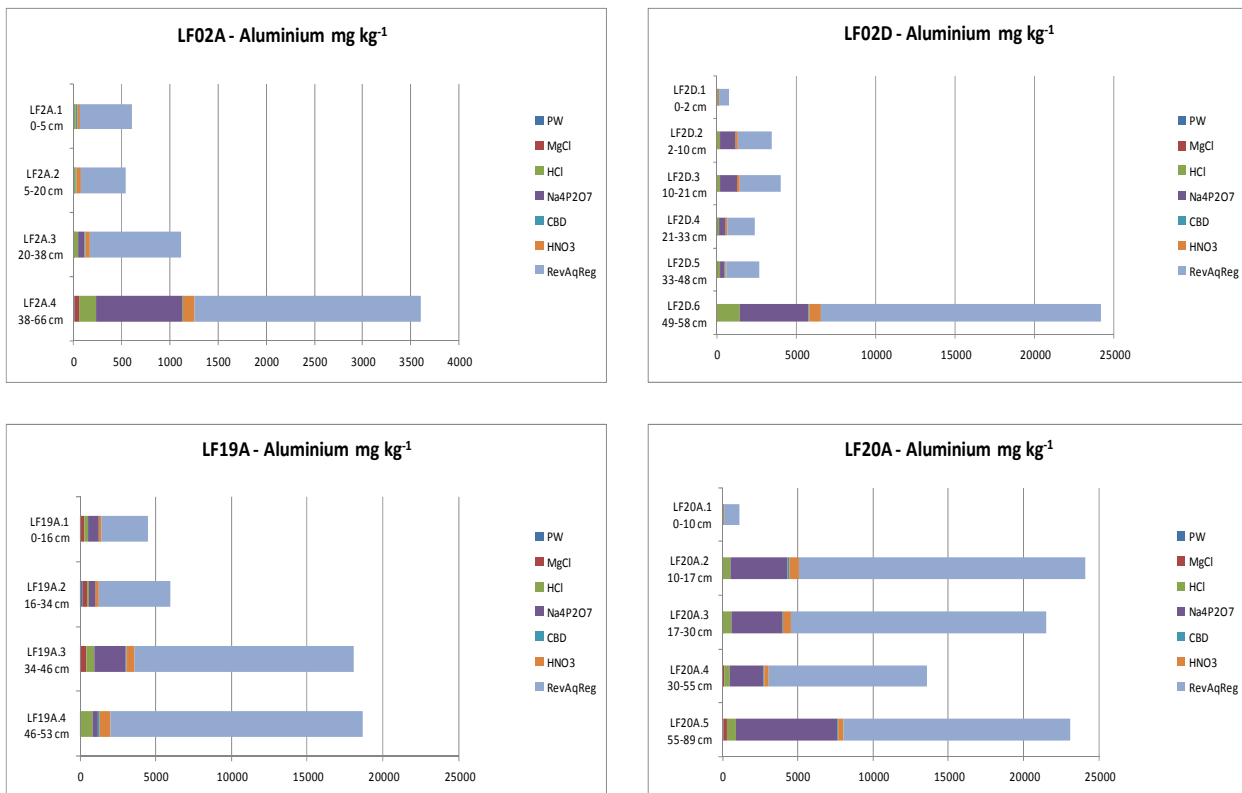


Figure 4-1 Sequential extraction data for Al in the subaqueous soil samples. Note the difference in scale for LF2A.

Aluminium was also present in the HNO_3 extraction step, but is unlikely to be derived from pyrite, probably being present in a more resistant phase (possibly a crystalline Fe oxide) than previous extractions released due to the higher strength of the nitric acid extraction.

The data are shown as percentages on Figure 4-2. The acid (HCl and HNO_3) extractions are both important in the shallow layers, with the organic fraction becoming more dominant at depth, and percentages of non-residual Al are generally lowest in the shallowest layer. However, the shallow soil layer in Dog Lake (LF19A) had the highest non-residual Al in the shallow soil layer and was present in a range of extraction steps. It was also in this profile that exchangeable Al was most significant.

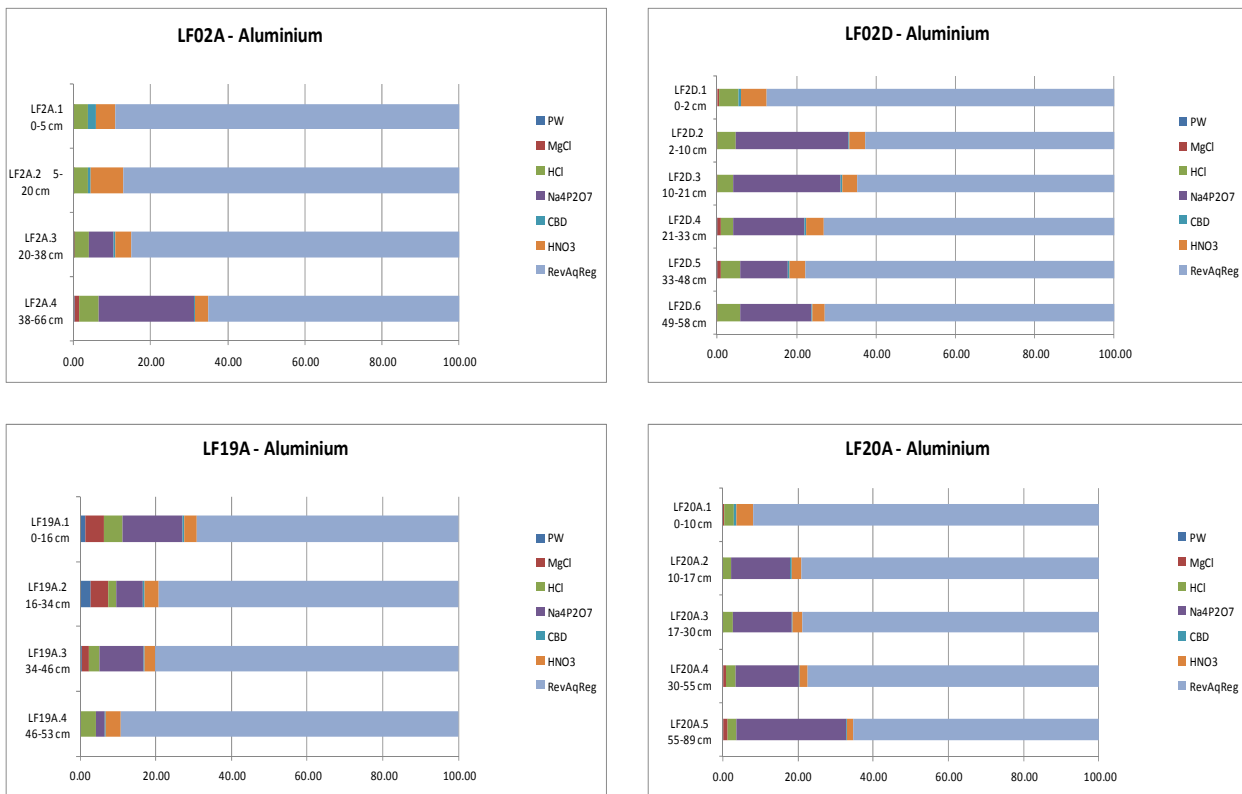


Figure 4-2 Sequential extraction data for Al in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.2 IRON (Fe)

The sequential extraction data for Fe are shown on Figure 4-3. The porewater concentrations presented previously (Figure 3-4) show a similarity to the exchangeable fraction (MgCl_2), being higher in Dog Lake and Boggy Lake and correlating with layers of high solute Fe. All samples had significant HCl extractant concentrations, most likely sorbed to a poorly crystalline Fe oxyhydroxide or sulfate phase. It is tentatively suggested that the presence of Fe in the dithionite (CBD) extraction is due to Fe derived from natrojarosite or its recrystallised product goethite as these were observed in the soils during sampling.

The high concentrations of Fe in the nitric acid extraction step is consistent with the presence of pyrite in deeper layers as evidenced from acid base accounting data (Appendix B). However, concentrations are lower than those found with the CRS method, indicating that there was Fe present in other sulfide forms apart from pyrite. It may also have been due to poor recovery of Fe or oxidative loss during sample preparation (Claff et al. 2010). The Fe mobilised in the residual fraction may represent Fe in insoluble mineral phases such as silicate minerals or crystalline Fe phases such as goethite not removed in previous extractions.

High concentrations of Fe were found in the MgCl_2 and HCl extraction steps in the surface sediments and deeper sediment layers, especially in LF19A and LF20A profiles (Figure 4-2). These sequential extraction steps were used to estimate the potentially labile and reactive phases of Fe in these sediments. Trace metals (e.g. As) are known to be associated to a high degree with Fe phases in sediments. The sequential extraction data suggests Fe (and possibly associated trace metals) may be in pools in sediments (especially subsurface sediments at LF19A and LF20A) that may be readily mobilised into porewater under changing environmental conditions (e.g. soil acidification).

The data are shown as percentages on Figure 4-2. The profiles from Point Sturt (LF02A and D) and Boggy Lake (LF20A) showed similar changes with depth for the relative proportions of the non-residual fractions:

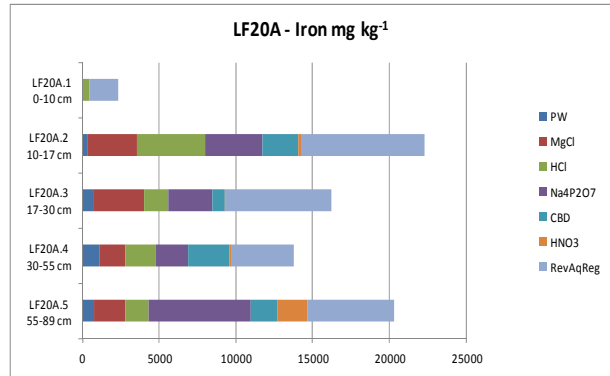
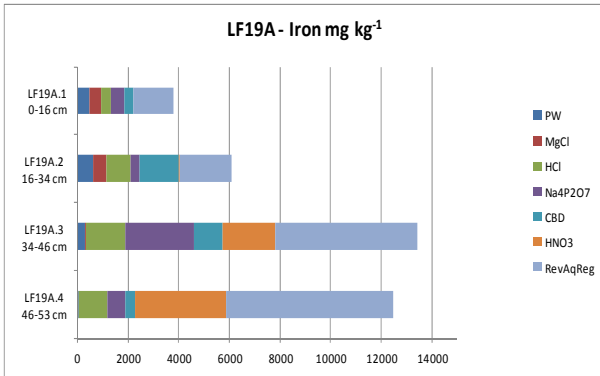
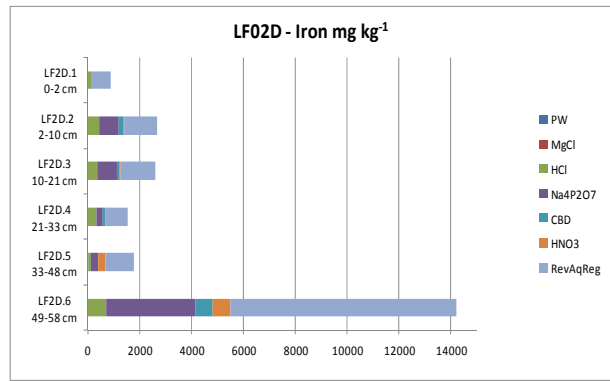
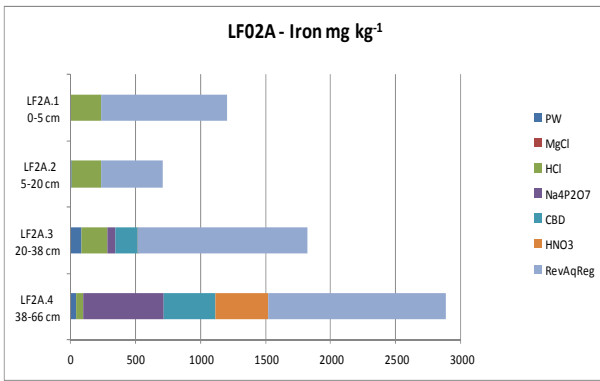


Figure 4-3 Sequential extraction data for Fe in the subaqueous soil samples. Note the differences in scale.

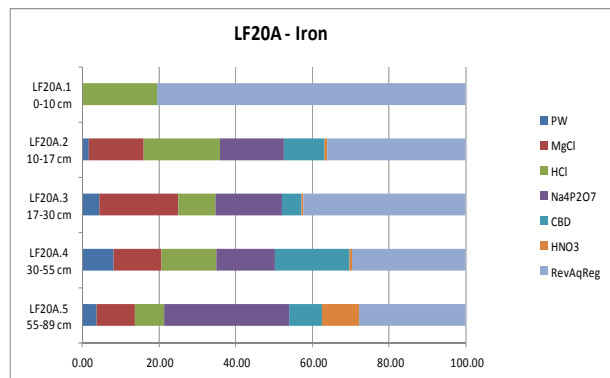
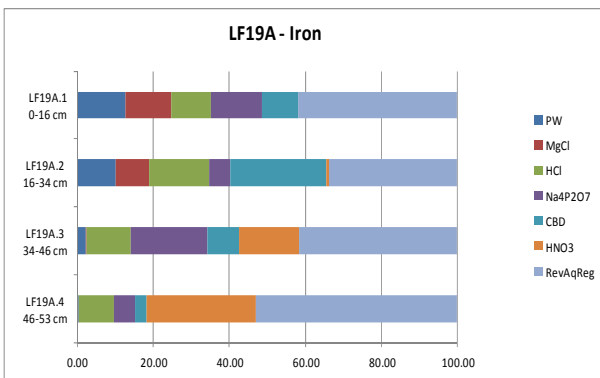
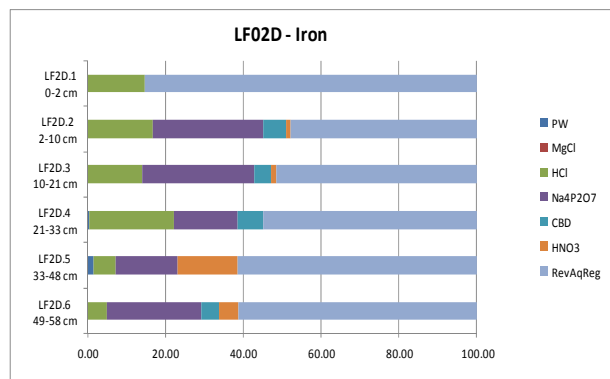
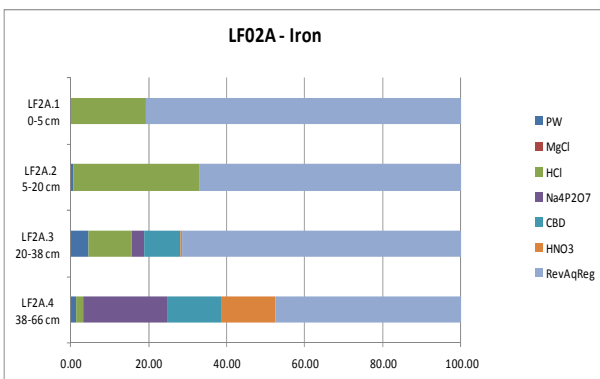


Figure 4-4 Sequential extraction data for Fe in the subaqueous soil samples showing the data plotted as percentages of the total.

the dominant fraction in the shallow layers was the HCl fraction, with the pyrophosphate fraction becoming important below this layer, and finally the nitric acid fraction being significant in the deepest soil layers

where Cr-reducible sulfide was present. The MgCl fraction was important at Boggy Lake, but largely absent in the Point Sturt soil extractions. Dog Lake was similar to Boggy Lake, but with a range of extractions containing Fe in the shallow layer (Figure 4-4).

4.2.3 MANGANESE (Mn)

The concentrations of Mn extracted in each sequential step is shown on Figure 4-5. The very high porewater concentrations at Point Sturt (LF02) and other site profiles in some soil layers have been discussed in section 3.2.5, and may be due to reductive dissolution of Mn(III,IV) solid phases and the present of very high amounts of colloidal material in some layers. Exchangeable Mn was present in the soil layers beneath the top layer, with the exception of Dog Lake (LF19A) where it was relatively high in all soil layers.

The dilute acid extraction (HCl) provided small amounts of Mn in all samples, and moderately high in the deeper parts of LF02D and LF19A. The 'organic' fraction contained some Mn mainly in deeper soil layers. There was little Mn in the dithionite extraction (CBD) implying that if more crystalline Fe oxide phases were present they contained little Mn in their structure.

Manganese formed a significant component in the nitric acid extraction and also in the residual fraction. It is not known if the Mn is present in a crystalline Fe oxide or within insoluble silicate minerals. The lability of Mn is high in the soils as indicated by high exchangeable Mn and high Mn concentrations in solution (Figure 3-5).

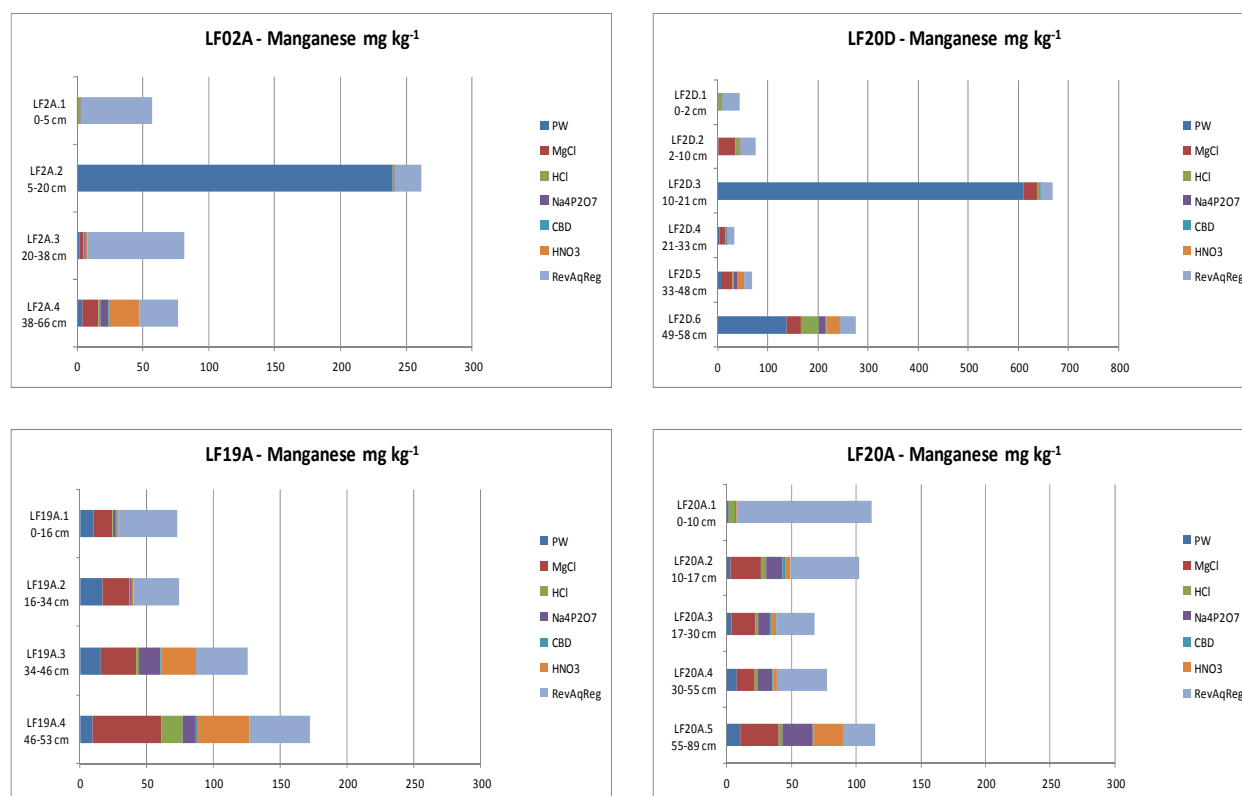


Figure 4-5 Sequential extraction data for Mn in the subaqueous soil samples. Note the differences in scale.

High concentrations of Mn were found in the MgCl₂, and HCl extraction steps in the surface and deeper sediment layers, especially in LF19A and LF20A profiles (Figure 4-3). These sequential extraction steps were used to estimate the potential labile and reactive phases of Mn in sediments. Trace metals (e.g. Co) are known to associate to a high degree with Mn phases in sediments. The sequential extraction data suggests Mn (and possibly associated trace metals) in sediments (especially subsurface sediments at LF19A and

LF20A) may be readily mobilised into porewater under changing environmental conditions (e.g. soil acidification).

The data are shown as percentages on Figure 4-6. This highlights better the soil layers with high dissolved Mn, the importance of residual Mn at shallow depth, increase in the proportions of non-labile Mn with depth and the importance of exchangeable (MgCl₂) Mn in the soil layers.

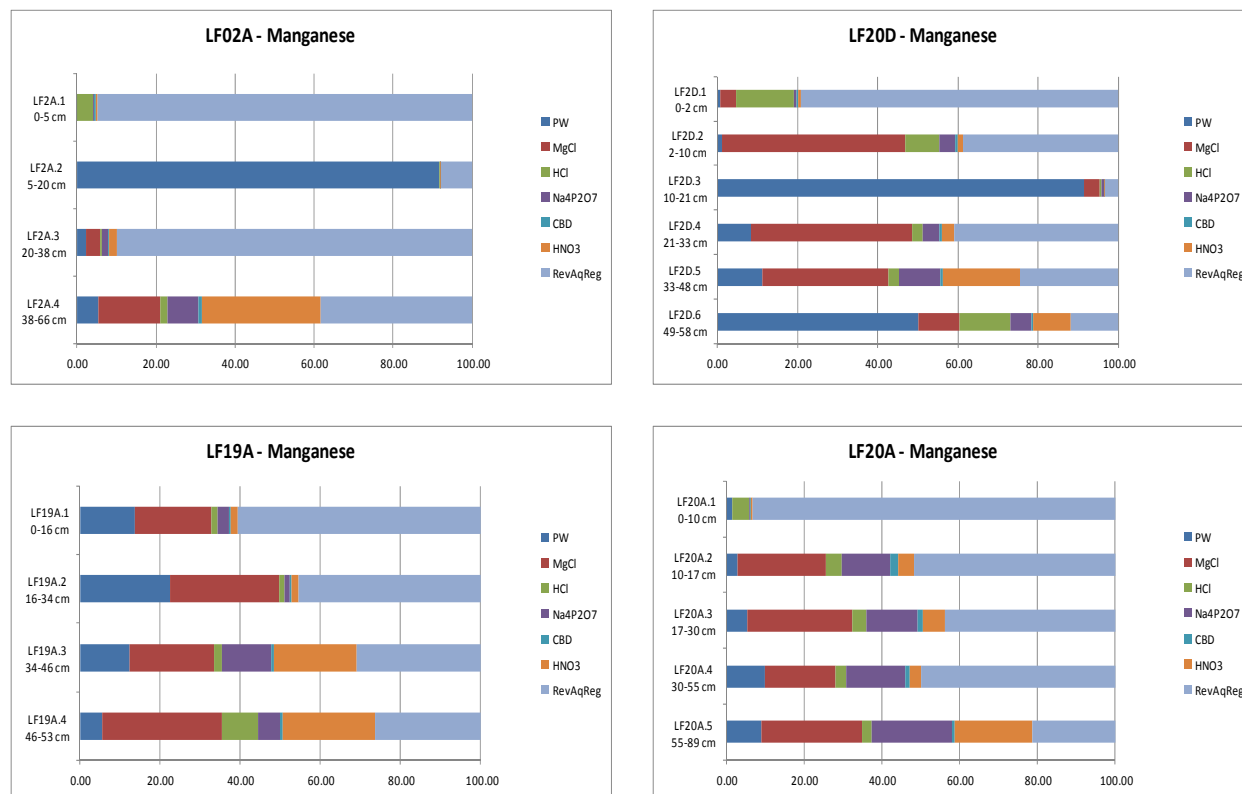


Figure 4-6 Sequential extraction data for Mn in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.4 BERYLLIUM (Be)

The sequential extraction data for Be are shown on Figure 4-7 and Figure 4-8. There is little information available for Be in natural waters, but it is known to be more mobile under acidic conditions (Edmunds & Trafford 1992). High concentrations have been noted in oxidised acid sulfate soils where the pH is low (Shand et al. 2010).

The lowest concentrations were present in LF02A, the deepest profile at Point Sturt. Beryllium was sufficiently labile that high solute concentrations were present in some samples from Dog Lake and Boggy Lake. Exchangeable Be was really only present in moderate concentrations in a few soil layers, with much higher concentrations in the HCl extract, possibly adsorbed to poorly crystalline Fe oxyhydroxides.

The 'organic' pyrophosphate extraction also showed moderately high concentrations of Be. Although little is known in detail about Be complexing with organic matter, high concentrations in coal and coal ash and its occurrence in some plants suggest that it may be important.

Lesser concentrations were derived from the nitric acid extraction, with most being typically present in the residual fraction. Similar to Fe, high concentrations of Be were found in the MgCl₂, and HCl extraction steps in surface and deeper sediment layers, especially in LF19A and LF20A profiles (Figure 4-7). This data suggests Be is in pools in sediments (especially subsurface sediments at LF19A and LF20A) that can be readily mobilised into porewater under changing environmental conditions (e.g. soil acidification).

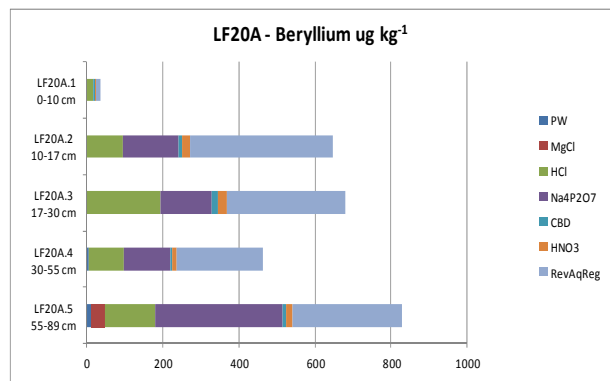
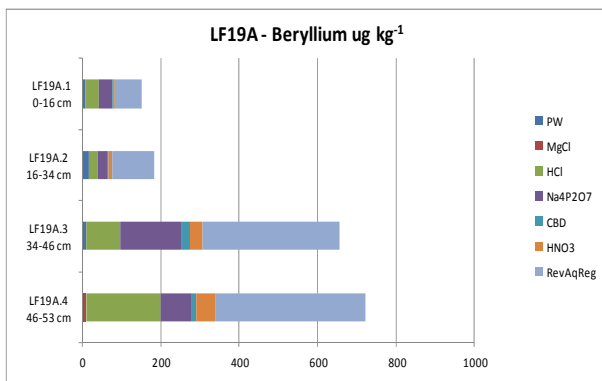
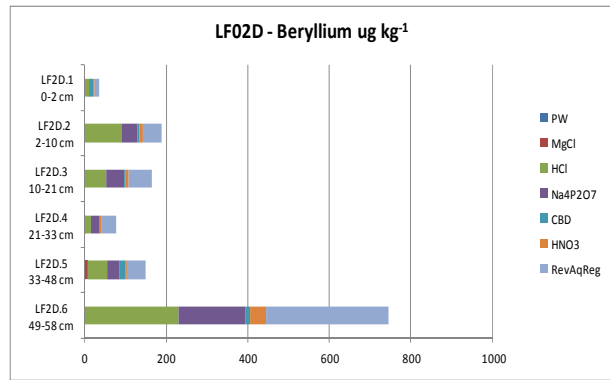
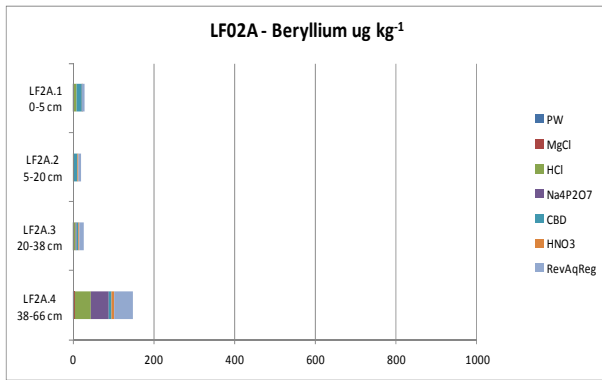


Figure 4-7 Sequential extraction data for Be in the subaqueous soil samples. Note the differences in scale.

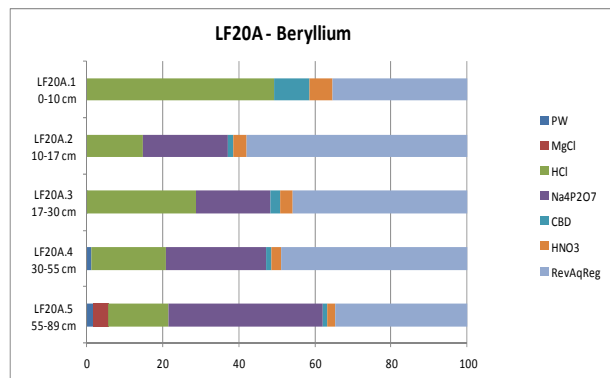
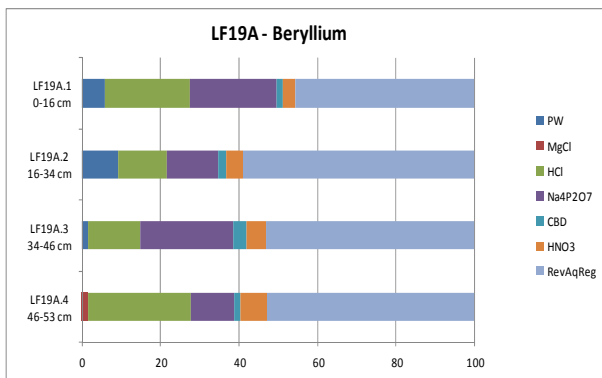
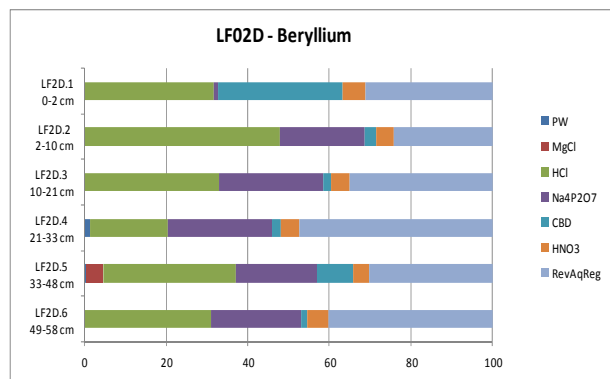
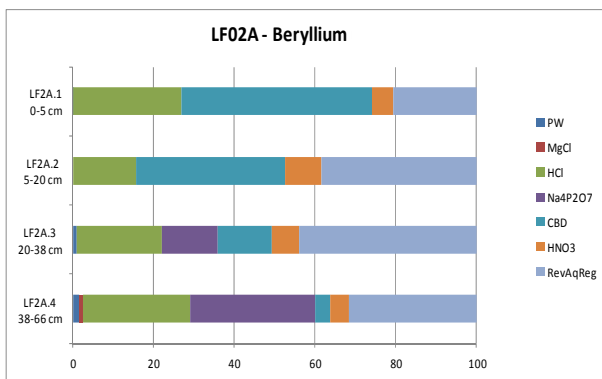


Figure 4-8 Sequential extraction data for Be in the subaqueous soil samples showing the data plotted as percentages of the total.

The data are plotted as percentages on Figure 4-8. The likely importance of Fe-oxide/oxyhydroxide mineral phases is suggested by the relatively high proportions of Be in the HCl and, in the shallow soil layers, the dithionite (CBD) extraction steps. The pyrophosphate concentrations and proportions also suggest that the organic fraction is important in binding Be, whilst low $MgCl_2$ extraction concentrations indicate little exchangeable Be in the soils. The presence of Be in the nitric acid extraction is unlikely to be related to its presence in sulfides as Cr-reducible sulfide was not present in all of these soil layers. As for Al, it is most likely to be associated with a poorly soluble Fe-oxide phase.

4.2.5 VANADIUM (V)

The sequential extraction data for V are shown on Figure 4-9. As with most trace elements, concentrations in profile LF02A were much lower than in the other profiles.

Despite very high dissolved concentrations in profile LF19A, most V is present in the solid phase. Exchangeable V was measured in all profiles, but with much higher concentrations in the HCl extraction. Relatively high concentrations were also associated with the pyrophosphate extraction in the deeper soil layers of profiles LF02D, LF19A and especially LF20A, where organic contents are quite high in these soil layers (Appendix C). Vanadium forms an oxyanion and is known to be sorbed especially at lower pH to organic matter. Vanadium was also present to a lesser degree in the dithionite and nitric acid extractions, and often high in the residual fraction.

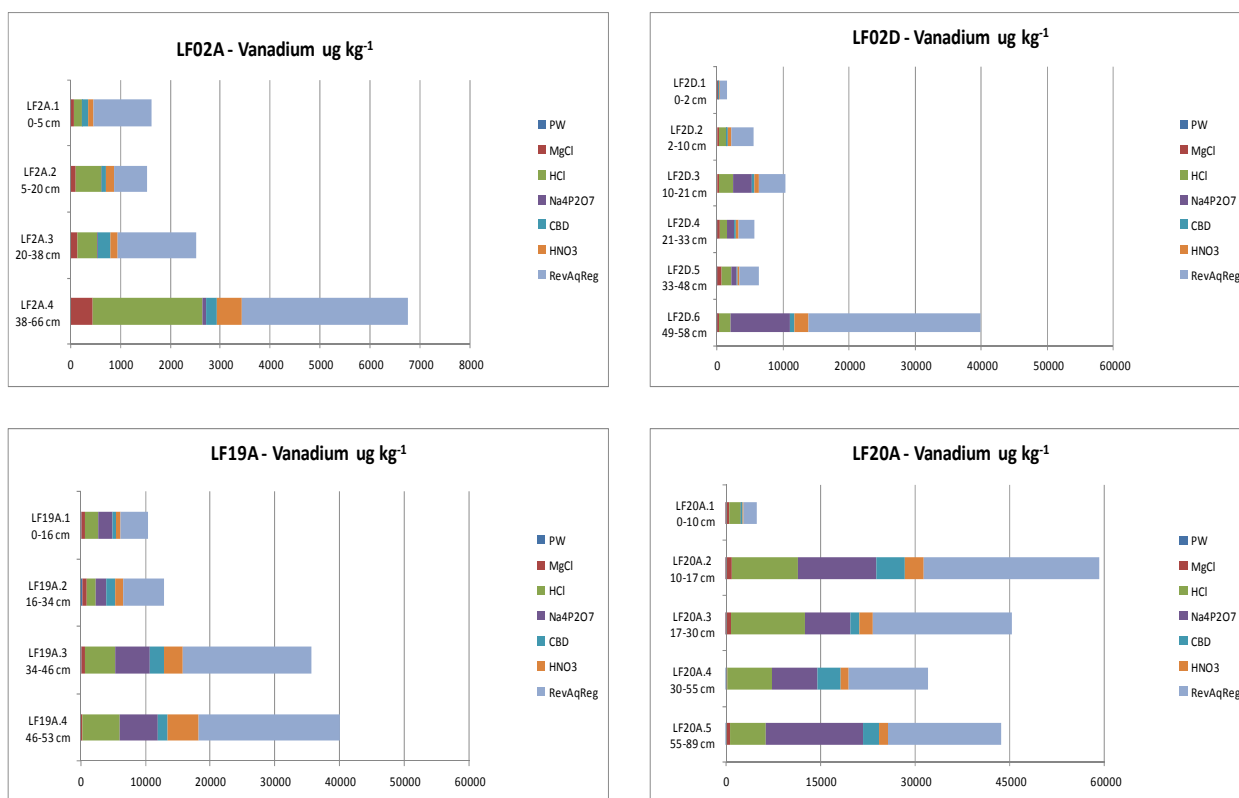


Figure 4-9 Sequential extraction data for V in the subaqueous soil samples. Note the differences in scale.

High concentrations of V were found in the $MgCl_2$, HCl and pyrophosphate extraction steps in surface and deeper sediment layers, especially in LF19A and LF20A profiles (Figure 4-9). The sequential extraction steps were used to estimate the potential labile and reactive inorganic and organic phases of V in these sediments. The data suggests V may be in pools in sediments (especially subsurface sediments at LF19A and LF20A) that can be readily mobilised into porewater under changing environmental conditions. These pools of V may represent a high potential hazard to sediment benthic organisms in dynamic acid sulfate soil systems.

The data are plotted as percentages on Figure 4-10, where the importance of the HCl and pyrophosphate extracts can be seen. Vanadium concentrations were negligible for the pyrophosphate extraction in LF02A, although present for LF02D (closest to shore), which may be a function of the lability of the organic matter (there was little difference in total organic C). Exchangeable V was also significant, and sufficient to cause water quality problems if mobilised into porewaters. The V in the nitric acid extraction, as with Al and Be, may be due to association with a crystalline Fe phase, since pyrite was not present in many of the soil layers.

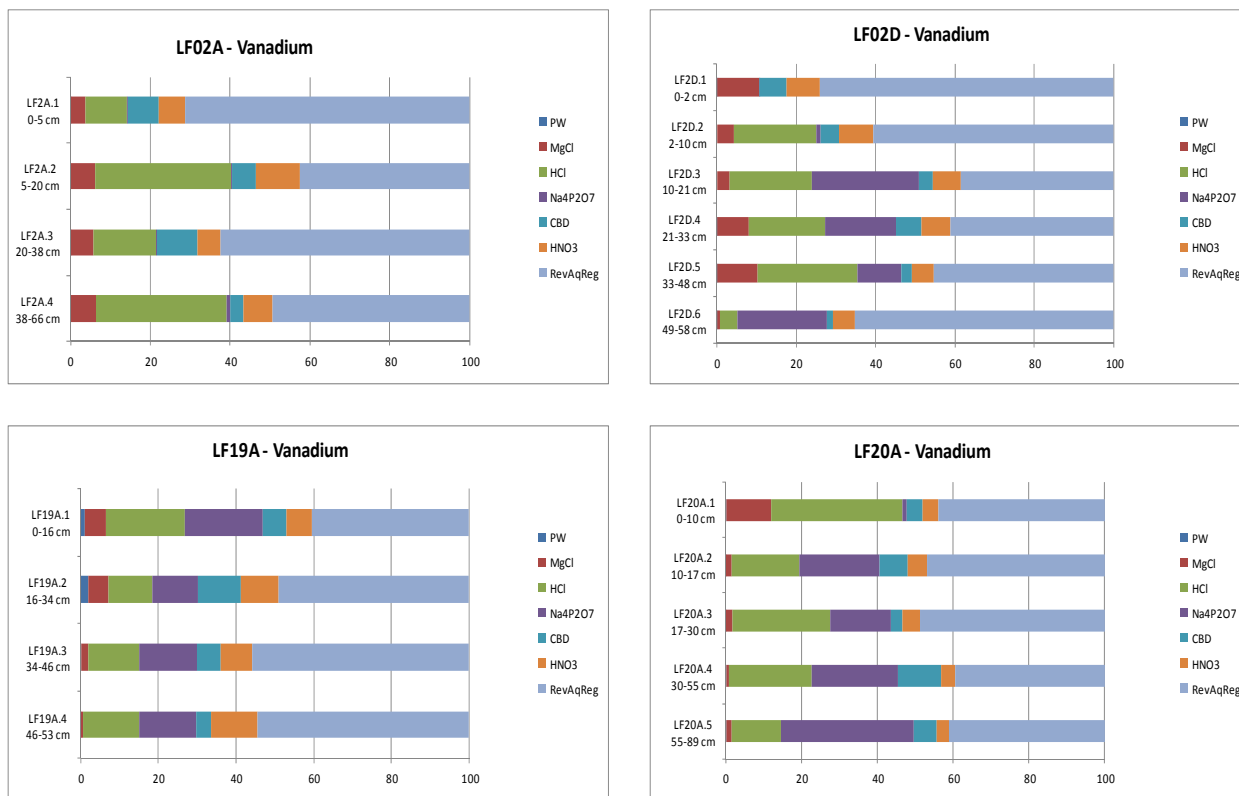


Figure 4-10 Sequential extraction data for V in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.6 CHROMIUM (Cr)

The sequential extraction data for Cr are shown on Figure 4-11. Chromium forms a number of inorganic and organic complexes, especially at higher pH, and is generally more mobile under acidic conditions. The dominant fraction of Cr is in the residual phase for all samples.

The fraction of Cr in the solution and exchangeable fraction is relatively small in comparison with other fractions, however concentrations in solution were moderately high, especially in Dog Lake (Figure 3-8). The weak HCl acid extraction, although not a dominant fraction, still has concentrations of concern (up to 2154 mg kg⁻¹) should they become bioavailable. The 'organic' fraction (pyrophosphate extraction) represents a major sink for Cr, especially in the deeper parts of the profiles. It is not clear if the Cr released is in the nitric acid phase or present in pyrite as the distribution shows little correlation with sulfide content; it may be that it is present in a more resistant mineral not extracted previously.

The sequential extraction data are plotted as percentages on Figure 4-12. The residual fraction is more clearly dominant in most soil samples, with the acidic fractions being important as well as the dithionite (organic) fraction in deeper layers.

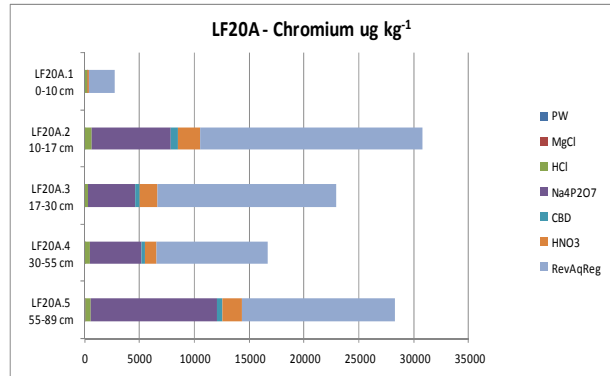
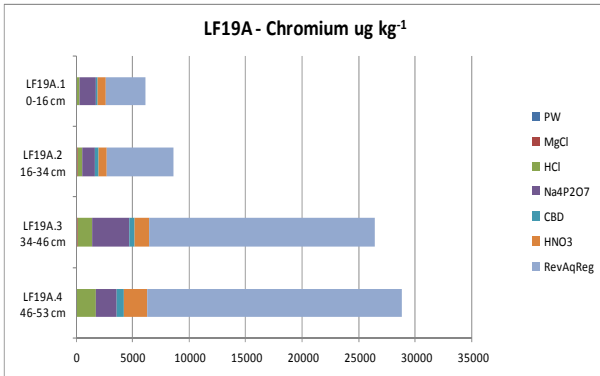
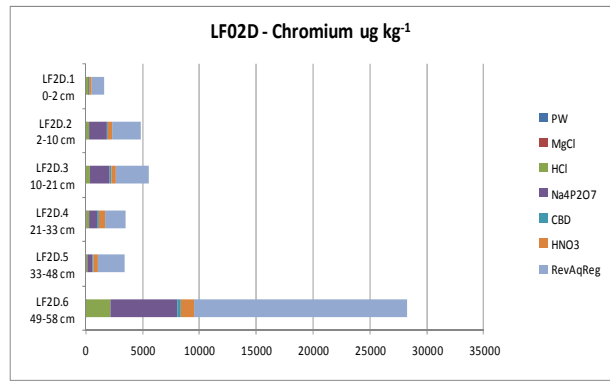
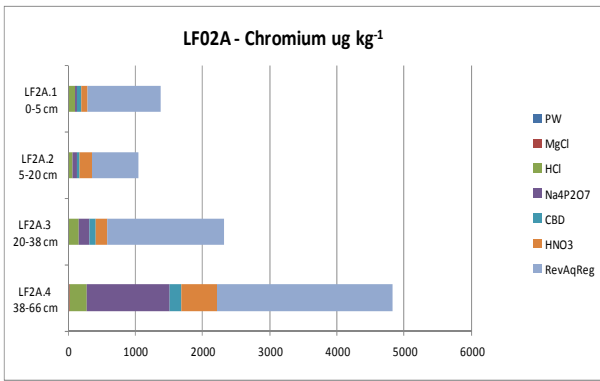


Figure 4-11 Sequential extraction data for Cr in the subaqueous soil samples. Note the differences in scale for LF02A.

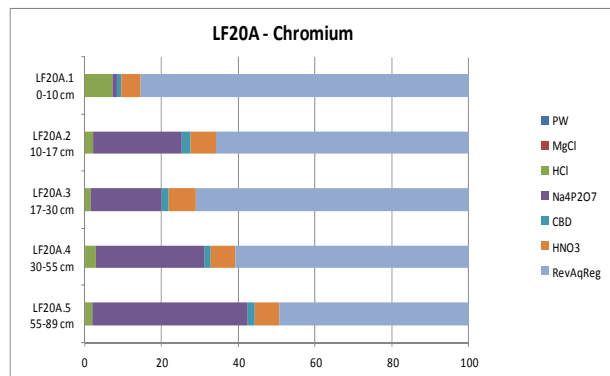
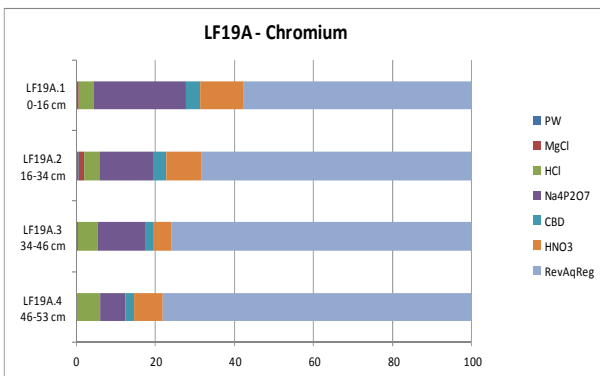
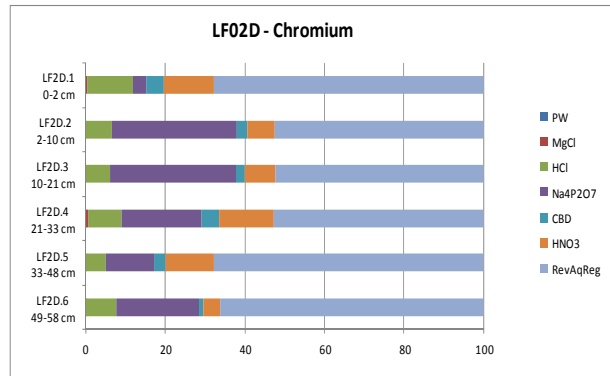
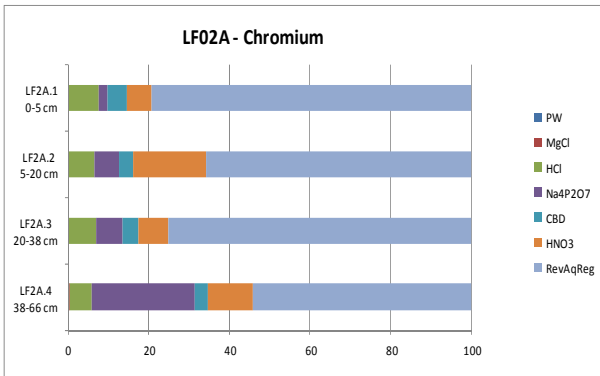


Figure 4-12 Sequential extraction data for Cr in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.7 NICKEL (Ni)

The sequential extraction data for Ni are shown on Figure 4-13. Nickel is common in the residual fraction. It is often associated with Mn oxides, but is also associated with Fe oxides, carbonate and organic matter (Christensen & Christensen 1999), and is scavenged by sulfide minerals in strongly reducing environments.

The porewater and exchangeable concentrations of Ni represent a hazard with concentrations up to more than 3 mg l^{-1} in solution (Figure 3-9) and $1250 \mu\text{g kg}^{-1}$ in the MgCl_2 extract. Concentrations were high in the HCl and pyrophosphate extractions in most soil layers. Nickel was also significant in the dithionite extract in some profiles, in general the deeper layers, but not dominant. The presence of high Ni in the nitric acid fraction is consistent with incorporation in pyrite.

High concentrations of Ni were found in the MgCl_2 , HCl and pyrophosphate extraction steps in deeper sediment layers, especially in LF20A profiles (Figure 4-7). The data suggests Ni may be in pools in sediments (especially subsurface sediments at LF19A and LF20A) that can be readily mobilised into porewater under changing environmental conditions (e.g. soil acidification,). The presence of significantly high Ni concentrations in the HNO_3 fraction is consistent with incorporation in pyrite and represents a potential hazard under changing environmental conditions that promote oxidation of pyrite. The mobilisation of Ni into porewater will depend on the solubility the pure/mixed Ni sulfide phases and reactions of released Ni in sediment porewater (e.g. precipitation, complexation, competitive exchange, etc.).

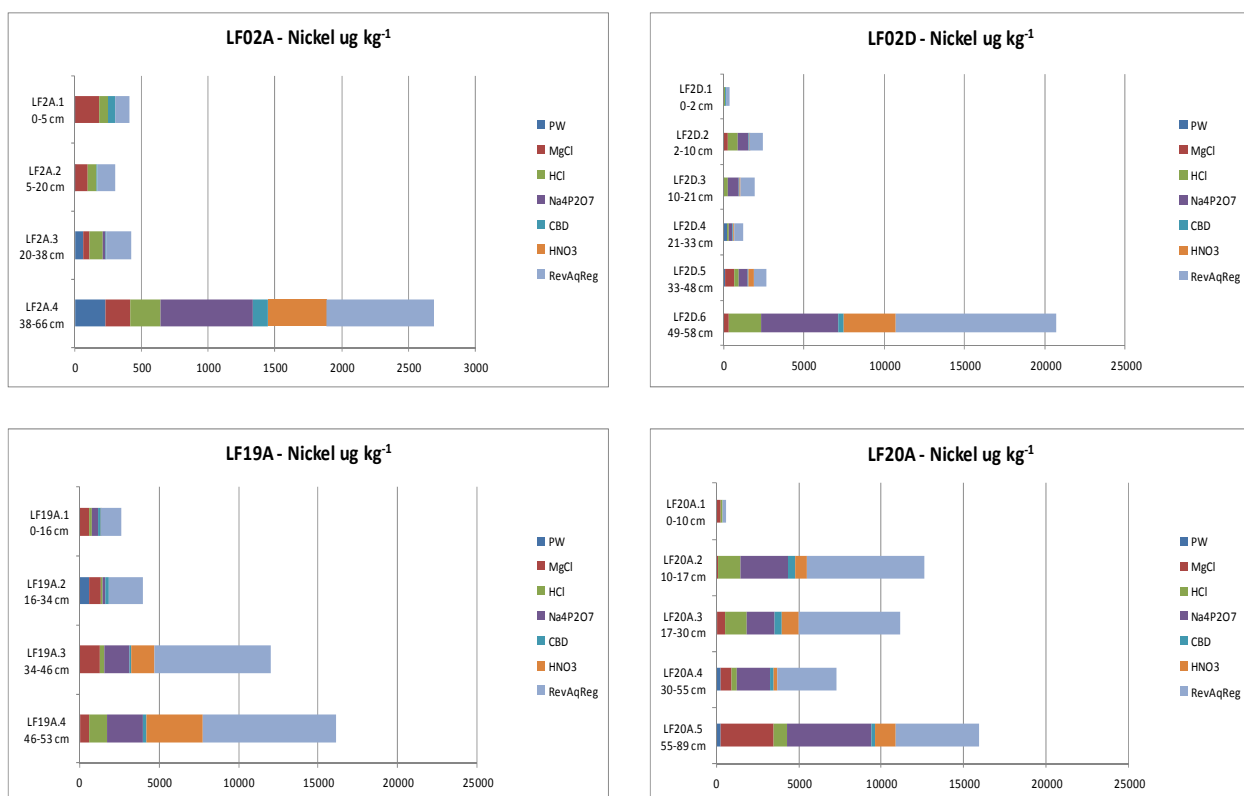


Figure 4-13 Sequential extraction data for Ni in the subaqueous soil samples. Note the differences in scale for LF02A.

The percentage plots show more clearly the differences in proportions for the different soil layers (Figure 4-14). The differences between the two Point Sturt profiles are clear, with exchangeable Ni being more important in the LF02A profile furthest from shore. Exchangeable concentrations were also high in Dog Lake and Boggy Lakes especially the shallowest soil layer. The pyrophosphate fraction was significant in most soil layers at depth, but like many other metals it was significant in this extraction in Dog Lake

(LF19A). For the HCl extraction, Ni was present in all soil layers, and also in the dithionite extract indicating a control by more crystalline Fe oxides. The data are also consistent with incorporation in pyrite in the deeper soil layers where Cr-reducible sulfide was present.

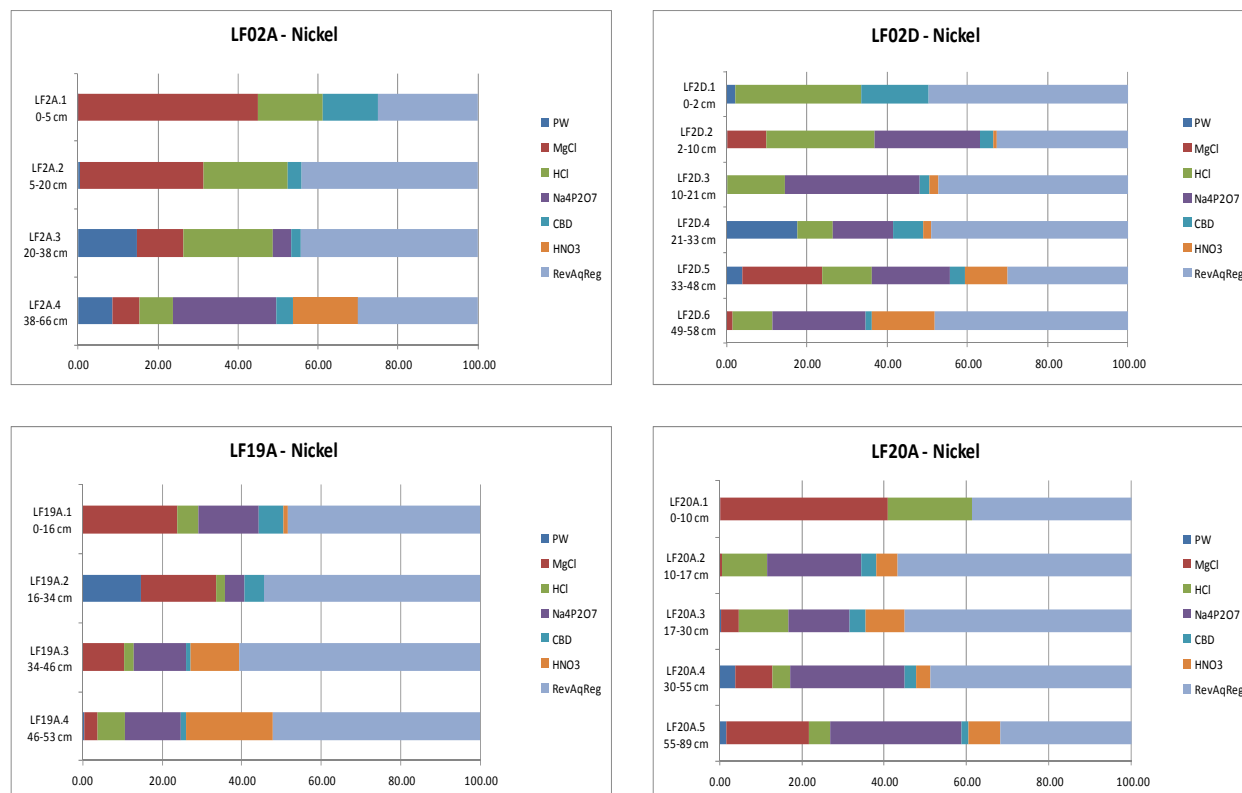


Figure 4-14 Sequential extraction data for Ni in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.8 ZINC (Zn)

The sequential extraction data for Zn are shown on Figure 4-15. The pattern for Zn is different to the other metal and metalloid data studied. Zinc in the residual fraction is often relatively small in comparison to other determinands, with the dominant fraction being in the dithionite (potentially the more crystalline Fe and Mn phases) extraction.

Zinc concentrations were high in the porewaters of all profiles (Figure 3-10) and this is consistent with it also being present in the $MgCl_2$ extraction representing potentially the exchangeable fraction. It was also present in deeper parts of the profiles in the weak acidic extraction, and likely associated with pyrite in the nitric acid extract. Significant concentrations were also found in the pyrophosphate extraction, which correlates with elevated organic C concentrations in these soils.

The unusually high concentrations of Zn in the dithionite extract may possibly be due to release from natrojarosite (as Zn is known to substitute for Fe^{3+} in jarosite) or a more crystalline 'aged' Fe oxide. These may also be responsible for the elevated Zn concentrations in the residual extraction.

Plotting the concentrations as percentages of the total highlights the shallower soil layers better (Figure 4-16), showing the importance of the pyrophosphate (organic) extraction and the exchangeable fraction.

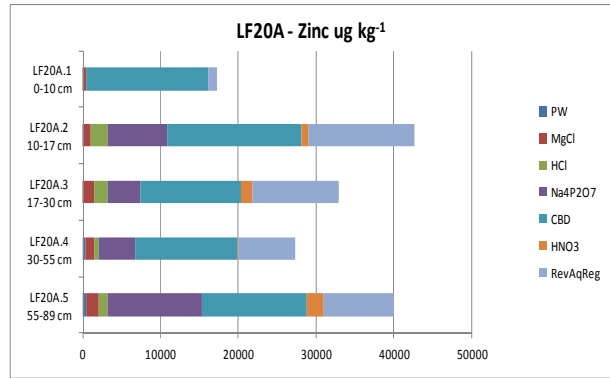
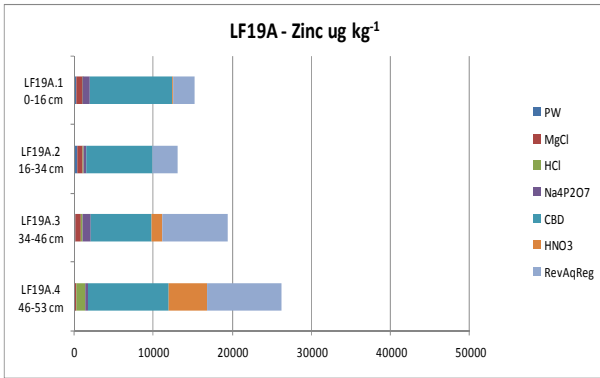
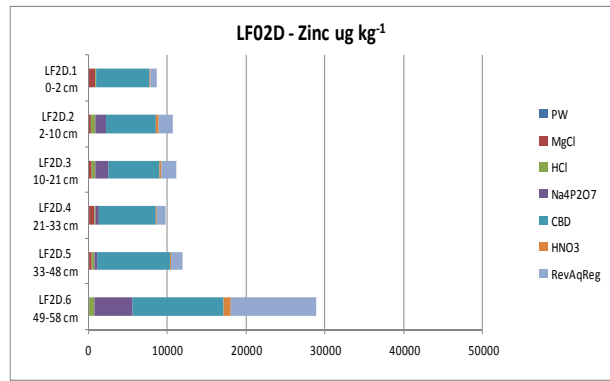
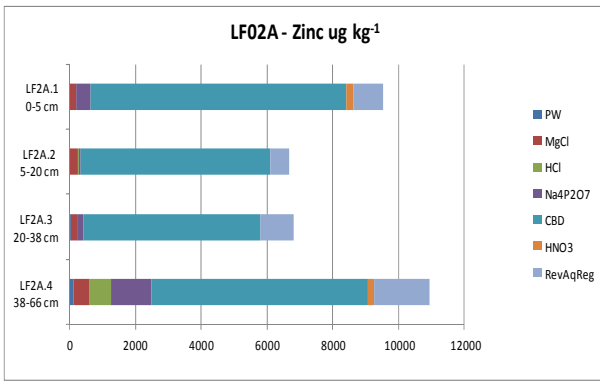


Figure 4-15 Sequential extraction data for Zn in the subaqueous soil samples. Note the differences in scale for LF2A.

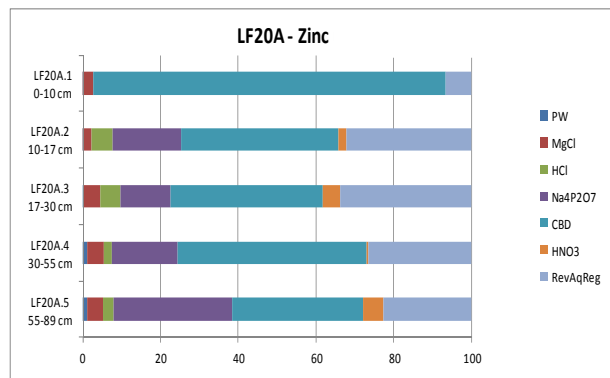
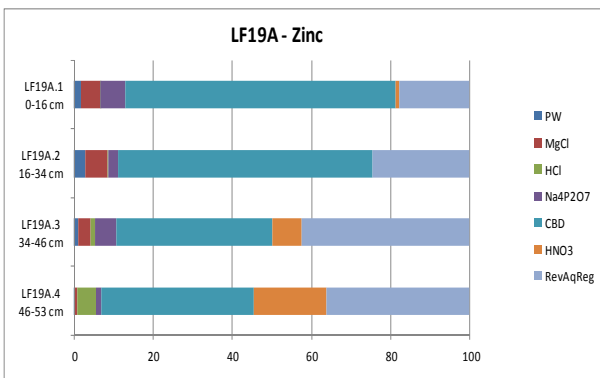
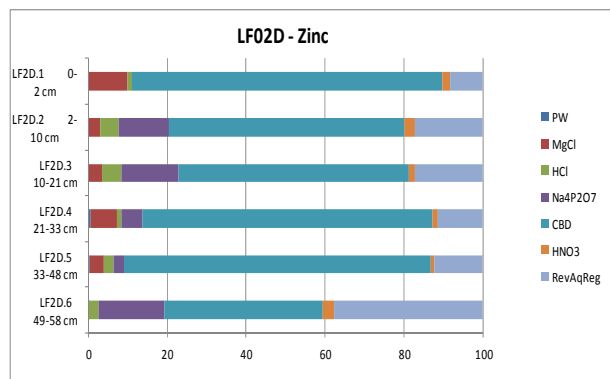
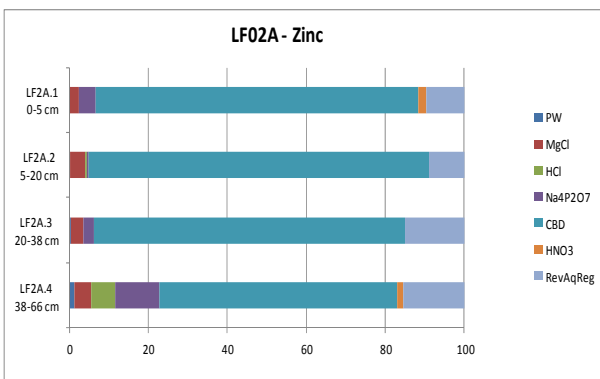


Figure 4-16 Sequential extraction data for Zn in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.9 ARSENIC (As)

The concentrations of As in each sequential step are shown on Figure 4-17. It was noted in the previous chapter that As concentrations were high in many porewater samples (Figure 3-11). Higher exchangeable (MgCl_2) As concentrations were mainly found in the deeper parts of the soil profiles, but was moderately high in all but the surface profile of Boggy Lake (LF20A).

The weak acid extraction step was important in all profiles, but more so in Boggy Lake where it and the 'organic' fraction are most important. At the other sites the 'organic' fraction and pyrite are dominant in the deeper soil layers. Arsenic was present in the residual fraction, but not as important in the more labile fractions, and most soil layers contained significant As in the dithionite extraction. The fractionation is consistent with the known behaviour of As, with strong adsorption of oxidised As species on Fe oxyhydroxide species and incorporation in sulfide minerals. Sodium pyrophosphate at pH 10 can extract amorphous oxides (Pickering et al. 1986) and promote the competitive exchange of HAsO_4^{2-} sorbed onto solid phases. However, the extent of association with the 'organic' fraction was surprising and further work is warranted to understand this strong association in the Lower Lakes soils.

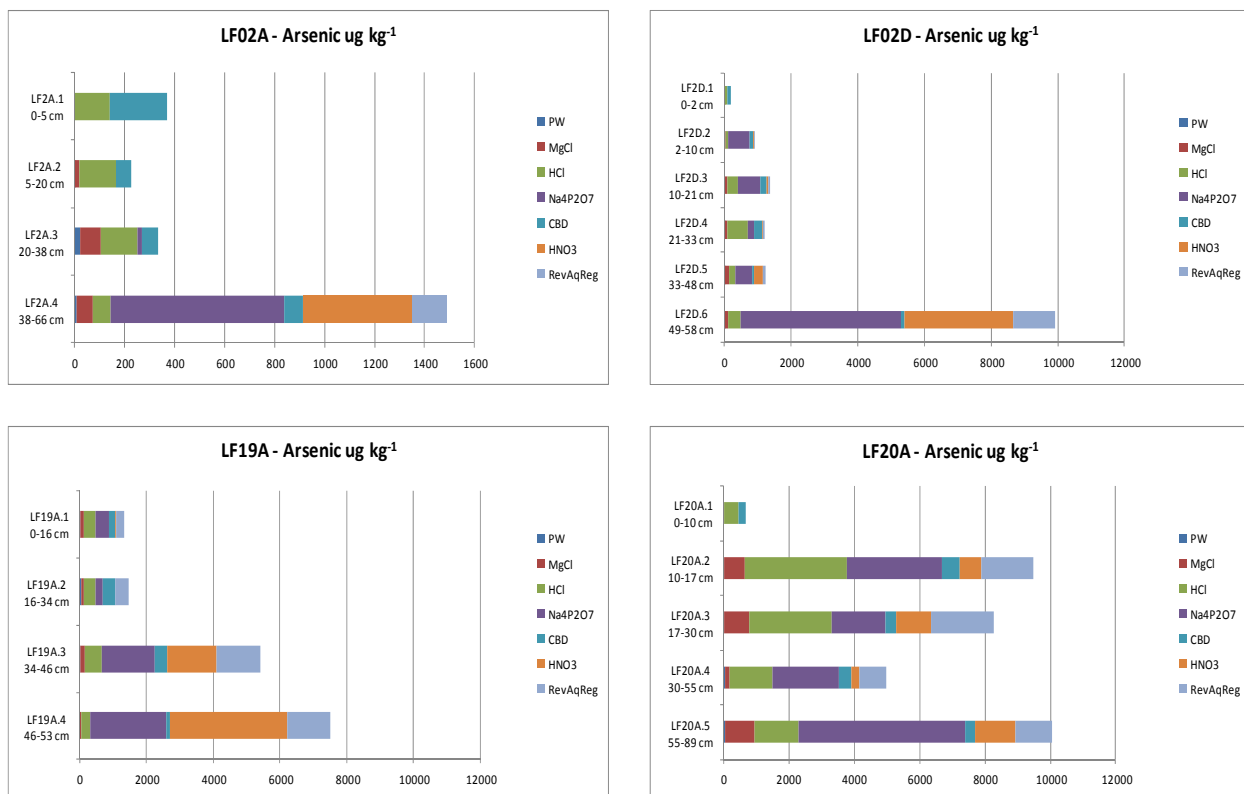


Figure 4-17 Sequential extraction data for As in the subaqueous soil samples. Note the differences in scale for LF02A.

The presence of high As concentrations in the HNO_3 fraction (deep sediment layers) is consistent with its presence in sulfide phases and represents a potential hazard under changing environmental conditions that promote oxidation. The mobilisation of As into porewater will depend on the solubility of pure/mixed As sulfide phases and its reaction once released into sediment porewater (e.g. precipitation, complexation, competitive exchange reactions, etc).

The data are plotted as percentages on Figure 4-18. The profile at Dog Lake (LF19A) shows that As was extracted in a number of extractions. The HCl and dithionite extractions were more significant in the upper part of the soil, whilst the nitric acid was more dominant in the lower parts, suggesting a shift in the

associated phases from Fe oxides/oxyhydroxides to incorporation in pyrite (consistent with Cr-reducible sulfide profiles at this site). The pyrophosphate was also significant in all soil layers, and residual As was relatively small compared with many of the metals.

The other profiles also showed high relative dithionite extractions, decreasing with depth, and nitric acid extraction being more important at depth. The pyrophosphate was present in all layers except the surface horizons. The most labile form (MgCl) was significant in most soil layers suggesting that the bioavailability is relatively high for As, and the dissolved As formed an important contributor to the total in several soil layers.

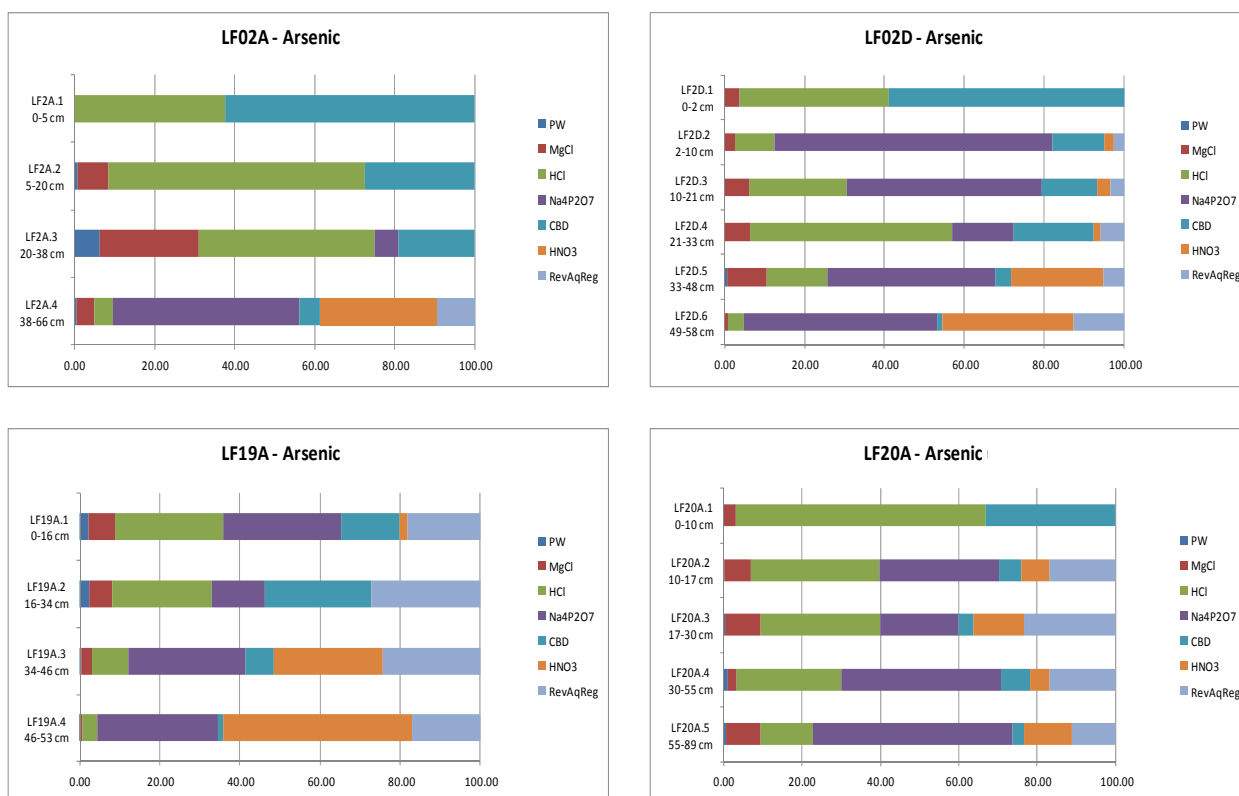


Figure 4-18 Sequential extraction data for As in the subaqueous soil samples showing the data plotted as percentages of the total.

4.2.10 LEAD (Pb)

The concentrations of Pb in each sequential step are shown on Figure 4-19. Lead is typically limited in solution by a strong affinity to sorb onto solid phases or form insoluble precipitates, and is generally present in solutions only under acidic conditions. Although the solute concentrations are low (Figure 3-12), these are significant due to the high toxicity of Pb in aquatic environments. The dominant fraction for many samples is the dilute acid extraction, hence it may be sorbed to poorly crystalline minerals. It was also present in the residual fraction to a significant degree. An association with pyrite is also suggested by a significant proportion from the nitric acid extraction. Exchangeable Pb was noted in some samples from Dog Lake and Boggy Lake, which potentially represents the highest risk under ambient conditions.

The presence of high Pb concentrations in the HNO₃ fraction (deep sediment layers) is consistent with its presence in sulfide phases and represents a potential hazard under changing environmental conditions that promote oxidation. The mobilisation of Pb into porewater will depend on the solubility of the pure/mixed Pb sulfide phases and its reactions once released into sediment porewater (e.g. precipitation, complexation, competitive exchange).

The data are plotted as percentages on Figure 4-20, highlighting better the proportions in the shallow soil layers which had lower concentrations of Pb. The importance of the HCl extraction is clearly seen in most

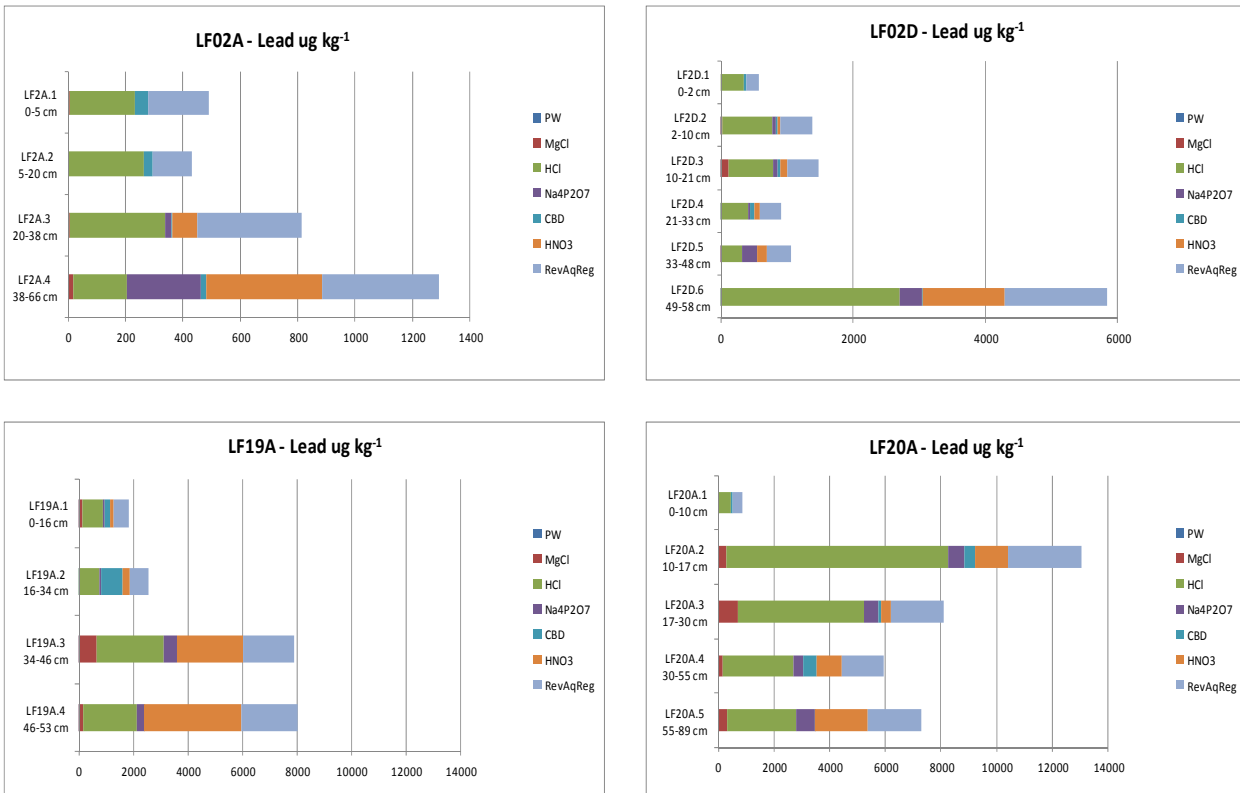


Figure 4-19 Sequential extraction data for Pb in the subaqueous soil samples. Note the differences in scale.

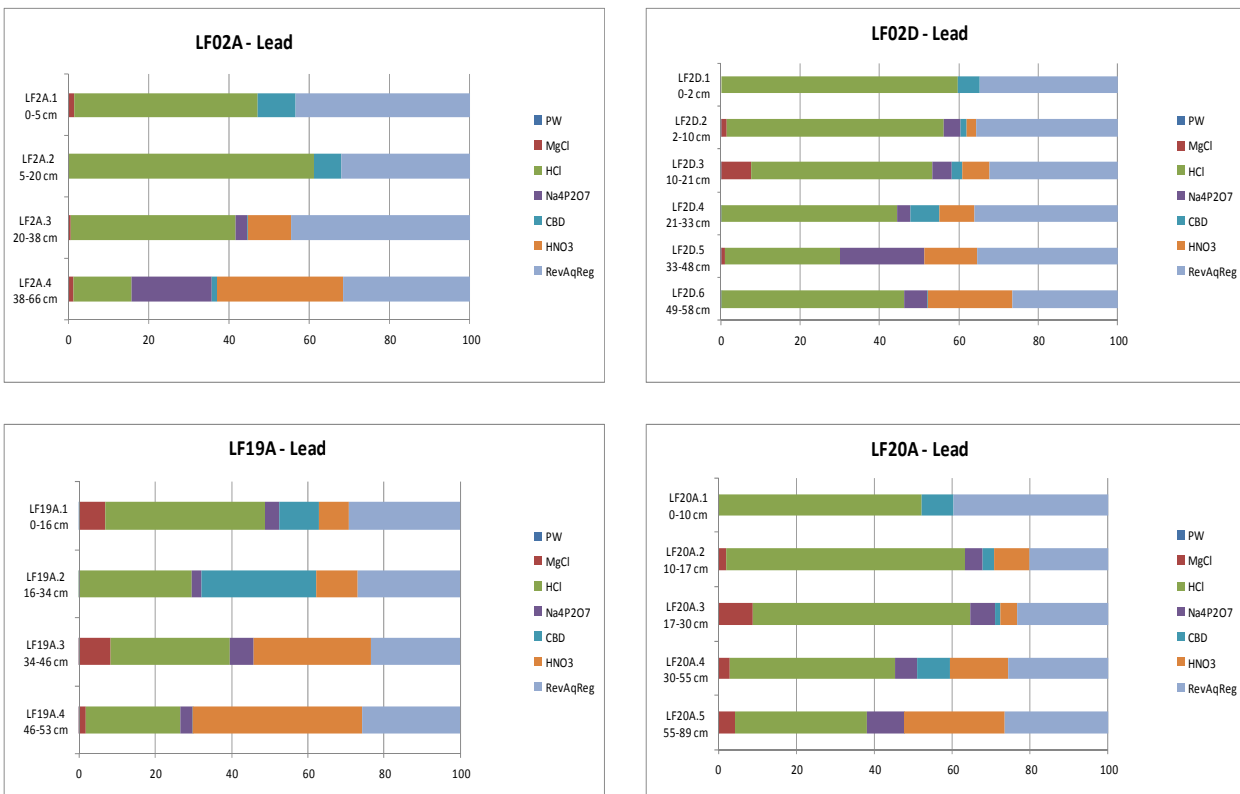


Figure 4-20 Sequential extraction data for Pb in the subaqueous soil samples showing the data plotted as percentages of the total.

soil layers. The nitric acid extract was higher in the deeper soil layers suggesting a relationship to pyrite, whilst the dithionite extraction was generally lower than for most other metals, indicating limited control by organic matter.

4.2.11 URANIUM (U)

The sequential extraction data for U are shown on Figure 4-21. The dominant fractions for U are from the weak extraction and the residual fraction. It is unlikely that there is any carbonate present in these soils as ANC was only a trace constituent in the upper soil horizons at Point Sturt (Appendix B). It is possible that U was originally present in carbonate minerals before the soils were acidified as U forms a strong complex with carbonate. Following acidification, U is most likely sorbed to poorly crystalline Fe oxyhydroxides (hence, the U has remained in the same extraction phase).

Uranium also appears to be associated with the 'organic' fraction consistent with its geochemical behaviour, with exchangeable U only being of significance in the weak acid extraction (HCl) in the deeper soils of LF02D and LF19A.

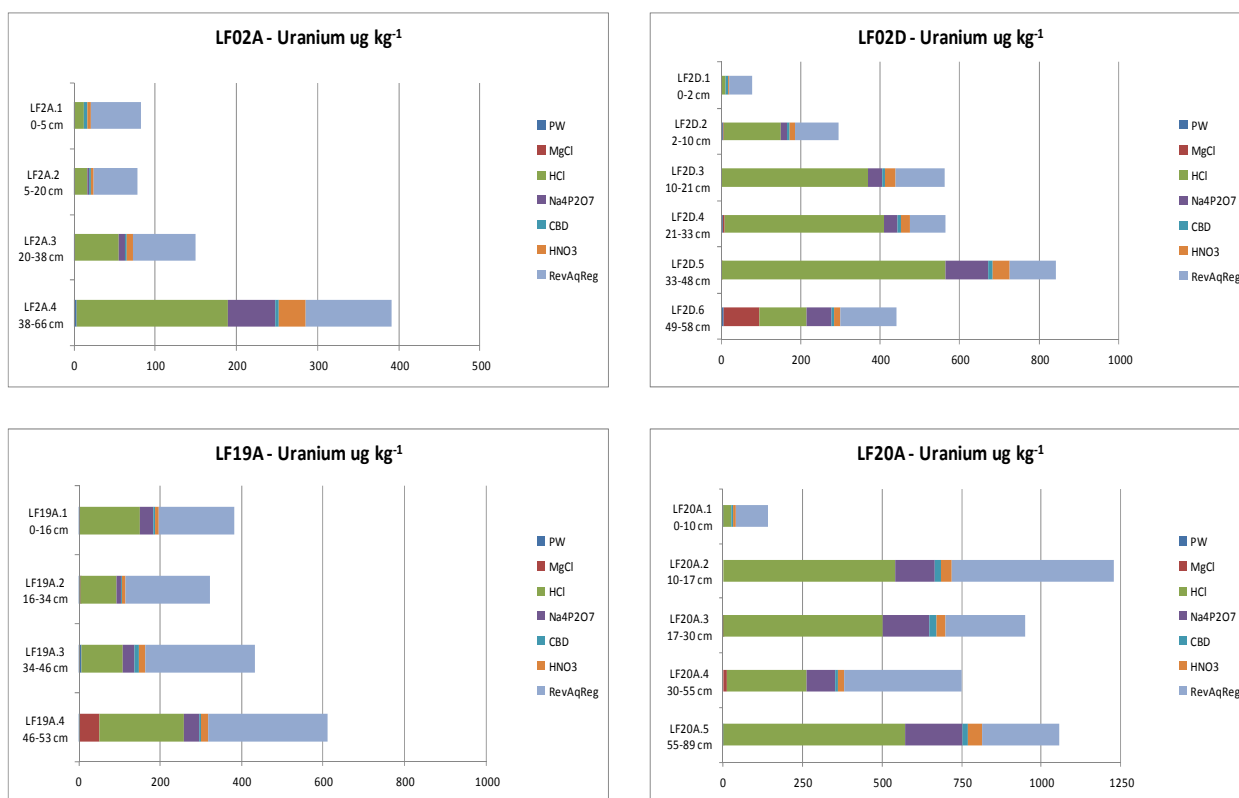


Figure 4-21 Sequential extraction data for U in the subaqueous soil samples. Note the differences in scale.

The percentage plots for the data (Figure 4-22) show more clearly the differences in relative proportions with depth. The amount of residual U is very variable being higher in the more sandy surface soil layers from Point Sturt and Boggy Lake. Exchangeable U was most abundant in deeper more clayey soils in profiles LF02D and LF19A (Figure 4-22). The dithionite extraction was a minor but significant source of U, and although the nitric acid extractant contained some U in all soil layers, it is likely to be due to some residual Fe oxides rather than sulfides.

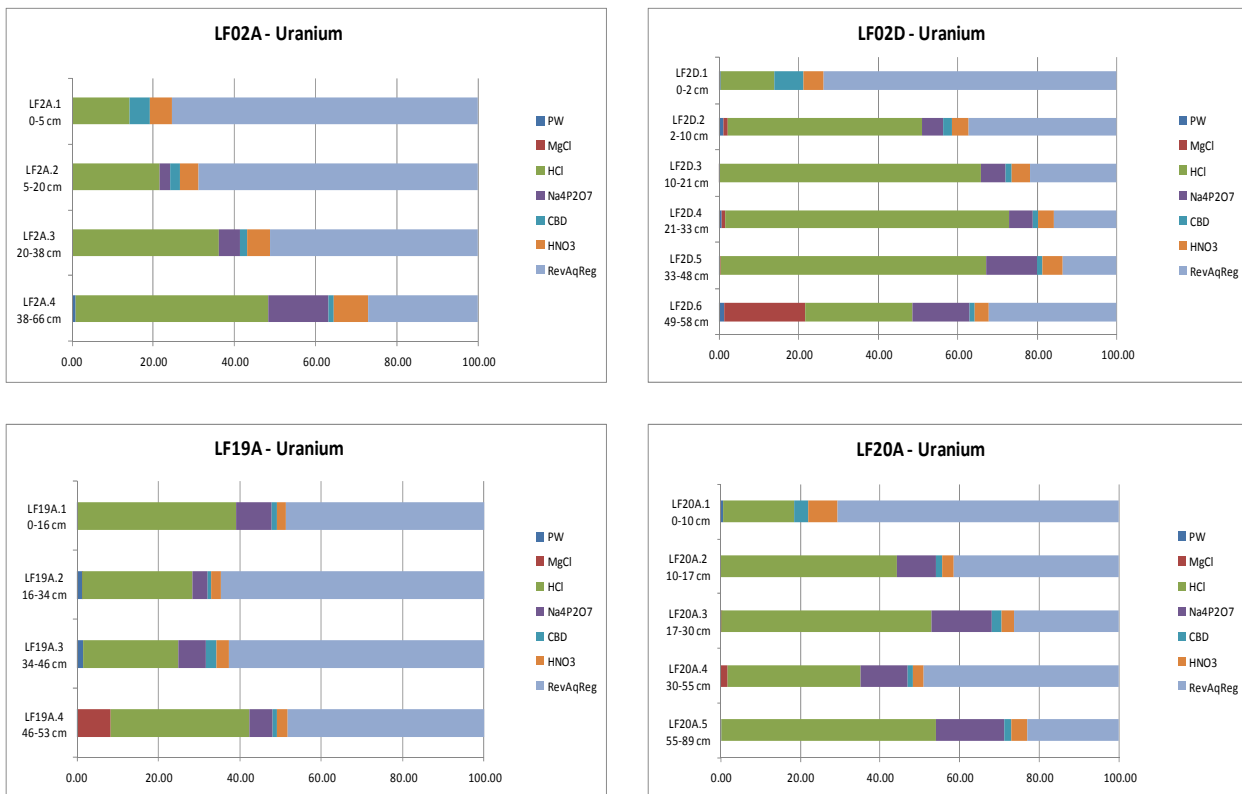


Figure 4-22 Sequential extraction data for U in the subaqueous soil samples showing the data plotted as percentages of the total.

4.3 Summary of sequential extraction chemistry

The sequential extraction data highlight the large number of trace metals and metalloids present in different soil fractions. Although the exchangeable fraction is often not the dominant fraction, it is generally sufficiently high to be of concern for a number of metals. The data show that most metals are present in a range of fractions, with the dilute acid and nitric acid fractions often being dominant. The percentages of metal and metalloid contaminants vary within each profile, and also between sites. The 'organic' fraction was important for a number of metals as well as the metalloid As. Zinc and uranium displayed significantly different behaviour, with the dithionite fraction being very important for Zn and the weak acid (HCl) extractions being important for U. The data provide a good basis for making predictions of metal and metalloid mobilisation under different future changes in geochemical scenarios, and a basis for which to ascertain in more detail the mineralogical phases present in the soils and their metal/metalloid associations.

The sequential extraction results highlight the importance of solid-phase speciation in examining the current and potential risk of metals in acid sulfate soils. In chapter 2, many porewater metal concentrations (actual hazard) (e.g. As) were found to exceed the 95% protection trigger values for freshwater (Table 3-1). A sequential extraction procedure was used to estimate the distribution of metals in sediment solid phases. The high concentration of many metals in the $MgCl_2$ and HCl extraction steps suggests metals in sediments (especially subsurface sediments) may be readily mobilised into porewater under changing environmental conditions such as soil acidification. The presence of high concentrations of metals (e.g. As) in the HNO_3 extraction step, operationally defined to be associated with sulfide phases, represents a potential hazard under conditions that promote oxidation and release of metals into porewater. These were, however, mainly present in the deeper soil layers.

5 Discussion

5.1 Introduction

This study on metal and metalloid concentrations in the soils, porewater and application of sequential extractions in selected profiles provides data with which to assess the degree of hazard from these contaminants and an indication of future risks if contaminants become available under different geochemical scenarios.

There is a wide range of metal and metalloid contaminants present at concentrations greater than ANZECC guidelines with significant spatial variability at a range of scales. The data are for selected sites and it is not currently possible to extrapolate the results over the Lower Lakes. The high metal contents may, for example, be due to hydrological and sediment sources from the Adelaide Hills to the north and west, which have been mined historically for metals. The following sections discuss in more detail the solution and 'solid-phase' partitioning of metals and metalloids and the implications for soil and surface water quality and ecology.

5.2 Solution phase partitioning of metals and metalloids

The importance of colloids in metal mobility and reactivity in sediments has been recognised for some time. A number of studies (Krom and Sholkovitz, 1978; Lyons et al. 1979; Moran & Moore, 1989) have attributed organic matter interaction as a primary factor in stabilising Fe and Mn colloids in anoxic porewaters. Krom and Sholkovitz (1979), in a study of anoxic porewaters in a Scottish Lake, found that 74-84 % and 3-17 % of the dissolved < 0.45 µm filtered Fe and Mn concentrations, respectively, were associated with high molecular mass phases. This highlights a need to take care when interpreting 'solute' concentrations using the industry standard 0.45 µm membrane filter, especially for Al, Fe and Mn. The presence of these metal oxide colloids may also exert a control on a range of metals and metalloids that easily sorb to mineral surfaces.

In sulfate reducing soils and sediments, metal sulfide precipitation may lead to the formation of metal-bearing colloids (Horzempa et al. 1979; Gammons et al. 2001; Moreau et al. 2004), which have the potential to transport metal contaminants traditionally are thought to be immobilised by sulfide formation (Kirk, 2004). Gammons and Franden (2001), in a study of H₂S-rich waters at a treatment wetland, found reducing conditions promoted bacterial sulfate reduction and precipitation of dissolved metals as sulfide minerals. Moreau et al. (2004) in an investigation of the size, submicron scale structure, and aggregation of ZnS formed by sulfate reducing bacteria found the earliest bacterially induced precipitates to be crystalline ZnS nanoparticles (1-5 nm). Colloids, such as submicron mineral phases, can thus act as carriers enhancing the mobility of often poorly soluble contaminants in sediments. Nanogoethite was shown to be the dominant reactive iron phase in a large variety of lacustrine and marine environments (van der Zee et al. 2003).

Colloidal particles of Al, Fe and Mn are likely to be less significant at low pH due to much higher solubility under acidic conditions (e.g. Figure 5-1). Shand et al. (2010), in a study of a wetland system, attributed high concentrations of Al, Be, Fe, Mn and the REE, at circumneutral pH surface waters and soil extractions, to colloidal particles that were not removed by 0.45 µm filters. This was substantiated by using smaller (0.2 µm) pore size filters, although it was considered likely that even finer membrane filters are necessary. The oxidation of acid sulfate soils leads to the release of metals and metalloids from the sulfide minerals present regardless of whether the soils acidify. However, low pH conditions allows a much greater solubility of metals and consequently the risks to the soil and nearby waters are increased due to much higher mobility. These metals and metalloids are often removed as the soils recover (return to their former higher pH and reducing conditions) and sorb onto, or be incorporated into, mineral phases.

The highest risks may be at intermediate Eh conditions where Fe and Mn are soluble (Figure 5-2). For the metalloids, which form oxyanions, such as As and selenium (Se), adsorption is much less at higher pH so they may also become mobile as the soils recover.

One of the key questions in this study was the role of colloids in the Lower Lake soils, which are considered to be in a gradual state of recovery i.e. pH is increasing. At the study sites, pH was not particularly high in most soil layers (Figure 2-4), the exceptions being in some of the surface soils, which had been flushed by infiltrating alkaline surface water, and the deep soils of profiles LF02D and LF19A. The data show that for the most part, the main contaminants are truly in solution: the concentrations of metals and metalloids are typically the same (within measurement error) in samples from the < 0.45 μm and < 3 kDa filtered solutions. The exception seems to be waters in the deepest soil layer from profile LF19A (Dog Lake) where the elements Al, Be, Ni, Zn and U (and also Co, the rare earth elements: REE's and yttrium: Y) were higher in the < 0.45 μm fraction indicating colloids were present. Interestingly, Fe was lower in the < 0.45 μm filter and the filter paper was brown: it may be the case that flocculation of Fe was induced by the filtering process. This does not appear to have had an impact on the transition metals Ni and Co.

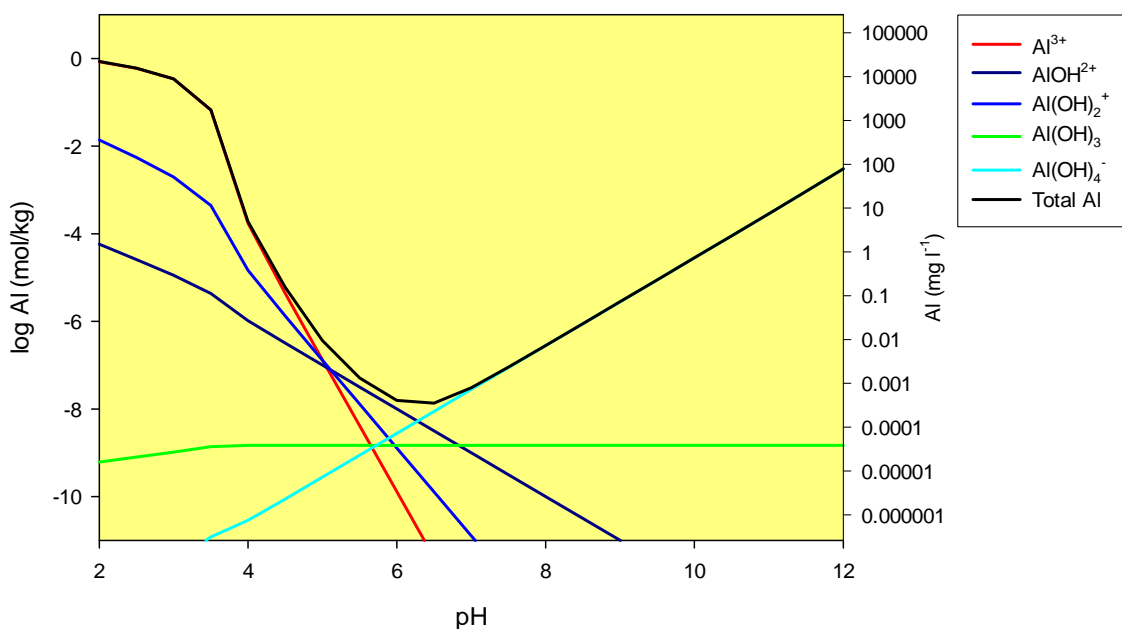


Figure 5-1 Solubility of gibbsite ($\text{Al}(\text{OH})_3$) in relation to pH (calculated using PHREEQC2). Total solubility is high under acidic and alkaline conditions with minimum solubility at circumneutral pH (from Shand et al. 2008).

The other samples which showed abundant colloidal formation were from Point Sturt for Mn (Figure 3-5). Two samples had extremely high colloidal Mn concentrations in the < 0.45 μm fraction. It would appear that colloids had no significant impact on other metal species.

The limited colloidal fraction in most samples is probably due to the relatively low pH in most soil profiles, as well as reducing conditions in deeper parts of the profile where pH is high. The formation of colloids are likely to become more important if pH continues to increase with soil recovery, and should be monitored as pH approaches circumneutral to slightly alkaline.

The ecotoxicological effects of metals associated with colloidal particles is poorly known e.g. do colloids behave in the same manner as dissolved constituents with regard to toxicological properties? It is known that they can't pass through membranes or attach to biotic ligands (receptor sites), but may be ingested or dissociate. Lombi et al. (2003), using alkaline amendments in soils, showed the mobility of fixed colloids to be significant, and increases with soil pH. The presence of significant amounts of metal associated with the colloidal phase may therefore pose an increased risk due to transport and change in lability in time and

space. On-going work in CSIRO is seeking to address this question as well as the role of contaminant mixtures.

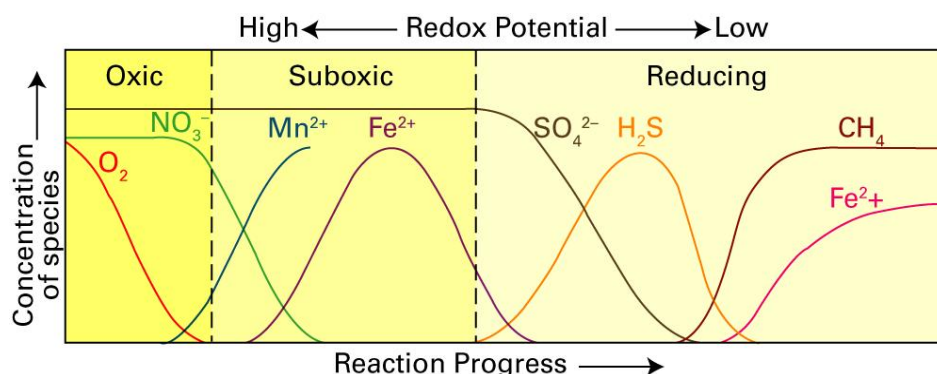


Figure 5-2 Progressive changes in redox species in an oxidising water through reaction with organic carbon (from Shand et al. 2007)

Another key question, not yet answered, is whether metal oxide colloids (with high concentrations of sorbed metals) are more commonly formed as a consequence of oxidation of acid sulfate soils followed by recovery i.e. it is not simply due to the higher pH. This would seem reasonable as you need oxidation to release the metals, but it is not clear as to whether acidification is necessary: acidification is known to affect the structure of clays, and these changes are irreversible, meaning, for example, that in cracking clay soils (vertisols) there will not be reversal of shrinkage or crack formation. Further work is required to determine these processes and the impact on ecotoxicity.

The lowest dissolved metal concentrations (for 3 of the 4 profiles - excluding Dog Lake) were typically either in the shallow soil layers, or the deep soil layers with higher pH and buffering capacity (LF02D and LF19A). The lower total dissolved sulfur (TDS) in the shallow layers is consistent with freshening of the soils during infiltration of lake water post-drought, and this also appears to have flushed the trace metal and metalloids downwards in the profile. The moderately high Na (a surrogate of salinity) and contaminant concentrations in the shallowest soil layer of Dog Lake (LF19A) is probably a function of poor permeability due to it being a clay-rich soil.

The mobility and bioavailability of metals in the dissolved and colloidal fractions of porewater samples is dependent on chemical properties such as pH. Increasing the pH of acidic sediments (e.g. addition of lime) as a remediation strategy may influence the mobility and bioavailability of metals in porewater. An increase in sediment pH may promote the formation and movement of colloids (e.g. clays and oxyhydroxide phases) and associated metals (Kaplan et al. 1996). The mobility, reactivity and potential bioavailability of metal contaminants associated with colloidal material in porewaters will depend on the physical and chemical properties of the particles (e.g. size and charge), strength of complexation (e.g. lability of associated metal), solubility (e.g. stability of pure or mixed sulfide phases), physical and chemical properties of the porewater (e.g. pH, ionic strength, DOC concentrations, etc.), solution and solid partitioning (e.g. sorption during transport, sieving, aggregation) and the biological route of exposure. On-going work in CSIRO is seeking to address this question of the formation of colloids and lability of metals in acidic sediments following the addition of lime or other alkaline remediation materials.

5.3 Solid phase partitioning of metals and metalloids

The data presented in Chapter 4 highlights the diversity of metals and metalloids present in the acid sulfate soils studied, and ascribed them to different fractions using a series of sequential extractions. Although care should be taken to ascribe these fractions to specific mineral phases, the study does highlight that metal and metalloid behaviour, in terms of mobility, is highly complex. For better predictive capacity and

understanding, future detailed laboratory and analytical work should be undertaken to link specific contaminants to specific mineral phases and sequential extraction phases/methodologies.

The fractionation of trace metals and metalloids is very unlikely to remain constant in these soils as they are transitioning from oxidised sulfuric materials back to sub-oxic and reducing (sulfidic) materials. As discussed in the section 5.2, the highest risk of metal mobilisation is generally the period of transition from highly oxidised soils (where metals and metalloids are often locked up in Fe and Mn oxide/oxyhydroxide and Fe hydroxysulfate minerals) to strongly reducing soils (where many metals and metalloids are locked up in Fe sulfide minerals). In between, Fe and Mn are soluble and mineral dissolution can release high concentrations of hosted metals and metalloids (Figure 5-2).

The metal and metalloid contaminants studied appear to be associated with a range of mineral phases as suggested by their presence in several extractions. The highest concentrations of contaminants in the Point Sturt profiles (LF02A and LF02D) were in the deeper heavy clays. The lowest concentrations were generally found in the Point Sturt sample (LF02A) furthest from shore. The sandy soils at this location were more coarse than nearer to shore, and it is likely that the uppermost soil layers were flushed during seicheing at lower water levels. Soil monitoring has shown that the salinity of the soils has been decreasing significantly since water levels rose (Baker et al. 2012).

The soils from Boggy and Dog Lakes typically contained higher metal concentrations in the extractions than Point Sturt, relating to the more clay-rich nature of the soils (the deepest heavy clay soil at LF02D was similar to these). The two top layers (0-34 cm) for Dog Lake and the top layer for Boggy Lake (0-10 cm) were more sandy and had lower concentrations in most extractants than deeper in these profiles.

Most metals and metalloids showed similar trends with the dominant fractions being from the HCl, pyrophosphate and HNO₃ extraction steps, as well as the residual phase. A general summary for the contaminants and their associated 'solid phase' fractions discussed in chapters 3 and 4 is shown on Table 5-1, highlighting typical dominant fractions in which metals were identified.

Table 5-1 Typical fractionation of contaminants derived from Sequential Extraction procedure. Large tick: generally a major fraction; small tick: often a moderate fraction or a major fraction in some profiles.

Extraction Contaminant	porewater	MgCl ₂	HCl	Na ₄ P ₂ O ₅	CBD	HNO ₃	Reverse Aqua Regia: residual
Al		√	√	√		√	√
Fe	√	√	√	√	√	√	√
Mn	√	√	√	√		√	√
Be			√	√	√	√	√
V		√	√	√	√	√	√
Cr			√	√		√	√
Ni	√	√	√	√	√	√	√
Zn		√	√	√	√		√
As		√	√	√	√	√	
Pb		√	√	√	√	√	√
U			√	√		√	√

Table 5-1 indicates the potential importance of poorly crystalline phases (HCl extraction), organic matter (pyrophosphate) and sulfide (HNO₃) as stores of metals and metalloids in these acid sulfate soil areas. Although it is not possible to deduce if these are indeed the controlling phases, the data are broadly consistent with the presence of Fe oxides, natrojarosite and sulfide that were present in these soils (Appendices A and B). Some metals were extracted during the nitric acid extraction in soils where Cr-

reducible sulfide was not present. It is likely that this extraction removes some relatively residual oxide phases, as the metal are also not typically incorporated in sulfide minerals. Claff et al. (2010b) noted that some Fe mineral phases (akaganeite, goethite, magnetite) were not fully extracted by the dithionite extraction, and that these minerals were present in the residual fraction. This is consistent with our Fe data, where extracted Fe in the nitric acid fraction correlated with Cr-reducible sulfide, but it is suggested that sorbed metals may be released during this extraction step.

It should be noted that although the bioavailable fraction (exchangeable: HCl) is not dominant in these soil layers, there are still sufficiently high concentrations to be of concern in these soils, as evidenced by some soil layers with very high porewater metal and metalloid concentrations. This is due to the much higher concentrations in the solid phase (mg kg^{-1}) compared to ANZECC Guideline concentrations (typically $\mu\text{g l}^{-1}$).

Although it appears likely that many metals have been flushed from the upper soil layers, especially sandy soils, a significant proportion has evidently not been transported out of the soil profiles. The data can be useful to understand the cycling of metals in soils during the recovery process, how these are modified by changes in mineralogy, and how they might be released under different changing environmental stressors.

Prior to oxidation, under the reducing conditions typical of the sub-aqueous soils (Fitzpatrick et al. 2008), a number of metals were probably locked up in reduced minerals such as pyrite. During the drying phase of the soils, pyrite oxidation led to the development of sulfuric conditions and the release of a range of metal and metalloid contaminants. Acidification of the soils would have also led to metal release from other minerals including clays resulting in elevated concentrations of metals such as Al and Be. Depending on the pH of the soil, most metals would have been incorporated into oxidation products, which may have included Fe minerals such as ferric oxyhydroxide, schwertmannite, natrojarosite or sideronatrite, or aluminium phases such as alunite, or organic matter. The sequential extraction data suggest that the contaminants are widely dispersed between different soil mineral phases. As the soils are in a state of transition, the proportions of these minerals are likely to change under different Eh-pH conditions and other thermodynamic constraints.

Some minerals such as natrojarosite and schwertmannite may be metastable, and likely to change over time into a more stable Fe mineral such as goethite, and with this, there is likely to be a release of some metals and metalloids. Poorly crystalline minerals also age with time, even under constant environmental conditions, and the more stable crystalline mineral phases will typically not be able to incorporate high trace element contents that are released to the soil porewaters or re-adsorbed by other mineral phases. Once very reducing conditions are returned to the soils, it is likely that reformation of sulfide minerals would scavenge many of the metals originally derived from sulfides. As discussed above, Fe and Mn oxides/oxyhydroxides/hydroxysulfate minerals are soluble under moderately reducing conditions, therefore the rate of change is critical to assessing the risks to biota and water bodies if transport is significant. Soil studies in the Lower Lakes (as elsewhere in the Murray-Darling Basin) have shown that recovery rates are generally very slow in most regions due to buffering by acid-generating mineral phases. It is therefore important to understand the amount and form of acidity, and the location and form of contaminants in the soil in order to develop geochemical models. This will facilitate informed prediction of metal mobility under different environmental scenarios.

The consecutive steps undertaken during the extraction procedure do not simply represent stronger extraction stages that can be used to predict a geochemical evolution. For example, where pyrite is present, oxidation of the soils might lead firstly to a release of metals and metalloids (step 5), and incorporation into oxide or sulfate minerals – earlier steps in the extraction process. Predictions, therefore, should be made on a scenario basis underpinned by sound geochemical knowledge of the processes controlling contaminant mobility. Laboratory experiments are currently underway at CSIRO to help establish the effects of drying followed by rewetting of soils from Dog Lake, and to establish in more detail the changes in soil porewater chemistry at a much finer resolution (e.g. using peepers). The competing effects of multiple exchange complexes and minerals will play a role in the redistribution of metal species over time. Hence further study of contaminant bioavailability should be undertaken as soils in the Lower Lakes continue to recover.

Further detailed study is required of metal and metalloid release in relation to; mineralogical transformations and ageing and (ii) changes in water level. It is well established that poorly crystalline minerals are less stable than crystalline mineral forms, hence the impacts from changing water levels may be more rapid than when the soils were originally oxidised.

5.4 Implications for water quality and ecology

Despite more than two years of inundation since the end of the drought, many of the subsurface soils previously exposed have not yet recovered to their previous condition in terms of pH and acidity (Baker et al. 2012). This study has shown that, for the sites studied, metal and metalloid concentrations remain very high, especially beneath the surface soil layer (which had circumneutral pH due to infiltration of Lake Alexandrina water). The surface soil layer at Dog Lake, however, was more saline than the other sites probably due to limited advection into the clay-rich soils at this location, and retained high metal concentrations in solution and as part of the solid phase.

The large flows from the River Murray immediately following the end of the drought in the Basin, helped to minimise adverse impacts from acid sulfate soils, due to dilution (and flushing through the wetland systems to the river), and to a high surface water head which helped to displace acidity and contaminants downwards into the soil profile. Nevertheless, with a slow return of the sub-soils to high pH and reducing conditions, contaminant hazards remain in many previously exposed sub-surface soils as evidenced by the soil porewater chemistry and potentially bioavailable contaminants in the soil layers. Recent dynamic batch studies of soils elsewhere in the Murray-Darling Basin (Shand et al. 2011 a,b,c) have shown the onset of reducing conditions may release Fe and Mn to solution along with oxyanions such as As. The oxyanions may thus continue to exert an impact long after metal cations have been removed from solution due to high pH. The impact of this change will be highly dependent on the transport in the system.

The contaminant hazards identified pose a risk to biota in two ways: firstly within the soil ecosystem itself, which has been severely affected by drought as well as acidification and contaminant release (the base of the food-web has been severely damaged); and secondly to mobilisation and transport of contaminants from the soil to overlying and surrounding water bodies e.g. by upward diffusive flux or advection if surface water head is decreased relative to sub-surface head. The development of an alkaline upper subaqueous soil in many parts of the Lake, or a shallow sulfidic sub-surface layer may act as a buffer to any upward flux of metals and metalloids, helping to remove them from solution (although the generation of H₂S may pose an alternative risk if significant), but the extent of such a buffering layer is not known in detail across the lake.

The chemical analysis of waters can be compared to existing water quality guidelines as a basis for predicting potential impacts on ecosystems. However, this does not directly demonstrate adverse biological effects. In addition, some of the studied porewaters contained a complex mixture of contaminants. The ecotoxicological effects of such a wide range of metals and metalloids in these soils are not established, and further work is recommended to establish the ecotoxicity of the soils. The guideline values for some metals have also been recalculated taking into account the hardness of the samples, because the uptake and toxicity for many metals is decreased due to competition from other solutes such as Ca and Mg responsible for water hardness. These should be treated with some uncertainty as the algorithms were developed for waters with lower hardness than present in most of the porewater samples. Hardness often correlates with alkalinity but these are and typically decoupled in acidic waters, hence the existing algorithms may not be directly applicable, and have the potential to be under protective to freshwater organisms (Markich et al. 2001).

6 Conclusions

This study presents a number of new findings including the role of dissolved vs. colloidal materials, and how metals and metalloids are partitioned in soils using a detailed sequential extraction process. It has shown that dissolved metal and metalloid concentrations in the study areas remain a concern, despite more than two years of high water levels in Lake Alexandrina. The previously exposed soils contain a number of metal and metalloid contaminants present in solution at concentrations above the ANZECC Guideline values for ecosystems, sometimes by several orders of magnitude.

The concentrations of solutes vary between sites, with Dog Lake and Boggy Lake typically having the highest contaminant porewater concentrations. The individual profiles studied also show large variations depending on soil type and hydrology as well as initial concentrations and solid phase speciation.

Soil porewater samples were filtered using different membrane filter pore sizes. The metal and metalloid contaminants were mainly present in solution (< 3 kDa), although Mn was present mainly as colloidal material (between 3 kDa and 0.45 μm) in two soil layers, and only occasionally were some metals present as colloids in some of the deeper soil layers.

The sequential extraction data highlighted the large differences in contaminant availability and potentially associated soil mineral phases. Individual contaminants were associated with a range of different fractions, from weakly-bound exchangeable to residual and are summarised in Table 5-1. The dominant solid phase speciation for contaminants often changed with depth e.g. Fe was largely present in the HCl extraction in shallow soil layers (suggesting it was present as a poorly crystalline oxide), with the nitric acid extraction (suggesting incorporation in pyrite) being more important at depth. This study has shown that the pyrophosphate extraction is very important in these soils, indicating that many contaminants are likely to be associated with organic matter. This was particularly true for Fe, Al, Ni, As, Cr, V and Be. In addition, the data show that these contaminants are likely to be associated with a range of minerals, as they were present in significant concentrations in a range of the extractions. For some elements, there was a dominant association e.g. Zn in the dithionite extraction, suggesting association with more crystalline oxide phases, and U and Pb in the HCl extraction, suggesting the major association with poorly crystalline oxide mineral phases. Although the exchangeable fraction formed a small part of the total, for some metals, they were still high enough to be of concern in relation to water quality limits.

The data provide a baseline from which to monitor the metal and metalloid hazards in Lake Alexandrina, and a much better basis to develop conceptual models for contaminant source and behaviour. Future sampling would be useful to understand the processes which determine how these contaminants change over time and how their potential availability is modified by e.g. redox changes or mineralogical transformations in the soil, such as mineral ageing or precipitation/dissolution. More detailed studies on determining the actual solid-phase speciation is recommended as a basis for contaminant-association and any reaction-transport model. The above recommendations would require both in-situ monitoring and detailed laboratory studies. In order to understand better the transport processes, fine resolution sampling is required e.g. using peepers or DGT samplers, which can provide information on likely transport mechanisms as well as better detailed contaminant profiles (Creeper et al. 2012). Future work could also focus on imposed changes e.g. wetting and drying, undertaken at least at soil core scale to better mimic reaction-transport in the complex profiles in the Lake. Finally, the impacts on soil ecosystem function and biodiversity of these complex contaminant mixtures are poorly understood and should be given some scope in future research programs.

7 References

- Antelo J, Fiol S, Gondar D, Lopez R, Arce F 2012 Comparison of arsenate, chromate and molybdate binding on schwertmannite: Surface adsorption vs. anion-exchange. *J. Coll. Inter. Sci.* 386, 338-343.
- ANZECC/ARMCANZ 2000 Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council/Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT, Australia.
- Auger, Y., Bodineau, L. And Leclercq S. 1999. Some aspects of vanadium and chromium chemistry in the English Channel. *Continental Shelf Research*, 19: 2003–2018.
- Baker, AKM, Fitzpatrick, RW, Shand, P, Simpson SL, Merry RH, and Thomas M (2010) Temporal variations in representative Acid Sulfate Soil environments around Lakes Alexandrina and Albert, South Australia. Prepared for The Murray Darling Basin Authority and South Australian Murray Darling Basin Natural Resources Management Board. Client Report, CSIRO: Sustainable Agriculture Research Flagship, 331 pp.
- Batley, G.E., Kirby, J.K. and McLaughlin, M.J. 2012. The fate and risks of nanomaterials in aquatic and terrestrial environments. Accepted for publication in the *Accounts of Chemical Research*, online July 2012 (DOI: 10.1021/ar2003368).
- Bin G, Xinde, C, Dong Y, Yongming L & Ma L 2011 Colloid Deposition and Release in Soils and Their Association With Heavy Metals. *Critical Reviews in Environmental Science and Technology*, 41:336–372.
- Brady, N.C. and Weil, R.R. 2002. *The Nature and Properties of Soils*. Thirteenth Edition, Pearson Education Inc, USA.
- Buffle, J. and Leppard, G.G. 1995. Characterisation of aquatic colloids and macromolecules. 2. Key role of physical structures on analytical results. *Environmental Science and Technology*, 29: 2176-2184.
- Christensen J. B. and Christensen T.H. 1999 Complexation of Cd, Ni and Zn by DOC from polluted ground water: a comparison of approaches using resin exchange, aquifer material sorption, and computer speciation models (WHAM and MINTEQA2). *Environ. Sci. Technol.* 33, 3231-3238.
- Claff, S.R., Burton, E.D., Sullivan, L.A., Bush, R.T., 2010a. Effect of sample pretreatment on the fractionation of Fe, Cr, Ni, Cu, Mn, and Zn in acid sulfate soil materials. *Geoderma* 159, 156–164.
- Claff, S.R., Sullivan, L.A., Burton, E.D., Bush, R.T., 2010b. A sequential extraction for acid sulfate soils: partitioning of iron. *Geoderma* 155, 224–230.
- Crans, D.C. and Tracey, A.S. 1998. The chemistry of vanadium in aqueous and nonaqueous solutions. In *Vanadium Compounds*; Tracey, A., et al.; ACS Symposium Series; American Chemical Society: Washington, DC.
- Creeper NL, Shand P, Fitzpatrick RW & Hutson J 2012 Behaviour of iron, aluminium and other selected metals following the rewetting of Inland Acid Sulfate Soils containing sulfuric material. In, Österholm P, Yli-Halla M & Edén P (eds.), 7th International Acid Sulfate Soils Conference in Vassa, Finland 2012: Towards Harmony between Land Use and the Environment. Geological Survey of Finland, Guide 56, 26-28.
- Denaix, L., Semlali, R.M. and Douay. F. 2001. Dissolved and colloidal transport of Cd, Pb, and Zn in a silt loam soil affected by atmospheric industrial deposition. *Environmental Pollution*, 113:29–38.

- DiCarlo, D. A., Yuniati, Z., Annette, D., Shree, G., Gao, B., and Steenhuis, T. S. (2006). In situ measurements of colloid transport and retention using synchrotron X-ray fluorescence. *Water Resources Research* 42, W12S05.
- Edmunds WM & Trafford JM Beryllium in river baseflow, shallow groundwater and major aquifers of the U.K. *Applied Geochemistry, Suppl. Issue No. 2*, 223-233.
- Fitzpatrick, R.W., Shand, P., Marvanek, S., Merry, R.H., Thomas, M., Raven, M., Simpson, S.L. & McClure, S. 2008 Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. CSIRO Land and Water Science Report 46/08.
- Gammons, C.H. and Frandsen, A.K. 2001. Fate and transport of metals in H₂S-rich waters at a treatment wetland. *Geochemical Transactions*, 2: 1-15.
- Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trends Anal. Chem.* 21, 451–467.
- Goody, D.C., Shand, P., Kinniburgh, D.G., & Van Riemsdijk, W.H. 1995 Field-based partition coefficients for trace elements in soil solutions. *Journal of Soil Science*, 46, 265-285.
- Horzempa, L.M. and Helz, G.R. 1979. Controls on the stability of sulfide sols: colloidal covellite as an example. *Geochemica et Cosmochimica Acta*, 43: 1645-1650.
- Hudson-Edwards KA, Wright K 2011 Computer simulations of the interactions of the (0 1 2) and (0 0 1) surfaces of jarosite with Al, Cd, Cu²⁺ and Zn. *Geochemica et Cosmochimica Acta*, 75: 52-62.
- Jensen, D.L., Ledin, A. and Christensen, T.H. 1999. Speciation of heavy metals in land-fill-leachate polluted groundwater. *Water Research*, 33:2642-2650.
- Kaplan, D.I., Summer, M.E., Bertsch, P.M. and Adriano, D.C. 1996. Chemical conditions conducive to the release of mobile colloids from ultisol profiles. *Soil Science Society of America Journal*, 60: 269-274.
- Kirk, G. 2004. *Biogeochemistry of submerged soils*. John Wiley and Sons.
- Kretzschmar, R. 1999. Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy*, 66:121–194.
- Krom, M.D. and Sholkovitz, E.R. 1978. On the association of iron and manganese with organic matter in anoxic marine porewater. *Geochemica et Cosmochimica Acta*, 42: 607-611.
- Lombi, E., Hamon, R.E., McGrath, S.P. and McLaughlin, M. 2003. Lability of Cd, Cu, and Zn in polluted soils treated with lime, beringite, and red mud and identification of a non-labile colloidal fraction of metals using isotopic techniques. *Environmental Science and Technology*, 37:979-984.
- Lyons, W.B., Gaudette, H.E. and Armstrong, P.B. 1979. Evidence for organically associated iron in nearshore pore fluids. *Nature*, 282: 202-203.
- Markich SJ, Brown PL, Batley GE, Apte SC & Stauber JL 2001 Incorporating metal speciation and bioavailability into water quality guidelines for protecting aquatic ecosystems. *Australasian Journal of Ecotoxicology*, 7, 109-122.
- McKeague JA & Day JH 1966 Dithionite and oxalate extractable Fe and Al as aids in differentiating various classes of soils *Can. J. Soil Sci.* 46, 13-22.
- Moran, S.B., and Moore, R.M., 1989, The distribution of colloidal aluminium and organic carbon in coastal and open ocean waters of Nova Scotia: *Geochimica et Cosmochimica Acta*, v. 53, p. 2519-2572.
- Moreau, J.W., Webb, R.I. and Banfield, J.F. 2004 Ultrastructure, aggregation-state, and crystal growth of biogenic nanocrystalline sphalerite and wurtzite. *American Mineralogist*, 89: 950-960.
- Morel, F.M.M. and Gschwend, P.M. 1987. The role of colloids in the partitioning of solutes in natural waters. In: Stumm, W. (Ed.), *Aquatic Surface Chemistry*. Wiley, New York.
- Nirel, PMV & Morel, FMM 1990 Pitfalls of sequential extractions. *Wat. Res.*, 24(8), 1055-1056.

- Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chem. Geol.* 214, 209–221.
- Ranville, J.F., Chittleborough, D.J. and Beckett, R. 2005. Particle-size and element distributions of soil colloids. *Soil Science Society of America Journal*, 69: 1173-1184.
- Ranville, J.F., Chittleborough, D.J., Shanks, F., Morrison, R.J.S., Harris, T., Doss, F., and Beckett, R. 1999. Development of Sedimentation field-flow fractionation-inductively coupled plasma mass-spectroscopy for the characterisation of environmental colloids. *Analytical Chimica Acta*, 381: 315-329.
- Rayment GE & Higginson FR 1992 Australian handbook of soil and water chemical methods, Inkata Press, Melbourne.
- Shand, P., Edmunds, W.M., Lawrence, A.R., Smedley, P.L. & Burke, S. 2007 The Natural (Baseline) Quality of Aquifers in England and Wales. British Geological Survey, 72pp. ISBN 978-085272595-5.
- Shand P, James-Smith J, Hodgkin, T, Fitzpatrick RW, McClure S, Raven M, Love A, Stadter M & Hill T. 2008. Ancient Acid Sulfate Soils in Murray Basin Sediments: Impacts on Borehole Clogging by $Al(OH)_3$ and Salt Interception Scheme Efficiency. In *Inland Acid Sulfate Soil Systems Across Australia* (Eds. Rob Fitzpatrick and Paul Shand). CRC LEME Open File Report No. 249. (Thematic Volume) CRC LEME, Perth, Australia, 129-136.
- Shand P, Merry R, Grocke S, Thomas M, Fitzpatrick RW, Thomas B, Baker A & Creeper N 2010 Water and soil quality impacts during reflooding of Nelwart Lagoon, South Australia. CSIRO: Water for a Healthy Country National Research Flagship. 158 pp.
- Shand P, Grocke S, Baker, AK, Smith L, Fiebiger C & Cozens G 2011a. Assessment of Acid Sulfate Soil Materials (Phase 2) Wellington North (Murrundi) wetland, South Australia. CSIRO: Water for a Healthy Country National Research Flagship.
- Shand P, Grocke S, Baker AK, Raven M, Smith L, Fitzpatrick RW, Fiebiger, C, Cozens, G 2011b. Assessment of Acid Sulfate Soil Materials (Phase 2) Swanport wetland, South Australia. CSIRO: Water for a Healthy Country National Research Flagship.
- Shand P, Baker, AK, Grocke, S, Raven M, Fitzpatrick RW, Smith L, Cozens, G & Fiebiger, C 2011c. Assessment of Acid Sulfate Soil Materials (Phase 2) Riverglades wetland, South Australia. CSIRO: Water for a Healthy Country National Research Flagship.
- Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B., Sparado, D.A. & Mosley, L. 2010 Climate-driven mobilisation of acid and metals from acid sulfate soils. *Marine and Freshwater Research*, 61, 129-138.
- Smith, E., Naidu, R. and Alston, A.M. 1998. Arsenic in the soil environment: a review. *Advances in Agronomy*, Academic Press, 64: 149-195.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Trefry, J. H. and Metz, S. 1989. Role of hydrothermal precipitates in the geochemical cycling of vanadium. *Nature*, 342: 531–533.
- van der Zee, C., Roberts, D.R., Rancourt, D.G. & Slomp C.P. 2003 Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. *Geology*, 31 (2003), pp. 993–996.
- Viraraghavan, T., Subramanian, K.S. and Aruldoss, J.A. 1999. Arsenic in drinking water-problems and solutions. *Water Science and Technology*, 40: 69-76.

Appendix A Sub-aqueous soil profile descriptions for studied sites

Soil descriptions from December 2011

Sample ID	Locality description	Sampling tool	Upper depth (cm)	Lower depth (cm)	Morphology
LFe02-A.1	Point Sturt North – Approximately 60 m offshore. Subaqueous (0.7 m).	Vibrating UWS	0	4	Pale brown (10YR 6/3) medium sand, some slightly coarse grains; uniform colour, loose; pH _f 7+; sharp wavy boundary.
LFe02-A.2			4	13	Grey (2.5 Y 5/1) loamy sand with 30% black (2.5 Y 2/0) medium to coarse, clear, prominent mottles which tend to be in horizontal bands (but not in the core described); few brownish fine to medium roots; sulfidic smell (from black mottles?); pH _f ~6; abrupt smooth boundary.
LFe02-A.3			13	25	Light grey (10YR 6/2) medium sand with the few darker horizontal bands, (one core has a weak yellowish band (pH _f 4 .5)), few very bright yellow (jarosite) mottles; few fine to medium roots stained brown; pH _f 5.5; clear smooth boundary.
LFe02-A.4			25	57	Dark grey (5Y 4/1) clayey sand with some darker (5Y 3/1) loamy sand to clayey sand diffuse layers to about 5 cm thickness; few coarse roots and plant remains; one core has 5 cm of dark brown peat; weak sulfidic smell; pH _f ~7 with 5.5 to 4 or less around orange stained plant material; sharp smooth boundary.
LFe02-A.5			57	69	Greyish green (5G 4/2) heavy clay with some sand grains, upper centimetres have a darker (organic?) colour; soft and moist, but drier than above; pH _f >7?
LFe02-D.1	Approximately 10 m offshore. Subaqueous (0.5 m).	Vibrating UWS	0	8	Grey (5Y 5/1) medium to coarse sand, some coarse grains; 30 to 40% black mottles in upper 5 cm, pale brown surface rind (oxidised); few coarse and more common fine roots; pH _f 5.8; abrupt smooth boundary.
LFe02-D.2			8	19	Greyish brown (2.5Y 5/2) clayey sand with 5% clear, prominent jarosite mottles; few dark brown, organic, old root channels; pH _f ~5; gradual boundary.
LFe02-D.3			19	31	Light grey (2.5Y 7/2) medium sand to clayey sand with 10% jarosite mottles and several 3 to 10 mm layers of dark brown organic; few old root channels; few fine roots; pH _f 3.9 to 4; sharp boundary.

Sample ID	Locality description	Sampling tool	Upper depth (cm)	Lower depth (cm)	Morphology
LFe02-D.4			31	47	Dark grey (5Y 4/1) clayey sand to loamy sand with diffuse darker (organic?) layering; few prominent old root channels with yellow to orange brown (core) colours; few fine roots; pH _f 3.9-4.2; sharp boundary.
LFe02-D.5			47	56	Greenish grey (5GY 5/1) heavy clay for 2 to 3 cm grading to hard CaCO ₃ (2 to 5 mm, 5GY 6/1); the clay layer varies between 3 and 10 cm among the cores.
LFe19-A.1	Dog Lake - Approximately 130 m offshore. Subaqueous (0.9 m).	Push tube	0	16	Greyish brown (10YR 5/2) loamy sand and darker sandy loam with common fine rootlets in the upper half of the layer. 5-10% yellow jarosite mottles throughout but more frequent at the base of the layer. Abrupt wavy boundary.
LFe19-A.2			16	24	Grey brown (2.5Y 5/2) loamy sand to clayey sand with up to 10-20% coarse jarosite mottles with diffuse edges and prominent near lower boundary. Clear wavy boundary.
LFe19-A.3			24	46	dark greenish grey (5GY 4/1) soft loamy clay with few fine prominent jarosite mottles associated with fine roots in the top 1-2 cm of layer. Paler at base. Clear boundary.
LFe19-A.4			46	53	Olive grey (5Y 4/2) heavy clay with some darker horizontal layer and some sand and mica. Slightly spongy and relatively dry.
LFe20-A.1	Boggy Lake - Approximately 300 m offshore. Subaqueous (0.9 m). These clayey samples were all too soft and wet to texture properly. All likely to be heavy clays as no coarse particle were felt.	UWS	0	10	Black (2.5Y 2/0) clay; very soft and sticky with monosulfide gel; decomposing plant remains; sulfidic smell; abrupt irregular boundary.
LFe20-A.2			10	17	Dark greyish brown (10YR 4/2) clay; two cores have a distinct brown layer in upper 2 cm; soft and sticky; few small, distinct, prominent jarosite mottles appear towards the base; pH _f 4.2; gradual boundary.
LFe20-A.3			17	30	Greyish brown (10YR 5/2) clay with 30% clear, medium, prominent jarosite mottles, coarser towards the base; soft and sticky, but a little firmer than above; weak residual structure which is mainly near vertical in two cores; few medium roots; pH _f 3.6; clear, irregular boundary.
LFe20-A.4			30	55	Dark grey (5Y 4/1) clay; soft and sticky; few to rare jarosite mottles along vertical root channels (5 mm diameter); few medium roots; very weak residual structure; diffuse boundary.
LFe20-A.5			55	89	Dark greenish grey (5GY 4/1) clay; very soft and sticky; may include some fine sand towards the base.

Appendix B Acid-Base Accounting Data

Sample Site	EAL lab code	TEXTURE (note 6)	MOISTURE CONTENT		ACID VOLATILE SULFUR (AVS) (% Sav WW) (note 3)	TITRABLE ACTUAL ACIDITY (TAA) (To pH 6.5)		Extractable sulfate sulfur (%S _{KCl})	REDUCED INORGANIC SULFUR (% chromium reducible S)		RETAINED ACIDITY (HCL extract) S _{NAS} (as %S _{HCL} - %S _{KCl})		TOTAL ORGANIC CARBON % C (note 4)	ACID NEUTRALISING CAPACITY (ANC _{BT})	NET ACIDITY Chromium Suite mole H ⁺ /tonne	LIME CALCULATION Chromium Suite kg CaCO ₃ /tonne DW (includes 1.5 safety Factor when liming rate is ^ve)	
			(% moisture of total wet weight)	(g moisture / g of oven dry soil)		pH _{KCl}	(mole H ⁺ /tonne)		(%Scr)	(mole H ⁺ /tonne)	(%S _{NAS})	(mole H ⁺ /tonne)					% CaCO ₃
<i>Method Info.</i>																	
						<i>(ACTUAL ACIDITY)</i>			<i>(POTENTIAL ACIDITY)</i>		<i>(RETAINED ACIDITY)</i>		<i>HCL-LECO</i>	<i>EUTRALISING CAPACITY</i>			
LFse02-A.1	C0099/1	Fine	14.2	0.2	<0.001	7.25	0	..	<0.01	0	..	0	0.03	0.01	2	-1	-0.1
LFse02-A.2	C0099/2	Fine	17.6	0.2	<0.001	6.72	0	..	0.01	6	..	0	0.11	0.00	0	6	0.5
LFse02-A.3	C0099/3	Fine	17.4	0.2	<0.001	6.24	3	..	0.01	6	..	0	0.06	..	0	9	0.7
LFse02-A.4	C0099/4	Fine	18.7	0.2	<0.001	5.03	20	..	0.13	81	..	0	0.22	..	0	101	7.6
LFse02-D.1	C0099/5	Fine	16.4	0.2	<0.001	7.57	0	..	<0.01	0	..	0	0.04	0.07	14	-9	-0.5
LFse02-D.3	C0099/6	Fine	22.2	0.3	<0.001	6.94	0	..	<0.01	0	..	0	0.11	0.00	0	0	0.0
LFse02-D.4	C0099/7	Fine	21.2	0.3	<0.001	6.07	4	..	<0.01	0	..	0	0.12	..	0	4	0.3
LFse02-D.5	C0099/8	Fine	21.0	0.3	<0.001	5.41	11	..	0.09	56	..	0	0.15	..	0	67	5.0
LFse02-D.6	C0099/9	Fine	24.0	0.3	<0.001	8.71	0	..	0.25	156	..	0	0.92	..	0	156	11.7
LFse19-A.1	C0099/10	Fine	27.0	0.4	<0.001	5.59	24	..	0.01	6	..	0	0.46	..	0	31	2.3
LFse19-A.2	C0099/11	Fine	18.7	0.2	<0.001	5.05	34	..	<0.01	0	..	0	0.14	..	0	34	2.6
LFse20-A.1	C0099/12	Fine	48.5	0.9	<0.001	4.73	69	..	0.10	62	..	0	2.04	..	0	131	9.8
LFse20-A.2	C0099/13	Fine	56.4	1.3	<0.001	3.90	159	0.161	0.03	19	0.137	64	2.74	..	0	241	18.1
LFse20-A.3	C0099/14	Fine	42.4	0.7	<0.001	4.21	104	0.120	0.08	50	0.136	63	1.32	..	0	217	16.3
LFse20-A.4	C0099/15	Fine	41.9	0.7	<0.001	4.17	113	0.219	1.20	748	0.061	28	0.86	..	0	890	66.7
LFse20-A.5	C0099/16	Fine	40.1	0.7	<0.001	5.13	18	..	1.05	655	..	0	0.59	..	0	673	50.5

- NOTE:**
- All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival (unless supplied dried and ground)
 - Samples analysed by SPOCAS method 23 (ie Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (Scr - Method 22B)
 - Methods from Ahern, CR, McElnea AE, Sullivan LA (2004). **Acid Sulfate Soils Laboratory Methods Guidelines**. QLD DNRME.
 - Bulk Density is required for liming rate calculations per soil volume. Lab. Bulk Density is no longer applicable - field bulk density rings can be used and dried/ weighed in the laboratory.
 - ABA Equation: Net Acidity = Potential Sulfidic Acidity (ie. Scr or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF (with FF currently defaulted to 1.5)**
 - The neutralising requirement, lime calculation, includes a 1.5 safety margin for acid neutralisation (an increased safety factor may be required in some cases)
 - For Texture: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clays
 - .. denotes not requested or required. '0' is used for ANC and Snag calcs if TAA pH <6.5 or >4.5
 - SCREENING, CRS, TAA and ANC are NATA accredited but other SPOCAS segments are currently not NATA accredited
 - Results at or below detection limits are replaced with '0' for calculation purposes.
 - Projects that disturb >1000 tonnes of soil, the 20.03% S classification guideline would apply (refer to acid sulfate management guidelines).**
 - Results refer to samples as received at the laboratory. This report is not to be reproduced except in full.



(Classification of potential acid sulfate material if: coarse Scr≥0.03%S or 19mole H⁺/t; medium Scr≥0.06%S or 37mole H⁺/t; fine Scr≥0.1%S or 62mole H⁺/t) - as per QUASSIT Guidelines

Appendix C Soil porewater data

See attached CD

Appendix D Soil extraction data

See attached CD

CONTACT US

t 1300 363 400
+61 3 9545 2176
e enquiries@csiro.au
w www.csiro.au

YOUR CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.

FOR FURTHER INFORMATION

CSIRO Land and Water

Paul Shand
t +61 8 8303 8513
e paul.shand@csiro.au
w www.csiro.au/en/Organisation-Structure/Flagships/Water-for-a-Healthy-Country-Flagship.aspx