

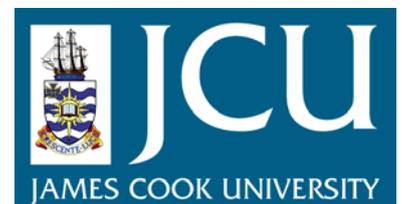
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6. FATE OF ELEMENTS RELEASED FROM ASS

6.1 Introduction

This chapter examines the fate of elements released from AASS and inundated AASS by investigating the geochemistry of drain and mouth sediments in the Firewood-Magazine Creek catchment. The objectives of Chapter 6 were: 1) to describe the mineralogy, geochemistry and element hosting of the drain sediments; 2) to investigate the drain sediments for enrichment in the elements mobilised from IAASS; and 3) to investigate the mouth sediments of Firewood Creek for element enrichments: a) relative to background creek systems; and b) from seawater inundation of AASS. Identifying the fates of the released elements was important because the effectiveness of seawater inundation as a remediation technique is highly dependent on it being able to prevent the off-site release of potential toxic elements.

The first sediments investigated for the elements released from ASS were drain sediments from the upper reaches of the Firewood Creek catchment. The Firewood Creek drain sediments were extremely fine, except for detrital minerals and organic matter. The drain sediments typically formed coatings on the beds and banks of the drains, suggesting that they formed by precipitation. Two types of drain sediments were readily discernable in the field: 1) black ooze (BO); and 2) orange flocculant (OF). The BO was physically similar and occurs in similar conditions, to material frequently referred to as monosulfidic black ooze (MBO). At East Trinity, the BOs were habitually overlain by the second type of drain sediment, the OFs. Though the BOs (i.e. MBOs) have received considerable attention (e.g. Bush et al., 2004; Smith, 2004; Smith and Melville, 2004; Hicks and Fitzpatrick, 2003; Bush et al., 2002a; Bush et al., 2002b; Fyfe et al., 2002; Sullivan and Bush, 2002), limited research has been conducted on the OF (e.g. Hall, 2002; Ferguson and Eyre, 1999). Furthermore, though numerous authors refer to the importance of the Fe-rich drain sediments as potential metal sinks in ASS environments (e.g. Smith and Melville, 2004; Smith, 2004; Hicks and Fitzpatrick, 2003; Fyfe et al., 2002), there are few studies into the chemical composition, or element hosting in either the BOs or OFs.

Here, the East Trinity drain sediments were described in terms of their chemical compositions (Al, As, Ba, Ca, Co, Cu, Fe, Ga, K, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Sc, Si, Sr, Ti, V, Y, Zn and Zr) and major mineralogies. Additionally, the importance of element hosting by sulfide and oxidised Fe phases was investigated using the MBCR-SEP. Elements examined using the MBCR-SEP were Al, Ba, Co, Cu, Fe, Ga, Mn, Na, Nb, Ni, Pb, Sc, Ti and Zn. The MBCR-SEP also provided an indication of element behaviour in the drain sediments under various environmental conditions.

The second set of sediments examined for the elements released from the AASS and IAASS were mouth sediments collected from the mouth of Firewood Creek. The Firewood Creek mouth sediments were clastic in nature and typical of tropical estuarine sediments (i.e. fine, black, organic-rich, with frequent shell grit). Hall (2002) previously investigated the geochemistry mouth sediments of Firewood Creek. Hall's (2002) data indicated that the elements lost from AASS and IAASS generally did not report in the sediments from the mouth of Firewood Creek. An additional set of mouth sediment data was used in combination with the data collected by Hall (2002) to further investigate the downstream impacts of the elements released from AASS and IAASS. The mouth sediments of Firewood Creek were investigated for their chemical composition (As, Ba, Ca, Co, Fe, Ga, K, Li, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Sr, Ti, V, Y, Zn and Zr). Element enrichment in the mouth sediments was identified by comparison with two sets of earlier sediments from Firewood Creek and background sediments that were described by Hall (2002).

The data and interpretations presented in this chapter provided new insights into the fate of elements released from oxidised and inundated ASS. Specifically, the drain and mouth sediments were investigated to identify if the elements released from ASS were retained on East Trinity, or released into Trinity Inlet. Furthermore, hosting of elements in the drain sediments was identified to establish the sizes of the labile element fractions and the behaviour of elements in the drain sediments under various environmental conditions (e.g. acidification, reduction or oxidation). The research further developed the work of Hall (2002) with regard to identification of the downstream geochemical impacts of elements released from AASS and inundated AASS. Finally, by combining the data on the elements lost from AASS and IAASS (Chapter 3), geochemical pathways in the ASS environment of East Trinity were clarified.

6.2 Methods

6.2.1 Drain Sediments

6.2.1.1 Sampling

Drain sediments were collected from the drains that serviced areas of IAASS in the Firewood-Magazine Creek catchment. The drains were installed during the drainage of East Trinity to facilitate the off-site movement of water. However, when seawater inundation restarted in the Firewood-Magazine Creek catchment, the drains facilitated movement of seawater onto the site.

The drain sediments consisted of two distinct types: fine grained 'Orange Flocculants' (the OFs) and slimy 'Black Oozes' (the BOs; see Figure 2.12). Both drain sediment types were found in slow flowing drains that facilitated movement of water on and off areas of AASS. During low tides, the drains carried soil-waters that seeped out of the inundated AASS. The BOs were always found

beneath the OFs, but were not always present. The OFs typically formed a film 2 to 5 mm thick over the BOs (when present). The OFs were orange-red (2.5Y 5/8 to 2.5Y 4/8), whereas the BOs were greenish-black (10Y 2.5/1).

Seventeen drain sediment samples were collected from the Firewood Creek system (Figure 2.9 and Table A.3 of Appendix A). Of these, 12 were OFs and 5 were BO. Details of the drain sediment sampling and storage are in Section 2.2.2. The drain sediment samples were photographed and described using Munsell colour charts (Munsell Color, 2000).

6.2.1.2 Soil pH and Oxidised Soil pH

The soil pH and oxidised soil pH of six drain sediments were measured using the method described in Section 2.4.

6.2.1.3 Mineralogical Analysis

The mineralogy of 4 drain sediment samples was determined using XRD. The drain sediment sample preparation for, and analysis by, XRD is detailed in Section 2.5. Samples were dried at 40 °C to avoid mineral transformation because of dehydration or structural water loss.

6.2.1.4 Elemental Analysis

Seventeen drain sediments were analysed using XRF at the AAC (Townsville). The XRF data for the drain sediments are given in Table G.1 of Appendix G. The drain sediment samples were processed (crushed) for analysis at the AAC. Further information on sample preparation and the XRF technique can be found in Section 2.6.1.1. The analytical quality of the XRF analysis is given in Section 3.2.3.4. The drain sediment XRF dataset consisted of: Al, As, Ba, Ca, Co, Cu, Fe, Ga, K, LOI, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Sc, Si, Sr, Ti, V, Y, Zn and Zr.

6.2.1.5 Modified BCR Sequential Extraction Procedure

The MBCR-SEP was used to identify elemental hosts in the BO and OF drain sediments. The MBCR-SEP is described in Section 2.7.7. The high purity water extraction step described in section 2.7.7 was not conducted on the drain sediments. The MBCR-SEP samples from the drain sediments were analysed for Al, As, Ba, Co, Cr, Cu, Fe, Ga, Mn, Na, Nb, Ni, Pb, Sc, Ti, V, Zn and Zr. Quality assurance of the elemental determination of the SEP samples is given in Chapter 5, Section 5.2.3. Correspondingly, the MBCR-SEP element dataset for the drain sediments was Al, Ba, Co, Cu, Fe, Ga, Mn, Na, Nb, Ni, Pb, Sc, Ti and Zn. The residual fractions of all drain sediments were determined directly (see section 5.2.3.4).

6.2.2 Creek Mouth Sediments

6.2.2.1 Sampling

Firewood Creek mouth sediments were collected by NRM&W staff from the sediment traps located outside the East Trinity bund wall (Figure 2.13). The Firewood creek mouth sediment traps were the same as those from which sediments were collected by Hall (2002) in early April 2004 (Figure 2.9). See Section 2.2.3 for details of the sampling and storage procedures.

6.2.2.2 Analysis

The mouth sediments were analysed for total element concentrations using ICP-MS/AES techniques at Australian Laboratory Services Pty. Ltd., Brisbane. Samples were digested with HF+HNO₃+HClO₄+HCl. The relevant elements determined were Al, As, Co, Ba, Ca, Fe, Ga, K, Li, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Sc, Sr, Ti, V, Y, Zn and Zr. The mouth sediments were dried and crushed before analysis (see Sections 2.6.1).

6.2.2.2.1 *Quality Assurance of Elemental Determination - ICP-MS/AES*

The analytical accuracy of mouth sediment analysis was established by submitting a sample of the international geochemical reference material GXR-3 (Appendix B, Table B.7). Section 2.9 details the QA thresholds and justification. Study elements that failed the accuracy assessment were Al, Cu and Sc. Consequently, Al, Cu and Sc were removed from the mouth sediment dataset. Standard concentration values for the GXR-3 SRM were not provided for Ga or Nb. Therefore, the accuracy of Ga and Nb could not be measured in the mouth sediments. Gallium and Nb have been included in the mouth sediment dataset, but caution must be exercised with their interpretation due to their accuracy being unconfirmed.

The analytical reproducibility of the ME-MS61 procedure was measured by inclusion of a replicate sample (Appendix B, Table B.8). Section 2.9 details the QA thresholds and justification. The reproducibility of all elements determined in the mouth sediments was acceptable. As a consequence, the mouth sediment dataset consisted of As, Co, Ba, Ca, Fe, Ga, K, Li, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, S, Sr, Ti, V, Y, Zn and Zr.

6.3 Results

6.3.1 Firewood Creek Drain Sediments

6.3.1.1 Soil pH and Oxidised Soil pH

The drain sediments generally had circum neutral soil pH values (Table 6.1). However, all the drain sediments reacted violently with H₂O₂ and became extremely acidic. This indicates that the drain

sediments are very sensitive to changes in the redox potential and can rapidly become extremely acidic.

Table 6.1. Soil pH (pH_F) and oxidised soil pH ($\text{pH}_{F\text{Ox}}$) values for the drain sediments collected from Firewood Creek catchment. OF is orange flocculant. BO is black ooze. The use of 'A' and 'B' in the sample ID indicates the samples were collected from the same location, with 'A' being for the OF sample and 'B' for the underlying BO sample.

Sample Type	FDS8A OF	FDS8B BO	FDS10A OF	FDS10B BO	FDS11A OF	FDS11B BO
pH_F	6.6	6.7	6.5	6.4	6.7	6.6
$\text{pH}_{F\text{Ox}}$	2.0	1.7	2.1	2.1	1.9	1.8

6.3.1.2 Mineralogy of Drain Sediments

Selected drain sediment samples were analysed using XRD to determine their major mineralogy (Table 6.2). Samples were dried at 40 °C to minimise mineral transformations. However, all black ooze samples turned orange during drying, making the dried black ooze samples indistinguishable from the dried orange flocculant samples. The transformation of the black ooze samples to orange flocculant samples is likely due to oxidation of reduced Fe compounds to oxidised Fe phases.

Quartz was the dominant mineral in all of the drain sediment samples analysed. Quartz is a common mineral in sediments because it is concentrated by its stability, chemical resistance, hardness and lack of cleavage (Deer et al., 1992). There are two sources of quartz to the drain sediments: the granites of the Murray Prior range located immediately behind East Trinity; and coastal sediments. The quartz identified in the drain sediments is likely to be from a combination of both sources.

Potassium and Na feldspar were identified in one of the drain sediment samples. The K and Na feldspars are essential constituents of acid igneous rocks and are abundant in granites (Deer et al., 1992). The abundance of K and Na feldspars in granites make the obvious source for the feldspars the nearby granites of the Murray Prior Range.

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$), dickite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$) and illite ($\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$), were all identified as major minerals in the drain sediments. Kaolinite and dickite are formed by weathering of feldspars, muscovite and other Al-rich silicates that involve the loss of K. If K is not lost during weathering, illite is likely to form (Deer et al., 1992). Quartz and the aluminosilicates represent the detrital mineralogy of the Firewood Creek drain sediments.

The only other major mineralogical components identified in the drain sediments beyond the detrital minerals were Fe and Al containing phases. All the drain sediments analysed display a ‘hump’ at 2.5 Å that is interpreted as being due to a poorly crystallised/cryptocrystalline Fe phase. Goethite (FeO·OH) also reports in all drain sediment samples. One other mineral identified in sample FSD01 was the ferrous Al-SO₄ mineral halotrichite (Fe²⁺Al₂(SO₄)₄·22H₂O). Goethite, halotrichite and the amorphous Fe phase likely precipitate in the drains from waters with high [Fe], [Al] and [SO₄]. Precipitation of the Fe in the drains may result from a transition of soil-waters from reducing in the ASS to oxidising conditions in the drains, or an increase in solution pH by the mixing of soil-waters with sea- or meteoric waters. Iron saturation because of drying could also cause precipitation. Aluminium precipitation is likely caused by either an increase in solution pH, or saturation effects.

Table 6.2. Minerals identified using XRD in four drain sediment samples collected from the Firewood Creek drains. Drain sediments were dried at 40°C to minimise mineral transformation. All drain sediments transformed to OF like material on drying.

	FSD01 (OF)	FSD02 (OF)	FSD05 (OF)	FSD06 (OF)
Most Abundant	Quartz	Quartz	Quartz	Quartz
↓↓↓	Kaolinite	Dickite	K feldspar	Goethite
↓↓	Halotrichite	Goethite	Albite	Albite
↓	Goethite, synthetic	Albite	Illite	
Least Abundant	Illite	Illite	Goethite	
Notes	Diffuse hump at 2.5Å Amorphous Fe phase			

6.3.1.3 Chemical Composition of Drain Sediments

As a group, the geochemistry of the drain sediments (i.e. the BO and OF) was dominated by LOI, Fe, Si and Al (Figure 6.1 and Table G.2 in Appendix G); but the chemical components displayed considerable variation over the dataset. The high concentration of LOI in the drain sediments reflects the wet, organic-rich nature of the environment from where the samples were collected (i.e. open drains servicing vegetated areas). The very high Fe concentrations are a result of Fe precipitation in the drains from waters moving out of AASS and IAASS. Silicon reflects the content of detrital minerals (e.g. quartz and aluminosilicates) that frequently make up a large portion of the drain sediment samples.

The considerable variation of the chemical composition of the drain sediments was demonstrated by the relative percent difference (R%D) of the 25th and 75th percentile (75th - 25th percentile R%D = (75th percentile - 25th percentile) / (average of 25th and 75th percentile) * 100). A 75th -

25th percentile R%D less than 100 % indicates that the difference between the 75th and 25th percentile is less than the average of the 25th and 75th percentile; whereas a 75th - 25th percentile R%D greater than 100 % indicates that the difference between the 75th - 25th percentile is greater than the average of the 25th and 75th percentiles.

The 25th - 75th R%D was greater than 100 % for Co, Ga, Cu, S, Sc, Pb and Nb, and between 100 % and 50 % for Mn, Na, Mg, P, Al, Si, Ni, Y, Zn, V, Rb, Sr, Ti, K, Fe and Zr. Only LOI, Ba, Ca and As had R%Ds between the 25th and 75th percentiles less than 50 %. The variations in element concentrations indicate that the drain sediments are a mixture of detrital minerals (Al and Si), organic matter (LOI) and Fe phases (Fe).

6.3.1.4 Comparison of Black Ooze and Orange Flocculant Drain Sediments

The BOs and OFs were investigated for geochemical similarities. The OFs always occurred on the surface of the drains and the BOs occurred immediately under the OFs, but were not always present. Though the BO and OF were associated with each other in the field, it was not known whether the two sediment types were chemically related. Therefore, the chemical compositions of the BOs and OFs were compared to identify if they shared geochemical properties (Figures 6.2 and 6.3). The statistical values used to construct Figures 6.2 and 6.3 are given in Table G.2 of Appendix G.

The likeness of chemical composition between the BO and OF samples was measured by the percentage of overlap of their element (and LOI) concentrations ranges. A large overlap of concentration ranges between sample groups indicates that the groups are similar. The percentage overlap of the element concentration ranges was calculated by taking the smallest maximum concentration from the largest minimum concentration and dividing it by the total concentration range of both sample groups (Concentration range overlap; CRO) = (largest minimum - smallest maximum concentration)/(concentration range of drain sediments) * 100). A CRO of 100 % indicates that the concentration range for the element in both groups is identical. A negative CRO occurs when there is no overlap of concentration ranges. Concentration ranges, rather than 25th and 75th percentiles, were used because of the small sample size of the BO group (n = 5).

The concentration ranges of all the chemical components from the BO and OF groups overlapped. Concentration ranges of twenty of the 27 elements compared overlapped by between 50 - 100 % (Al, Ca, Co, Fe, Ga, K, LOI, Mg, Na, Nb, Ni, P, Pb, Rb, Sc, Si, Sr, Y, Zn and Zr). Arsenic, Ba, Mn, S, Ti and V had CROs of between 25 - 50 %. Only Cu had a CRO of less than 25 % (i.e. 12 %). The overlap of the concentration ranges indicates that elemental composition of the BO and OF are similar.

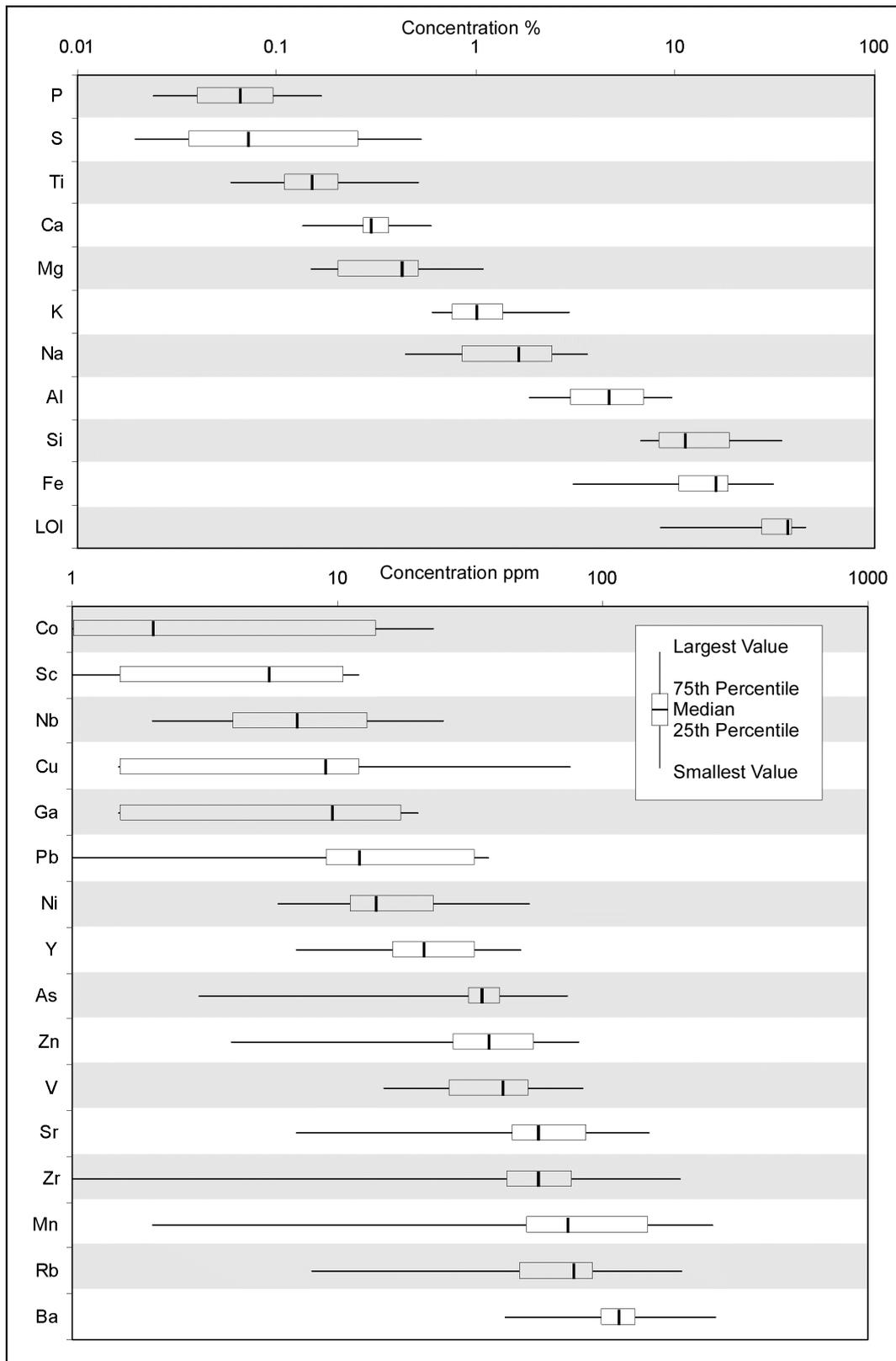


Figure 6.1. Firewood Creek drain sediment chemical composition. Components were determined using XRF method and concentrations are described by median, 25th percentile, 75th percentile, smallest and largest values from a population of 17 samples. Components are displayed in ascending median concentrations.

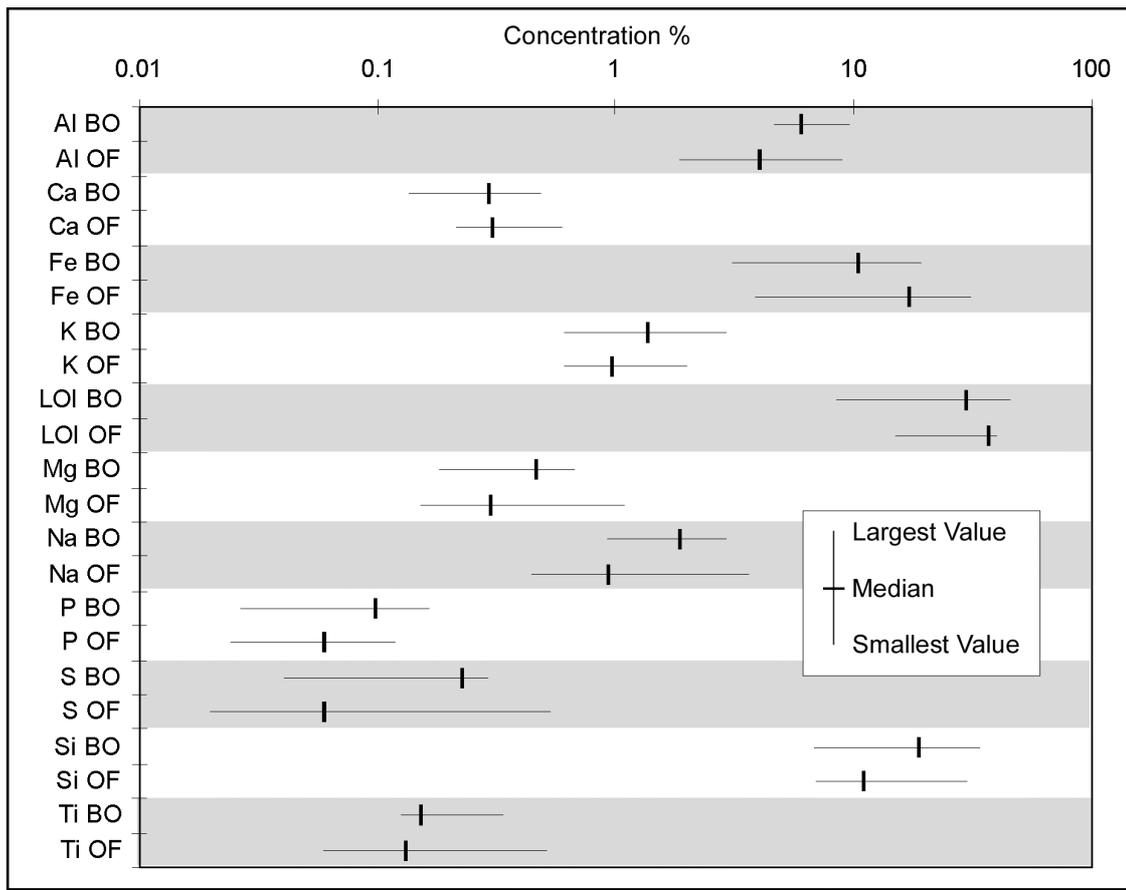


Figure 6.2. Comparison of major chemical components in black ooze (BO) and orange flocculant (OF) drain sediments from Firewood Creek. Chemical components were determined by XRF. Chemical component concentrations are compared by median, smallest and largest values from 12 orange flocculant and 5 black ooze samples.

6.3.1.5 Correlation of Chemical Components in Drain Sediments

Correlation was used to identify relationships between the chemical components in the drain sediments (Table 6.3). Spearman’s coefficient of correlation was used because of the non-parametric nature of much of the data. Correlation coefficients were calculated using the XRF data. Only the correlation coefficients for the elements of interest (Al, As, Co, Cu, Fe, Mn, Ni, Pb, S, Sc, Ti, V and Zn) with all the dataset elements are given.

The correlations indicated that Si, K and Rb represent the detrital mineral geochemistry of the drain sediments. Silicon correlated strongly with K and Rb (both $a = 0.001$) and moderately with Zr ($a = 0.01$). The association of Si with Zr suggests that Zr is hosted by zircon ($ZrSiO_4$). The strong correlation between Si, K and Rb demonstrate that the elements are hosted together. The likely

hosts of K, Rb and Si in the drain sediments are K-feldspar and illite. Hosting of K, Rb and Si in aluminosilicates is supported by the insignificant, but positive, correlation of K, Rb and Si with Al.

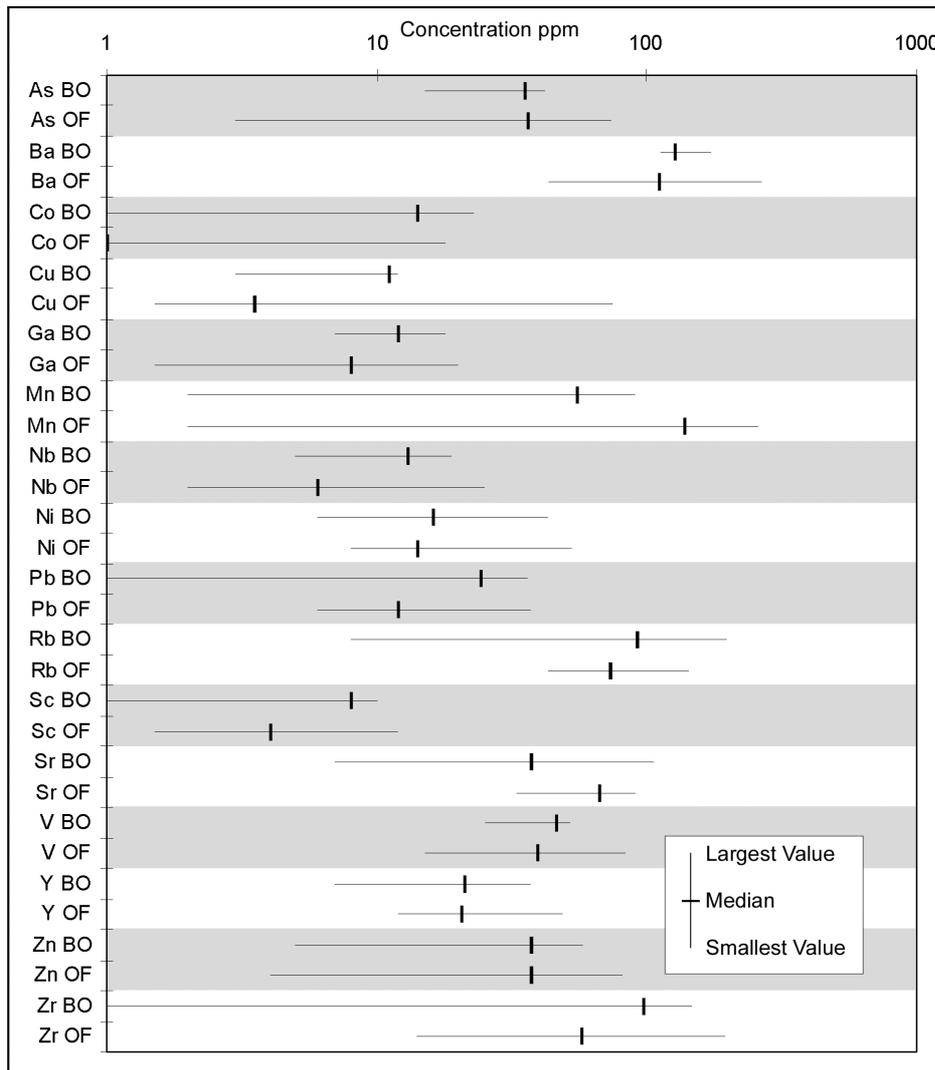


Figure 6.3. Comparison of trace elements in black ooze (BO) and orange flocculant (OF) drain sediments from Firewood Creek. Elements were determined by XRF. Element concentrations are compared by median, smallest and largest values from 12 orange flocculant and 5 black ooze samples.

Iron dilutes the concentration of K, Rb, Si and Zr in the drain sediments. The dilution of Si, K, Rb and Zn by Fe was demonstrated by the strong inverse correlations with K ($a = 0.001$), Rb ($a = 0.001$) and Si ($a = 0.001$) and the weak inverse relationship with Zr ($a = 0.05$). The dilution of detrital mineral element concentrations by Fe indicates that a large amount of Fe is being precipitated in the drains from soil-waters flowing out of IAASS and AASS. Furthermore, the inverse relationship of Fe with K, Rb and Si shows that the geochemistry of the drain sediments is a mixture of elements from at least two sources: K, Rb, Si and Zr from detrital minerals (quartz, feldspars and zircon) and Fe that precipitates from waters exiting AASS and inundated AASS.

Table 6.3. Correlation matrix for the drain sediments from Firewood Creek system. Only the correlation coefficients for the elements of interest (Al, As, Co, Cu, Fe, Mn, Ni, Pb, S, Sc, Ti, V and Zn) with all the dataset elements are given. Strong correlations ($\alpha = 0.001$) are shown in both bold and italic, moderate correlations ($\alpha = 0.01$) in bold and weak correlations ($\alpha = 0.05$) in italic. Spearman's coefficient of correlation was used because of the non-parametric nature of the data.

	Al	As	Co	Cu	Fe	Mn	Ni	Pb	Sc	Ti	V	Zn
Al	1.000											
As	-0.014	1.000										
Co	0.646	-0.420	1.000									
Cu	<i>0.606</i>	0.105	0.247	1.000								
Fe	-0.472	0.230	-0.688	<i>-0.518</i>	1.000							
Mn	-0.363	-0.234	-0.091	-0.484	0.377	1.000						
Ni	0.417	<i>0.586</i>	-0.135	0.371	0.246	-0.447	1.000					
Pb	0.221	0.043	0.248	0.374	-0.369	0.140	-0.087	1.000				
Sc	0.747	0.192	0.335	0.692	-0.126	-0.308	0.790	0.310	1.000			
Ti	0.815	-0.202	0.746	0.461	<i>-0.531</i>	-0.166	0.077	0.229	<i>0.544</i>	1.000		
V	<i>0.532</i>	-0.202	0.420	-0.046	0.019	0.352	0.167	-0.136	0.287	<i>0.488</i>	1.000	
Zn	0.710	0.154	0.402	0.469	-0.348	-0.097	0.279	0.451	0.889	<i>0.509</i>	0.439	1.000
LOI	-0.215	0.430	-0.423	-0.254	0.655	0.339	0.375	-0.453	-0.014	-0.360	0.140	-0.235
Na	0.302	0.449	0.007	0.212	0.085	-0.444	<i>0.553</i>	0.010	<i>0.603</i>	0.257	-0.276	0.068
K	0.229	-0.169	0.618	0.135	-0.766	-0.185	-0.253	0.261	-0.040	<i>0.499</i>	0.133	0.222
Rb	0.240	-0.254	0.638	0.164	-0.761	-0.078	-0.280	0.386	0.016	0.482	0.184	0.264
Mg	0.332	<i>0.525</i>	-0.007	0.198	0.180	-0.296	0.631	0.011	0.654	0.302	-0.097	0.120
Ca	-0.167	0.400	-0.382	-0.354	0.622	0.224	0.383	-0.328	0.025	-0.088	0.111	-0.227
Sr	-0.014	0.178	0.082	-0.090	-0.052	0.120	0.027	0.084	0.279	0.345	0.041	0.102
Ba	0.434	0.093	0.416	0.092	-0.265	-0.386	0.224	-0.133	0.299	<i>0.603</i>	0.065	0.116
Y	<i>0.499</i>	0.175	<i>0.517</i>	0.114	-0.310	0.026	0.146	0.300	0.387	0.275	0.473	0.781
Zr	0.257	-0.472	0.636	-0.022	<i>-0.530</i>	0.230	-0.436	0.256	-0.009	0.629	0.430	0.200
Nb	0.780	0.026	0.711	0.315	-0.454	-0.367	0.303	0.235	<i>0.533</i>	0.805	0.280	0.476
Ga	0.789	0.413	<i>0.505</i>	0.762	<i>-0.542</i>	<i>-0.518</i>	<i>0.547</i>	0.483	0.766	<i>0.562</i>	0.060	0.858
Si	0.197	-0.266	<i>0.549</i>	0.190	-0.833	-0.292	-0.352	0.321	-0.012	0.424	-0.058	0.237
P	<i>0.557</i>	0.390	0.184	0.337	0.063	0.076	0.445	0.070	0.436	0.317	0.472	0.417
S	0.316	0.323	0.005	0.056	0.317	-0.233	<i>0.517</i>	-0.189	<i>0.587</i>	0.299	-0.016	0.071

In addition to Fe, K, Rb and Si, the correlations showed that Al forms a third important component to the drain sediment geochemistry. Aluminium had a high, but insignificant, inverse correlation coefficient with Fe, suggesting that Al was diluted in the drain sediments by the input of Fe. Furthermore, the lack of significant correlation between Al and Si, K, or Rb suggests that there is a source of Al to the drain sediments in addition to Al from detrital minerals. A source of Al to the drain sediments is precipitation from soil-waters. Aluminium can be released from clays under acidic soil conditions (Evangelou, 1998; Nriagu, 1978). Furthermore, the occurrence of the mineral halotrichite suggests that the drain waters carry high concentrations of Al. Although not identified in the XRD analysis, Al hydroxides may also occur in the drain sediments and hence be important hosts for Al.

The importance of Al was evident from the number of positive correlations with other elements. Aluminium correlates strongly with Ga, Sc, Ti and Zn ($a = 0.001$), moderately with Co ($a = 0.01$) and weakly with Cu and V ($a = 0.05$). Aluminium containing minerals identified in the drain sediments included kaolinite, illite and halotrichite; but other Al phases were likely to occur in the samples such as gibbsite ($\text{Al}(\text{OH})_3$). Kaolinite, illite and gibbsite are able to adsorb metals on exchange sites or absorb elements into their mineral lattice. The correlation with Al indicates that Ga, Sc, Ti, Zn, Co, Cu and V are either incorporated into a crystal lattice with Al, or adsorbed on exchange sites of clays or Al hydroxides.

Cobalt and Cu correlated negatively with Fe ($a = 0.01$ and $a = 0.05$, respectively). The inverse relationship of Co and Cu with Fe indicates that Co and Cu are not being effectively adsorbed or precipitated with Fe phases (e.g. goethite and amorphous solids) in the drains.

Arsenic, Mn and Ni did not have any diagnostic correlations. Arsenic correlates only with Ni ($a = 0.001$). Arsenic and Ni did not correlate significantly with Al, Fe, or Mn; but the largest positive correlation coefficient with Al, Fe and Mn for both As and Ni is with Fe (0.242 and 0.369 respectively). The positive correlation with Fe indicates that As and Ni are more strongly associated with Fe than with Al and Mn, suggesting that As and Ni occur more with Fe phases than with Mn or Al (i.e. clays) in the drain sediments. The only significant correlation Mn displayed was a weak inverse relationship with Ga.

The only correlations with S were Sc and Ni (weak and positive in both cases). This indicates that element hosting in the drain sediments by sulfur was either not particularly significant, or was obscured by the high concentrations of S in the drain sediment environment (i.e. from seawater and oxidised ASS).

Finally, Ti and Nb correlated strongly. The strong correlation of Ti with Nb suggests that Nb was hosted with Ti by detrital Ti oxides (e.g. anatase, brookite or rutile; Deer et al, 1992).

6.3.1.6 Element Hosting in Drain Sediments

The MBCR-SEP was used to identify element fractions in the OF and BO drain sediments. The MBCR-SEP determines four chemically defined element fractions: 1) acid extractable; 2) reducible; 3) oxidisable; and 4) residual fractions. The results from the MBCR-SEP are reported for both the BO and OF drain sediments. Three drain sediment pairs were examined using the MBCR-SEP: FSD08A and B; FSD10A and B; and FSD11A and B. Each drain sediment pair consisted of an OF sample that was collected from above a BO sample. The samples were grouped into BO and OF

sets. The element fractions are presented as the percentage of the element occurring in the 4 fractions determined by the MBCR-SEP in the BO and OF sample sets (Figure 6.4).

The only significant hosts of Fe in the BO and OF were the residual and reducible fractions. Iron was largely hosted in the residual fraction by both the OF (54 %) and BO (76 %). The majority of the outstanding Fe was hosted in both drain sediment types in the reducible fraction. However, the OFs hosted twice as much Fe in the reducible fraction (43 %) as the BO (21 %). The increased amount of Fe in the reducible fraction of the OF compared to the BO indicates that the OF samples contain considerably more oxidised Fe phases.

The hosting of Al in the two drain sediment types was similar. Most Al was hosted by the residual fraction (84 - 86 %), but a significant amount (10 - 11 %) also occurred in the reducible fraction. The hosting of Al in the residual phase suggests that Al is mostly hosted by aluminosilicates and other resistant phases. However, about 10 % of the Al also occurred in the reducible fraction indicating that Al is present in oxidised phases (e.g. in an Al oxyhydroxide or substituting for Fe in goethite).

More than 90 % of the Ba, Ga, Nb, and Ti occurred in the residual fraction of both drain sediment types. The lack of significant proportions of Ba, Ga, Nb and Ti in any fraction except the residual indicates that the elements are hosted by resistant minerals (e.g. aluminosilicates, silicates and oxides).

Sodium primarily reported in the acid extractable fraction of the drain sediments. This indicates that Na was mostly hosted by carbonates, was adsorbed onto surfaces, or was incorporated in readily soluble minerals. Sodium did not report significantly (i.e. at greater than 10 %) in any other fraction except the acid extractable fraction, indicating that Na is largely hosted by exchange sites, carbonates and soluble minerals.

Cobalt reported differently in the BO and OF drain sediments. In the OF, Co reported in the (in descending order) residual (41 %), acid extractable (27 %), reducible (22 %) and oxidisable (10 %) fractions. In contrast, Co in the BO samples occurred in the (in descending order) acid extractable (33 %), residual (27 %), oxidisable (26 %) and reducible (14 %) fractions. In both the BO and OF drain sediments, a large portion of the Co was hosted by resistant minerals (e.g. aluminosilicates) and more than a quarter of the Co was associated with exchange sites. However, more than twice as much Co was hosted by reduced phases (e.g. sulfides) in the BO than the OF. Moreover, 50 % more Co was hosted by oxidised phases (e.g. Fe oxides and oxyhydroxides) in the OF than in the BO.

Scandium reported only in significant proportions (greater than 10 %) in the oxidisable and residual fractions of the drain sediments. The occurrence of Sc indicates that it is hosted by a combination of reduced minerals (e.g. sulfides) and resistant minerals (e.g. aluminosilicates, silicates and oxides) in the drain sediments.

Nickel was the only element that occurred at more than 50 % of its total concentration in the oxidisable fraction. The remaining Ni was hosted by the residual fraction (21 - 23 %), the reducible fraction (8 - 12 %) and the acid extractable fraction (7 - 11 %). The high proportion of Ni in the oxidisable fraction indicates that Ni is associated with reduced phases in both the BO and OF drain sediments.

Copper occurred largely in the residual fraction of both drain sediments (79 % in the BO and 87 % in the OF). The only other significant occurrence of Cu was in the oxidisable fraction of the BO, where Cu reports at 16 %. The occurrence of Cu indicates that it is hosted largely by resistant minerals, with a small proportion being hosted by oxidisable phases (e.g. sulfides) in the BO.

Lead only reported at greater than 10 % in the residual and reducible fractions of both the BO and OF. Lead occurred in the residual fraction of the BO and OF at 66 % and 81 %, respectively and in the reducible fraction at 31 % and 14 %, respectively. The distribution of Pb in the drain sediments indicates that the main hosts are resistant minerals (aluminosilicates, silicates and oxides) and reducible phases (e.g. Fe oxides and oxyhydroxides).

The occurrence of Zn in the two drain sediment types was similar. Zinc occurs in the residual fraction of the BO and OF at 58 % and 64 %, respectively, in the oxidisable fraction at 10 % and 12 %, in the reducible fraction of both sediment types at 15 % and in the acid exchangeable fraction at 17 % and 10 %, respectively. The MBCR-SEP shows that most Zn was hosted in resistant phases, with the remainder distributed across the other three fractions.

The majority of the Mn in BO drain sediments reported in the residual fractions (84 %), indicating that Mn is hosted by resistant minerals (aluminosilicates, silicates and oxides). Manganese in the OF was distributed between the residual (62 %), acid extractable (21 %) and reducible (13 %) fractions. The hosting of Mn in the OF is primarily by resistant minerals, but significant proportions are also hosted by exchange sites and incorporation into oxidised phases (e.g. Fe oxides).

The data indicate that the drain sediments share a similar elemental composition, displaying very high Fe and generally low trace element concentrations. This suggests that: 1) the two types of drain sediment share a common genesis; and 2) the drain sediments are not significant sinks for

trace metals released alongside Fe from the oxidised/inundated ASS. Finally, element hosting differed between the BOs and OFs, with the BOs frequently reporting higher residual and oxidisable fractions, than the OF.

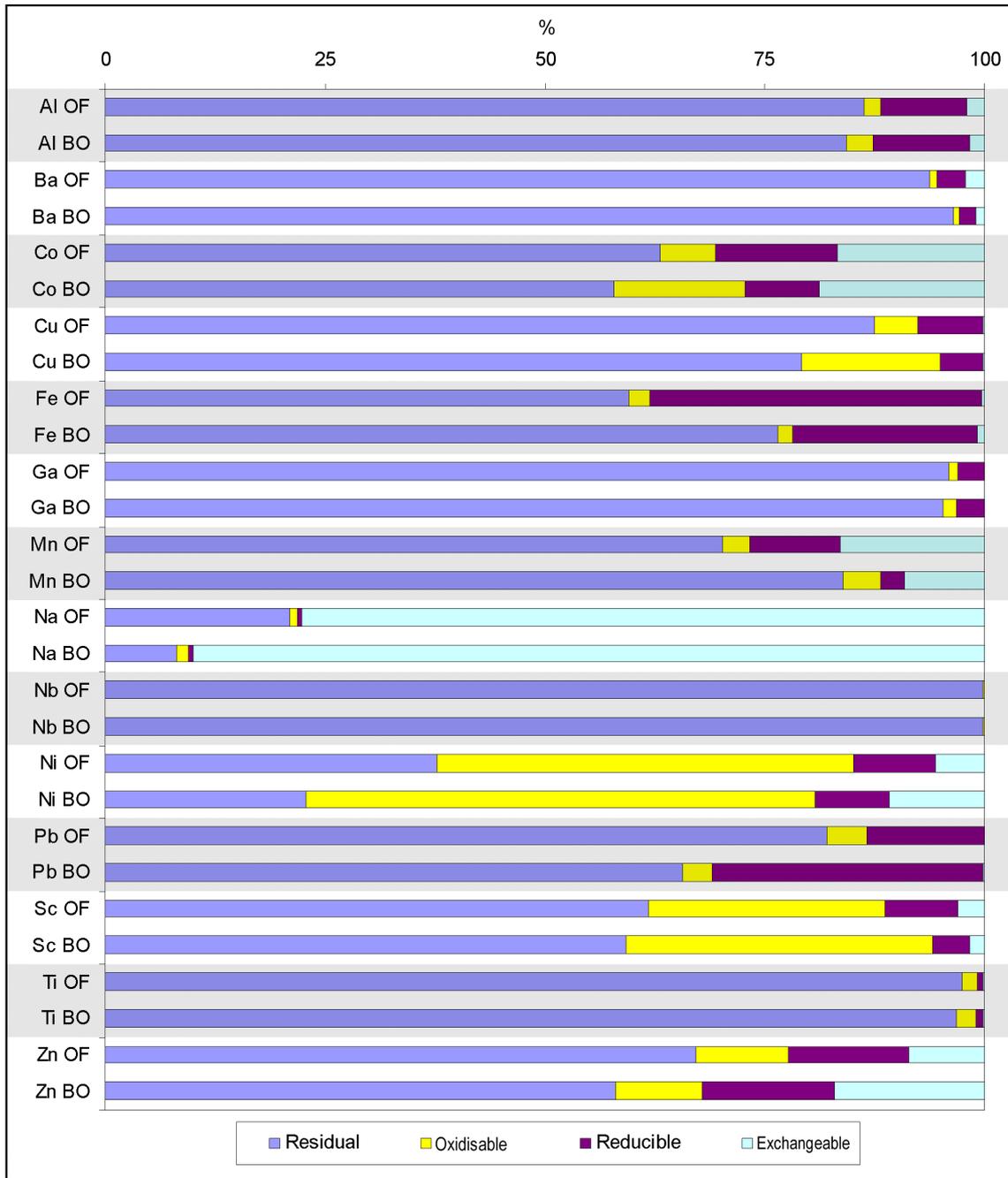


Figure 6.4. Percentage of elements hosted by acid extractable, reducible, oxidisable and residual fractions in the drain sediments as determined using the MBCR-SEP. Results are the average of 3 orange flocculants (OF) and 3 black ooze (BO) samples.

6.3.2 Geochemistry of Mouth Sediments

6.3.2.1 Chemical Composition of Mouth Sediments

Median, 25th percentile, 75th percentile, minimum and maximum values were used to describe the elemental composition of the mouth sediments from Firewood Creek (Figure 6.5). All elemental data for the mouth sediments from Firewood Creek are given in Table H.1 of Appendix H. The three most abundant elements in the mouth sediments were Fe, K and Na. Cobalt, Nb and Ga were the least abundant elements in the mouth sediments of Firewood Creek.

The Firewood Creek mouth sediments collected in 2004 displayed limited variations in elemental concentrations. The variation of element concentration was measured by calculation of the R%D between the 25th and 75th percentile (see Section 4.3.1.2). A small 25th - 75th percentile R%D indicates that the element concentrations in the sample set are similar, whereas a large 25th - 75th percentile R%D indicates that the element concentration range is large. No element in the mouth sediments of Firewood Creek had a 25th - 75th percentile R%D of more than 50 %. Elements that varied between 25 - 50 % are Ca, Co, Li, Mg, Mn, Ni, P, S and Zn. Arsenic, Fe, Ga, Na, Nb, Pb, Sr, Ti, V, Y and Zr varied between 25 - 10 %. Only Ba, K and Rb varied by less than 10 %. The low variation of concentrations in the mouth sediments indicates that sediments are geochemically homogeneous.

6.3.2.2 Element Correlation in Mouth Sediments

Correlation was used to identify relationships between elements in the mouth sediments from Firewood Creek collected in April 2004 (Table 6.4). Spearman's coefficient of correlation was used because of the non-parametric nature of much of the data. Elements were determined in the mouth sediments using a HF+HNO₃+HClO₄+HCl digest and ICP-MS/AES analysis (Section 2.8.5) rather than XRF analysis. Therefore, some elements that are hosted by resistant minerals (e.g. Zr, Ti) may report at concentrations below their true values. Only the correlation coefficients for the elements of interest (i.e. As, Co, Fe, Mn, Ni, Pb, Ti, V and Zn) with all the dataset elements are given.

Iron was associated with As, Co, Ni, Pb, V and Zn in the Firewood Creek mouth sediments. Iron correlated strongly ($\alpha = 0.001$) with Pb, moderately ($\alpha = 0.01$) with Zn and weakly ($\alpha = 0.05$) with As, Co and Ni. The lack of correlation between Fe and S suggests that Fe is not significantly associated with sulfides in the mouth sediments. Furthermore, the correlation of Fe with Ni, Pb and Zn, in the absence of significant correlations with S, indicates that Ni, Pb and Zn are associated with Fe phases (e.g. akaganeite (β -FeO·OH), goethite (α -FeO·OH)). In contrast, the significant correlations between As, Co and S suggest that As, Co and Fe are partly hosted by sulfides.

The numerous correlations with Li suggest that clay minerals are important hosts for Co, Ni, Ti, V and Zn. Lithium is frequently structurally combined in clays and Li concentration has been used as a proxy for the clay content of sediments (Loring and Rantala, 1992). In the Firewood Creek mouth sediments, Li correlated strongly with Co, Ni and Zn, moderately with Ti and weakly with Fe and V ($a = 0.05$). Therefore, the correlations indicate that Co, Ni, Ti, V and Zn are associated with clay minerals.

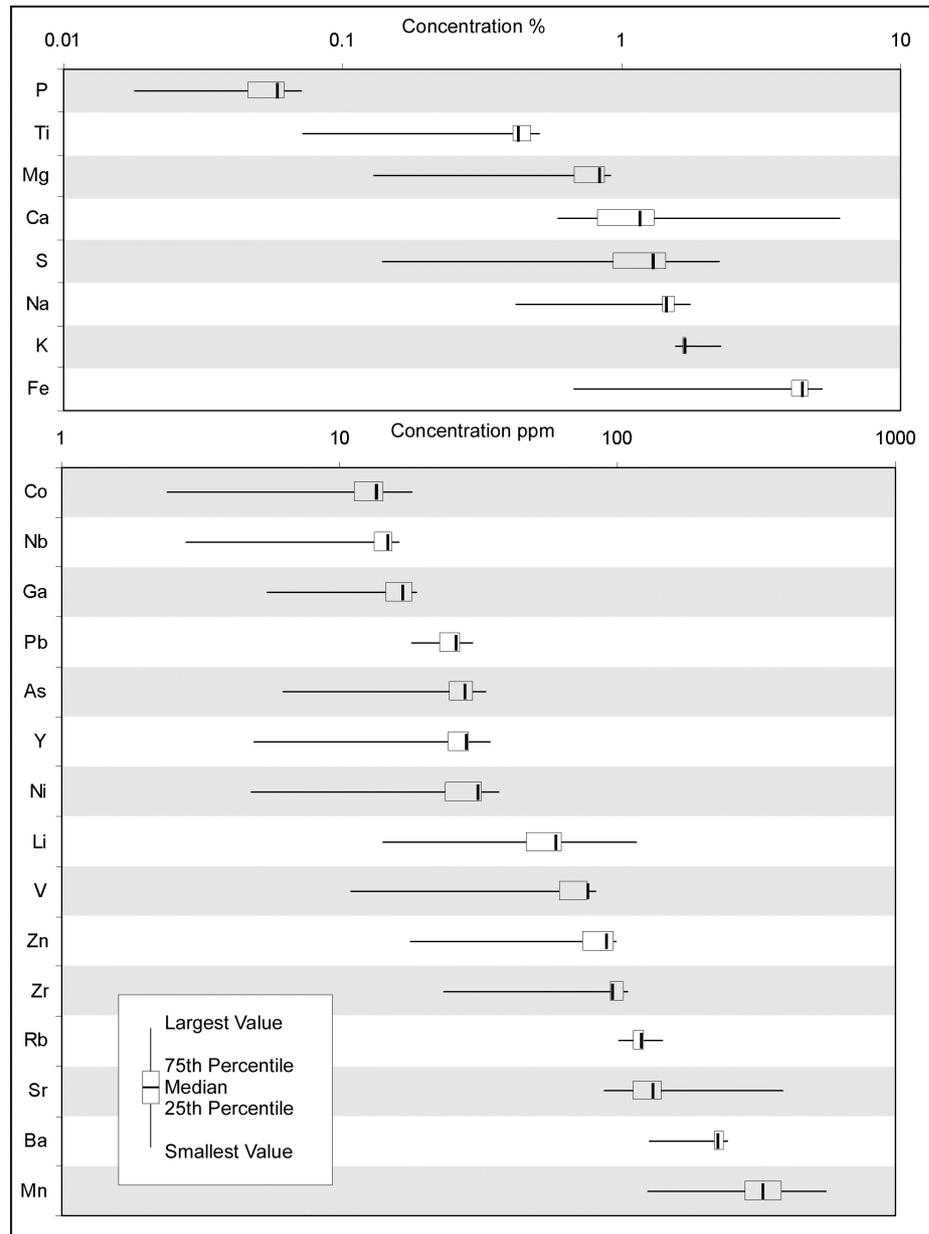


Figure 6.5. Chemical composition of mouth sediments from Firewood Creek. Component were determined using ICP-MS/AES after HF+HNO₃+HClO₄+HCl digest. Element concentrations are described by median, 25th percentile, 75th percentile, smallest and largest values from a population of 13 samples. Components are displayed in ascending median concentrations.

Table 6.4. Correlation matrix for April 2004 mouth sediments from Firewood Creek. Only the correlation coefficients for the elements of interest (As, Co, Fe, Mn, Ni, Pb, Ti, V and Zn) with all the dataset elements are given. Strong correlations ($\alpha = 0.001$) are shown in both bold and italic, moderate correlations ($\alpha = 0.01$) in bold and weak correlations ($\alpha = 0.05$) in italic. Spearman's coefficient of correlation was used because of the non-parametric nature of the data.

	As	Co	Fe	Mn	Ni	Pb	Ti	V	Zn
As	<i>1.000</i>								
Co	0.511	<i>1.000</i>					Alpha <i>n = 13</i> 0.001 <i>0.791</i> 0.010 <i>0.698</i> 0.050 0.555		
Fe	<i>0.692</i>	<i>0.626</i>	<i>1.000</i>						
Mn	<i>0.637</i>	0.286	0.555	<i>1.000</i>					
Ni	0.489	<i>0.890</i>	<i>0.692</i>	0.368	<i>1.000</i>				
Pb	<i>0.648</i>	0.462	<i>0.885</i>	<i>0.604</i>	0.478	<i>1.000</i>			
Ti	0.264	<i>0.753</i>	<i>0.670</i>	0.451	<i>0.775</i>	<i>0.566</i>	<i>1.000</i>		
V	0.250	<i>0.648</i>	<i>0.666</i>	0.446	<i>0.767</i>	<i>0.601</i>	<i>0.952</i>	<i>1.000</i>	
Zn	0.324	<i>0.721</i>	<i>0.781</i>	0.144	<i>0.757</i>	<i>0.703</i>	<i>0.733</i>	<i>0.776</i>	<i>1.000</i>
Li	0.324	<i>0.918</i>	<i>0.599</i>	0.110	<i>0.846</i>	0.440	<i>0.747</i>	<i>0.690</i>	<i>0.835</i>
Na	0.363	0.516	<i>0.648</i>	<i>0.604</i>	0.495	<i>0.676</i>	<i>0.687</i>	<i>0.565</i>	0.450
K	0.084	-0.229	-0.336	0.101	-0.190	-0.274	-0.224	-0.128	-0.467
Rb	0.259	0.053	0.137	0.317	0.084	0.195	0.100	0.196	-0.030
Mg	0.275	<i>0.698</i>	<i>0.736</i>	0.478	<i>0.780</i>	<i>0.665</i>	<i>0.945</i>	<i>0.946</i>	<i>0.775</i>
Ca	-0.211	-0.477	-0.260	0.133	-0.465	-0.349	-0.338	-0.357	-0.516
Sr	0.302	-0.049	0.231	<i>0.670</i>	-0.016	0.154	0.099	0.042	-0.138
Ba	-0.024	0.506	0.226	0.440	0.530	0.238	<i>0.815</i>	<i>0.784</i>	0.398
Ga	0.515	<i>0.820</i>	<i>0.741</i>	0.470	<i>0.894</i>	<i>0.571</i>	<i>0.877</i>	<i>0.894</i>	<i>0.783</i>
Y	0.469	<i>0.725</i>	<i>0.763</i>	0.071	<i>0.670</i>	<i>0.660</i>	0.480	0.469	<i>0.898</i>
Zr	0.511	<i>0.571</i>	<i>0.577</i>	<i>0.808</i>	<i>0.566</i>	<i>0.637</i>	<i>0.753</i>	<i>0.756</i>	0.432
Nb	0.440	<i>0.813</i>	<i>0.709</i>	0.549	<i>0.824</i>	<i>0.648</i>	<i>0.945</i>	<i>0.922</i>	<i>0.721</i>
P	0.132	0.423	0.538	0.060	0.275	0.544	0.445	0.369	<i>0.643</i>
S	<i>0.665</i>	<i>0.560</i>	0.429	0.445	0.368	0.374	0.407	0.268	0.198

6.4 Discussion

The fate of the elements released during the oxidation of PASS and inundation of AASS are discussed using the results from the analysis of the drain and mouth sediments of Firewood Creek. Particularly important is the determination of whether elements released from the ASS are being released into Trinity Inlet. Furthermore, if elements are being released from the ASS, has seawater inundation of the ASS increased the rate of element release.

6.4.1 Drain Sediments

MBOs, of which the East Trinity BO drain sediments largely consist, are a well documented phenomenon in ASS environments (e.g. Bush et al., 2004; Smith, 2004; Smith and Melville, 2004; Hicks and Fitzpatrick, 2003; Bush et al., 2002a; Bush et al., 2002b; Fyfe et al., 2002; Sullivan and Bush, 2002). MBOs form from ASS leachate that has high concentrations of Fe and SO_4 , in stagnant or slow flowing drains rich in organic matter (Smith and Melville, 2004). The MBOs are reported to be of importance in ASS environments because of their potential to acts as sinks for

potentially toxic elements (Smith, 2004; Smith and Melville, 2004). Metal and metalloid scavenging in the MBOs is largely thought to be by S^{2-} that is formed during reduction. This is because sulfide has been identified as the primary control of metal (Cd, Cu, Fe, Mn, Ni, Pb and Zn) concentrations in sulfidic waters (Dyrssen and Kremling, 1990) and anoxic sediments (Simpson et al., 1998).

At East Trinity, the BOs are intimately associated with OF drain sediments. Though the BOs have received significant attention, limited investigation has been conducted on the geochemistry of OFs or their role as potential element sinks (e.g. Hall, 2002; Ferguson and Eyre, 1999).

Here, discussion of the East Trinity drain sediments focuses on the formation of the drain sediment, the role of the drain sediments as sinks for elements mobilised from the ASS and the differences in element hosting between the BO and OF. Clarification of these issues will increase the understanding of the risks posed by the drain sediments, as well as assist with the development of effective management techniques for the drain sediments on East Trinity and in other ASS environments.

6.4.1.1 Drain Sediment Formation

At East Trinity, the drain sediments are likely to have formed from flocculated Fe^{3+} phases that precipitated in the drains servicing areas of ASS. Formation of the drain sediments from flocculation of Fe precipitates is supported by the similar Fe normalised median element values for the drain sediments and suspended particles from Firewood Creek reported by Hall (2002) (Table 6.5). All of the Fe normalised element values from the drain sediments are of the same magnitude as those from Hall's (2002) suspended particles.

Furthermore, both sets of suspended particles described by Hall (2002) and the OF drain sediments have goethite and a range of other oxidised Fe phases in their major mineralogy. The similar Fe normalised element values and mineralogies of the Firewood Creek drain sediments and suspended particles indicates that the drain sediments formed from flocculation of the suspended particles. Therefore, the elemental composition of the drain sediments at East Trinity is largely preordained by the elemental composition of the suspended particles.

The mechanism of Fe precipitation in the egressing ASS soil-waters is likely due to increased solution pH or salinity (due to mixing of waters), or increased pE from exposure to the atmosphere. Steep pH and salinity gradients have been identified as the cause of Fe and Al precipitation in drains of the catchment of the lower Richmond River by Ferguson and Eyre (1999).

Table 6.5. Comparison of median element concentrations and Fe normalised median concentrations of Firewood Creek drain sediments and suspended particle geochemistry from Firewood Creek reported by Hall (2002). The “Flocculants 1” sample set was collected before a period of trial seawater inundation. The “Flocculants 2” sample set were collected during a period of trial seawater inundation.

	Firewood Ck Drain Sediments (n = 17)		Firewood Ck Flocculants 1 (n = 11)		Firewood Ck Flocculants 2 (n = 9)	
	[Median]	Fe Norm	[Median]	Fe Norm	[Median]	Fe Norm
Fe %	15.99	1.00	16.9	1.00	11.7	1.00
Al %	4.63	0.29	2.62	0.16	2.99	0.26
As ppm	35	2.19	26.95	1.59	16.1	1.38
Cu ppm	9	0.56	8.72	0.52	18.9	1.62
Mn ppm	74	4.63	27.2	1.61	93	7.95
Ni ppm	14	0.88	2.53	0.15	6.18	0.53
Pb ppm	12	0.75	25.7	1.52	31.5	2.69
Zn ppm	37	2.31	55.3	3.27	103	8.80

6.4.1.2 Geochemical Relationship of the BOs and OFs

Comparison of the Fe normalised element values in the OFs and BOs show that: 1) the elemental compositions of the BOs and OFs from East Trinity are generally similar; and 2) the BOs are enriched relative to the OFs in Al, As, Co, Cu, Ni, Sc, V, Pb, Y and Zn, but depleted in Mn (Table 6.6). The similar elemental composition suggests that the BOs and OFs are geochemically related. The fact that the BOs and OFs are geochemically related is supported by their occurrence in the field. Where both drain sediments were present, the OFs were always found overlying and in contact with, the BOs. The relationship between the BOs and OFs is further demonstrated by the dried BOs and OFs samples. Drying of BOs and OFs samples resulted in an identical product (i.e. very fine orange powder mixed with detrital minerals).

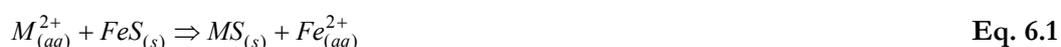
The likely mechanism for the formation of the BO at East Trinity is the partial reduction of OF drain sediments. MBOs (i.e. BOs) form in slow or non-flowing drains containing water with high Fe, SO₄ and organic matter concentrations (Smith, 2004; Smith and Melville, 2004).

The differences in the Fe normalised element values between the BO and OF is largely explained by the smaller Fe concentration in the BO. The larger Fe normalised element values in the BO generally occur without significant increase in the actual concentration of the element (e.g. Al, As, Ni, Sc, V, Y and Zn). Instead, the increase in the Fe normalised element values in the BO is due to a lower [Fe].

Table 6.6. Comparison of Fe normalised median values in the Black Ooze (BO) and Orange Flocculant (OF) samples.

	Orange Flocculants (n = 12)		Black Oozes (n = 5)		BO Fe Norm/ OF Fe Norm
	[Median]	Fe Normalised	[Median]	Fe Normalised BO	
Fe %	17.0	1.00	10.3	1.00	1.00
Al %	4.0	0.24	5.9	0.58	2.42
As ppm	36	2.12	35	3.41	1.61
Co ppm	1	0.06	14	1.36	22.67
Cu ppm	3.5	0.21	11	1.07	5.10
Mn ppm	137	8.06	55	5.36	0.67
Ni ppm	14	0.82	16	1.56	1.90
Pb ppm	12	0.71	24	2.34	3.30
Sc ppm	4	0.24	8	0.78	3.25
V ppm	39	2.29	46	4.48	1.96
Y ppm	20.5	1.21	21	2.05	1.69
Zn ppm	37	2.18	37	3.61	1.66

The low [Fe] in the BO may be due to the loss of Fe during reduction. A possible mechanism for the loss of Fe from the BO is given by Smith and Melville (2004), who identify that trace metals (Cd, Cu, Ni, Pb and Zn) can displace Fe from monosulfides to form insoluble metal sulfides (Equation 6.1). A second mechanism that may explain the decreased Fe content of the BO is the release of Fe²⁺ during the reductive dissolution of Fe³⁺ oxyhydroxides by H₂S (Afonso and Stumm, 1992).



Ferrous Fe is soluble under transitional/mildly acidic to near neutral conditions in ASS environments (see Figure 4.4). Where limited sulfide is available (e.g. during the transformation of OF to BO), Fe may not be effectively immobilised and therefore remain in solution. The extended mobility of Fe²⁺ could result in its depletion from the BO.

Further evidence of the BO forming from the OF can be seen in the behaviour in Mn. Manganese is not enriched in the BO because it is mobile under reducing conditions (see Figure 4.3, diagram b). Hence, Mn is immobile in OF, but mobile in the BO. The mobility of Mn in the BO leads to its depletion relative to OF.

6.4.1.3 Drain Sediments as Element Sinks

At East Trinity, the drain sediments are generally not an effective sink for elements mobilised from ASS by oxidation or inundation. Firstly, the drain sediments have lower median concentrations of Al, Co, Cu, Mn, Ni, Pb, Sc, V, Y and Zn relative to the ASS described in Chapter 3 (Table 6.7). Only Fe and As have higher median concentrations in the drain sediments than in the ASS.

Table 6.7. Median values of Al, As, Co, Cu, Mn, Ni, Pb, Sc, V, Y and Zn in the East Trinity ASS and drain sediments (XRF data).

	ASS [Median] (n=21)	Drain Sediments [Median] (n=17)
Fe %	3.26	15.99
Al %	7.99	4.63
As ppm	25	35
Co ppm	6	2
Cu ppm	12	9
Mn ppm	138	74
Ni ppm	19	14
Pb ppm	26	12
Sc ppm	14	6
V ppm	70	42
Y ppm	25	21
Zn ppm	50	37

Secondly, the poor trapping (or incorporation) of elements mobilised from the ASS by the drain sediments is demonstrated using Fe normalised element concentrations. The Fe normalised element concentrations are used to compare the composition of the drain sediments with the assemblages of the elements mobilised from the oxidised and inundated ASS. The assemblages of elements mobilised from the AASS and IAASS are calculated using the AASS, IAASS and PASS group median values presented in Chapter 3. The mobilised elements are found by subtracting the median element concentration in the AASS or IAASS from the median element concentration in their ASS profile respective PASS group. The element concentrations in the mobilised element assemblages for the AASS and IAASS are then normalised to their Fe concentrations. Equations 6.2 and 6.3 summaries the Fe normalisation process for the mobilised element assemblages for AASS and IAASS, respectively.

$$Fe \text{ normalised } [x] = \frac{\left(\begin{bmatrix} \tilde{x} \\ \tilde{x} \end{bmatrix}_{PASS} - \begin{bmatrix} \tilde{x} \\ \tilde{x} \end{bmatrix}_{AASS} \right)}{\left(\begin{bmatrix} \tilde{Fe} \\ \tilde{Fe} \end{bmatrix}_{PASS} - \begin{bmatrix} \tilde{Fe} \\ \tilde{Fe} \end{bmatrix}_{AASS} \right)} \quad \text{Eq. 6.2}$$

$$Fe \text{ normalised } [x] = \frac{\left(\begin{bmatrix} \tilde{x} \\ \tilde{x} \end{bmatrix}_{PASS} - \begin{bmatrix} \tilde{x} \\ \tilde{x} \end{bmatrix}_{IAASS} \right)}{\left(\begin{bmatrix} \tilde{Fe} \\ \tilde{Fe} \end{bmatrix}_{PASS} - \begin{bmatrix} \tilde{Fe} \\ \tilde{Fe} \end{bmatrix}_{IAASS} \right)} \quad \text{Eq. 6.3}$$

Normalising the chemistry of the drain sediments and the assemblage of the elements mobilised from ASS to their Fe contents allows for the direct measure of element trapping by the drain sediments. The comparison assumes that the Fe that forms much of the drain sediments is released from the oxidised and inundated ASS along with the other elements that are of interest. Therefore,

if the drain sediments are effectively trapping the trace elements mobilised in the ASS concurrently with Fe, the drain sediments should have similar Fe normalised values to the assemblage of elements mobilised from ASS.

The limited occurrence of the elements mobilised from the ASS in the drain sediments is demonstrated by the large number of elements reporting Fe normalised values less than 1 (Table 6.8). Where the Fe normalised element values for the drain sediments are less than the Fe normalised element values for the mobilised element assemblages, it indicates that the drain sediments have a lower proportion of that element than has been mobilised from the ASS. This suggests that the element with the lower Fe normalised value has not been incorporated into the drain sediments as effectively as Fe.

Table 6.8. Comparison of median Fe normalised element values of the Firewood Creek drain sediments and the assemblages of elements mobilised (relative to PASS) from the AASS and IAASS groups (see Chapter 3).

	Drain Sediments Fe Norm	Mobilised from AASS Fe Norm	Mobilised from IAASS Fe Norm
Fe %	1.00	1.00	1.00
Al %	0.29	1.83	0.22
As ppm	2.19	1.37	-
Co ppm	0.13	21.93	4.79
Cu ppm	0.56	8.22	1.67
Mn ppm	4.63	382	110
Ni ppm	0.88	17.82	6.04
Pb ppm	0.75	6.85	3.96
Sc ppm	0.34	2.74	-
V ppm	2.63	23.30	0.83
Y ppm	1.31	5.48	2.08
Zn ppm	2.31	37.01	11.46

Elements in the drain sediments that have lower Fe normalised values than in the elements mobilised from the ASS are Co, Cu, Mn, Ni, Pb, Y and Zn. This indicates that Co, Cu, Mn, Ni, Pb, Y and Zn have not been as effectively incorporated into the drain sediments as has Fe. Aluminium, Sc and V have Fe normalised values in the drain sediments between the mobilised element Fe normalised values from the AASS and IAASS groups. This suggests that Al, Sc and V occur in the drain sediments in similar proportion to that mobilised from the oxidised ASS. The only element that has a higher Fe normalised value in the drain sediments than that in the mobilised elements is As. This suggests that As is being preferentially trapped by the drain sediments. Arsenic is known to strongly associate with Fe (oxyhydr)oxides (Hudson-Edwards, 2003) and sulfates such as jarosite (Hudson-Edwards et al., 2005). Accumulation of As on Fe-precipitates is a possible mechanism that explains the enrichment of As (relative to Fe) in the drain sediments.

6.4.1.4 Trace Elements in Drain Sediments

Poor incorporation of trace elements into the drain sediments is reflected in their low trace element concentrations. Low trace metal content in MBOs has been previously reported by Fyfe et al. (2002). The authors suggested two reasons for the low metal concentrations of MBOs: restriction of metal adsorption/coprecipitation by rapid formation of the MBO; or preferentially trapping of trace elements by the Fe oxides that frequently occur in association with the MBOs. At East Trinity, the elemental composition of the drain sediments has been shown to be a product of suspended Fe precipitate particle element concentrations. Furthermore, the low concentration of trace elements in the drain sediments is due to inefficient element scavenging by the suspended particles.

Finally, in comparison to other ASS environment drain sediments (e.g. MBOs), the drain sediments from East Trinity have lower trace element concentrations. This is demonstrated by comparison of the total element concentration of the East Trinity drain sediments with that of MBOs from the Tweed River floodplain described by Smith and Melville (2004, estimated from Figure 6 therein; see Table 6.9). The East Trinity drain sediments contain more Fe than those from the Tweed River MBOs, but less Al, Mn, Ni, Pb and Zn.

Table 6.9. Comparison of total concentration and Fe normalised values in the Firewood Creek drain sediments and the Tweed River floodplain monosulfidic black oozes. The median concentrations for the Tweed River floodplain are estimates from Figure 6 of Smith and Melville (2004).

	Firewood Ck Drain Sediments (n = 17) [Median]	Fe Norm	Tweed River Floodplain [Estimated Median]	Fe Norm
Fe %	15.99	1.00	7.00	1.00
Al %	4.63	0.29	7.90	1.13
Mn ppm	74	4.63	600	85.71
Ni ppm	14	0.88	25	3.57
Pb ppm	12	0.75	90	12.86
Zn ppm	37	2.31	100	14.29

6.4.1.5 Comparison of Drain Sediments with Sediment and Soil Quality Guidelines

The chemical composition of the East Trinity drain sediments are compared with sediment quality guidelines (Table 6.10). ANZECC and ARMCANZ (2000) provides Interim Sediment Quality Guidelines (ISQG) for As, Cu, Pb, Ni and Zn. The use of the guidelines has previously been discussed in Section 3.4.1.3.

The elements in the drain sediments that exceeded the sediment quality guidelines were As, Cu and Ni (Table 6.10). Arsenic exceeded the ISQL-Low and the soil EIL value in more than 75 % of the samples and the highest value for As exceeded the ISQL-High value. Only the highest concentration of Cu in the drain sediments exceeded the ISQL-Low value. More than 25 % of the drain sediment sample exceeded the ISQL-Low value for Ni, but only the largest value exceeded the ISQL-High value. The toxic effects of As and Ni have been reported in Section 3.4.1.3. Toxic concentration of Cu are known to damage the liver and bone marrow (Smith and Huyck, 1999).

Examination of the drain sediment chemical composition with the sediment quality guidelines indicates that As is the primary concern to the environment in terms of toxicity, with Ni and V also potentially being able to produce toxic effects. In spite of exceeding the ISQG-Low threshold, Cu is unlikely to be of concern because it generally occurs in non-environmentally significant concentrations in the drain sediments.

Table 6.10. Comparison of East Trinity drain sediments with ANZECC and ARMCANZ (2000) interim sediment quality guidelines. East Trinity drain sediment values in bold exceed the corresponding guideline value/s.

	Sediment Quality Guidelines		East Trinity Drain Sediments (n = 17)				
	ISQG-Low ¹	ISQG-High ²	Smallest	25th %tile	Median	75th %tile	Largest
As ppm	20	70	3	31	35	41	74
Cu ppm	65	270	1.5	1.5	9	12	75
Ni ppm	21	52	6	11	14	23	53
Pb ppm	50	220	1	9	12	33	37
Zn ppm	200	410	4	27	37	55	81

¹ Interim Sediment Quality Guideline (ISQG) - Low: “probable-effects concentration” threshold, below which biological effects rarely occur.

² Interim Sediment Quality Guideline (ISQG) - High: “probable-effects concentration” threshold, below which biological effects possibly occur. Concentrations at or above the ISQG-High represent concentrations within which frequent biological effects are expected.

6.4.2 Element Hosting in the Drain Sediments

This section examines element hosting in the drain sediments as determined using the MBCR-SEP. See Section 5.4.1 for a full discussion on the use of SEPs.

6.4.2.1 Use of the Modified BCR Sequential Extraction Procedure

The MBCR-SEP used to examine the drain sediments did not include the water-soluble extraction employed with the ASS samples (Chapter 5). This meant that the water-soluble fraction of the drain sediments was incorporated into the AE fraction (the first step of the SEP).

The only deviations from the MBCR-SEP used with the drain sediments from East Trinity were an increase in the volume of H₂O₂ added at the third step and the use of a HF+HNO₃+HClO₄+HCl digest of the residual rather than the recommended aqua regia digest. Additional H₂O₂ was added to ensure it was present in excess. This was done because of the expected high sulfide and organic matter content of the samples. The HF+HNO₃+HClO₄+HCl digest was used for the residual phase because it gave a more complete digestion than the aqua regia method. Though the changes are minor, they must be considered if the MBCR-SEP data from the drain sediments are compared with MBCR-SEP results from other geological media.

6.4.2.2 Element Fractions in the Drain Sediment

The results of the MBCR-SEP show that there is only a small difference in the element hosting between the OF and BO drain sediments despite the distinct colouration used to distinguish the drain sediment types in the field. This is demonstrated by the comparison of the averaged element values (percentage) reporting in each fraction in the OF and BO (Table 6.11). The fraction sizes in the two drain sediments did not differ by more than 3 %. A larger proportion of elements reported in the reducible fraction of the OF compared to the BO. By contrast, a reversed trend occurred for the oxidisable fraction. This was expected, as the OF were known to be composed largely of oxidised Fe phases and sulfide was expected to be significant in the BO.

Table 6.11. Averaged element percentages reporting in the MBCR-SEP fractions in the BO and OF drain sediments from East Trinity.

	OF % Average	BO % Average
Acid Extractable	10	11
Reducible	9	8
Oxidisable	8	11
Residual	73	70
Sum	100	100

6.4.2.2.1 *Acid Extractable Fraction*

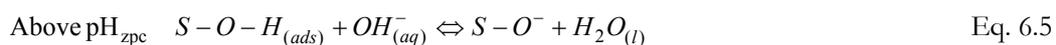
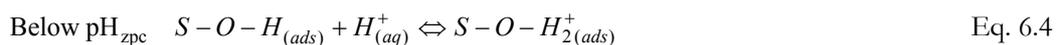
The AE fraction determined by the MBCR-SEP consists of elements that are dissolved in porewaters, hosted by readily soluble (evaporites) and acid soluble (carbonates) minerals and elements adsorbed on soil material surface charges. The major mineralogy of the drain sediments consists of quartz, clays (illites and kaolinite) and various oxidised Fe phases. No carbonate minerals and only one possible evaporite (halotrichite) were identified in the major mineralogy of the drain sediments. The lack of carbonates and limited evaporites suggests that the main contributor to the acid extractable fraction in the drain sediments are exchange sites on clays and on oxidised Fe phases (e.g. goethite and amorphous Fe oxyhydroxides). Organic matter is likely to also play an important role in element adsorption in the drain sediments.

Adsorption is the process by which a chemical species becomes associated with a charged (two-dimensional) surface by electrostatic forces or chemical bonds (Evangelou, 1998). Absorption differs from adsorption by involving incorporation of a chemical species into a three-dimensional lattice (Stumm and Morgan, 1996). Ad- and ab-sorption are frequently referred to using the collective term of sorption, particularly where the precise process is not known (Stumm and Morgan, 1996).

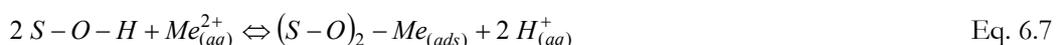
Adsorbed chemical species form either inner- or outer-sphere complexes with charged surfaces. An outer-sphere complex is a relatively weak electrostatic association between a charged surface and a hydrated ion (i.e. cation and base are separated by one or more H₂O molecules, Stumm and Morgan, 1996). A cation held by an outer-sphere complex can easily be exchanged by other cations capable of forming outer-sphere complexes (Evangelou, 1998). In comparison, an inner-sphere complex is a relatively strong complex between a charged surface and an unhydrated cation that involves covalent bonding with surface ligands, commonly O (Stumm and Morgan, 1996). An inner-sphere complexed cation can only be effectively exchanged by cations that are also capable of forming inner-sphere complexes (Evangelou, 1998).

Sorbing surfaces have two types of surface charge: permanent (or pH independent) charge and variable (pH dependent) charge (Evangelou, 1998). Permanent charge is due to isomorphic substitutions and lattice defects and is the main source of surface charge for smectite and vermiculite clays (Langmuir, 1997). Variable surface charge is largely the product of functional group ionisation on mineral surfaces (Langmuir, 1997) and is dependent on the pH and composition of the interface solution. Oxides, hydroxides, phosphates and carbonates frequently display variable surface charge (Langmuir, 1997). In the presence of water, oxide surfaces are generally covered with hydroxyl groups (Stumm and Morgan, 1996). Soil organic matter may also have substantial variable charge due to carboxylic (RCOOH), enolic (R=C(OH)R) and alcoholic (ROH) functional groups (Evangelou, 1998).

The method by which pH regulates surface charge and metal adsorption can be described by competition between H⁺ and other cations for the negative surface charges (Stumm and Morgan, 1996). The pH value at which the net charge on a variable charge surface (substance) is zero is referred to as the point of zero charge (pH_{pzc}). Below the pH_{pzc} the variable charge surface becomes positively charged (Equation 6.4; Evangelou, 1998). By contrast, at pH values above the pH_{pzc}, the variable charge surface becomes negatively charged and available for cation adsorption (Equation 6.5; Evangelou, 1998). Therefore, as pH drops, negative charges on the variable charge surface become progressively protonated and cation adsorptive capacity on the surface decreases.



Adsorption of metal cations by variable charge surfaces is pH dependent because the formation of surface complexes is competitive (e.g. metal ions compete with H^+ , see Equations 6.6 and 6.7 for monodentate and bidentate examples; Stumm and Morgan, 1996). Additionally, H^+ is able to displace outer-sphere complexes by forming inner-sphere complexes with the surface, effectively displacing the outer-sphere complex (Equation 6.8 where ‘...’ indicates an outer-sphere complex and ‘—’ an inner-sphere complex). Consequently, cation adsorption by a variable charge surface increases with increasing pH (Smith, 1999).



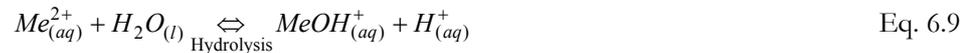
At East Trinity, the elements in the drain sediments that report at more than 10 % in the acid extractable fraction are Co, Mn, Na, Ni and Zn. Seawater is the likely source of the Na in the AE fraction of the drain sediments. The low concentration of elements other than Co, Mn, Na, Ni and Zn in the AE fraction indicates two possible circumstances. Firstly, the AE fraction is not generally significant (with the possible exception of Co, Mn, Ni and Zn) in the East Trinity drain sediments. Or secondly, the AE extraction of the MBCR-SEP failed to effectively extract all adsorbed elements.

The importance of adsorption in the accumulation of elements by the drain sediment (particularly the OF) was demonstrated by Hall (2002). Hall (2002) examined Fe-rich precipitates in the creeks of East Trinity and reported that metal and metalloid concentrations in the precipitates correlated with the pH of the creek water. From this, Hall (2002) concluded that adsorption controlled the concentrations of Al, Ca, Cu, Cr, Mn, Ni, Pb and Zn in the suspended Fe precipitates. The drain sediments form from the flocculation and deposition of the suspended particle, therefore Hall’s (2002) premise that adsorption controls the concentration of Al, Ca, Cu, Cr, Mn, Ni, Pb and Zn is explored with regard to the MBCR-SEP result from the drain sediments.

The AE fraction results for the drain sediments partly support Hall’s (2002) premise with regard to Co, Mn, Ni and Zn (AE fraction 33 - 7 %). However, Al, Cu and Pb report in only very small proportions (< 2 % for Al, < 0.8 % for Cu, Cr and Pb) in the AE fraction of the drain sediments. This suggests that though adsorption may be an important initial process in the scavenging of elements from solution by the Fe precipitates, many of the adsorbed elements are transferred (e.g. by sorption, precipitation, or co-precipitation) to other chemical fractions in the drain sediments.

This indicates that the AE fraction is unlikely to be a major source of Al, Ba, Cu, Fe, Ga, Nb, Pb, Sc and Ti to the environment.

Though transferral of adsorbed elements may occur, there is also evidence that the AE extraction of the MBCR-SEP failed to desorb strongly adsorbed cations in the drain sediments. Adsorption of individual metal ions occurs over a pH interval of 1 - 2 units (Stumm and Morgan, 1996). The range of pH values over which metal ion adsorption occurs is referred to as the adsorption edge. The position of the adsorption edge depends on the adsorbing substrate and the adsorbate. The adsorption of metal cations by a specific variable charge surface can be predicted (to some degree) by the cations hydrolysis constants (Evangelou, 1998). This is because a metal's hydrolysis constant is indicative of the strength of the covalent bonds formed with lattice ions (Hall, 1998). The greater the hydrolysis constant of the metal, the lower the adsorption pH (see Equations 6.9 and 6.10; Evangelou, 1998).



$$pK_a = -\log\left(\frac{[MeOH_{(aq)}^+] \times [H_{(aq)}^+]}{[Me_{(aq)}^{2+}]}\right) \quad \text{Eq. 6.10}$$

Correlation of cation adsorption order with hydrolysis constants is demonstrated by Figure 9.12b (from Stumm and Morgan, 1996). Figure 9.12b shows the order of cation adsorption on hydrous Fe³⁺ oxide with increasing pH as Cr³⁺, Pb²⁺, Cu²⁺, Zn²⁺ and Ni²⁺. This adsorption order correlates with each cation's respective hydrolysis constant (Table 6.12).

Table 6.12. Hydrolysis constants of selected metals species with relationship to adsorption strength and exchange pH. Cations in bold reported in significant proportions in the MBCR-SEP acid extractable fraction of the drain sediments from East Trinity.

	Strongest	←	Adsorption Strength			→	Weakest
Form	Cr ³⁺	Pb ²⁺	Cu ²⁺	Zn²⁺	Ni²⁺	Co²⁺	Mn²⁺
pK _a	4.0 ¹	7.7 ^{1,2}	7.9 ²	9.0 ^{1,2}	9.5 ²	9.9 ²	10.6 ¹
	Lowest	←	Exchange pH			→	Highest

¹ Hydrolysis constant from Burgess (1978).

² Hydrolysis constant from Erdemoğlu and Sarikaya (2006).

A general order of sorption that applies to the divalent transition metals is the Irving-Williams order. The adsorption strength predicted by the Irving-Williams order for divalent transition elements is: Cu²⁺ > Zn²⁺ ≥ Ni²⁺ > Co²⁺ > Fe²⁺ > Mn²⁺ (Langmuir, 1997). Langmuir (1997) states that there is evidence that the adsorption tendency of divalent transition elements by hydrous oxides often follows the Irving-Williams order. The Irving-Williams order is followed by the

adsorption edges displayed by the cations adsorbed on Fe (oxyhydr)oxides in Figure 9.12b from Stumm and Morgan (1996, see Figure 6.6) and Figure 4.22 from Evangelou (1998).

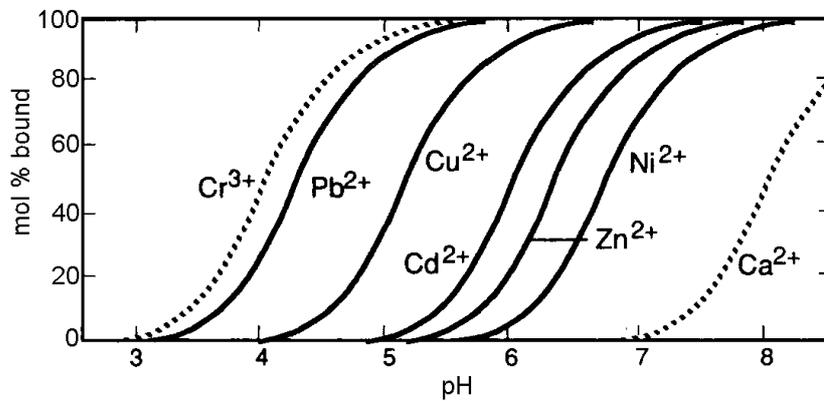


Figure 6.6. Sorption edges for Cr^{3+} , Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} on hydrous ferric oxide (after Figure 9.12b from Stumm and Morgan; 1996).

In the drain sediments from East Trinity, Co, Mn, Ni and Zn report in the AE fraction between 33 and 7 %. By contrast, the occurrence of Cu and Pb report in the AE fraction was negligible (0.8 %, 0.2 % and 0.2 %, respectively). According to the hydrolysis constants and Irving-Williams order, Pb^{2+} and Cu^{2+} will be more strongly adsorbed than Co, Ni and Zn. The likely adsorbing materials are the oxidised Fe phases. This indicates that the AE extraction may have only been strong enough to desorb the less strongly adsorbed cations (Co, Mn, Ni and Zn) and not the more strongly bound cations (Cu and Pb), from the adsorption surfaces in the drain sediments. A possible reason for this is the pH of the AE selective extraction. Equations 6.11 and 6.12 detail calculation of the pH of the AE extraction. The AE solution was found to have a pH of approximately 2.85. The pH of the AE extraction may not be low enough to exchange the more strongly adsorbed cations (e.g. Cu and Pb).

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[0.11 \text{ M}]} \quad \text{Eq. 6.11}$$

$$\text{pH of } 0.11 \text{ M } \text{CH}_3\text{COOH} = -\log\left(\sqrt{K_a \times [\text{CH}_3\text{COOH}]}\right) \approx 2.85 \quad \text{Eq. 6.12}$$

Though there is a distinct possibility that the AE extraction failed to dissolve some strongly adsorbed cations, it still provides an indication of the elements likely to be mobilised from the drain sediments under moderately acidic conditions. An event, such as a flush of acidic soil-water, could cause the release of Co, Mn, Ni and Zn from the drain sediments. However, ASS waters have been reported with pH values well below 2.85; e.g. White et al. (1997) reported ASS discharge with a pH of 1.6. In such situations, the AE fraction of the MBCR-SEP may not provide a valid indication of elements mobilised by a flush of acidic ASS water.

6.4.2.2.2 Reducible Fraction

In the drain sediments, the source of the reducible element fraction was largely hydrous Fe oxides. Hydrous oxides of Mn and Fe are well known 'sinks' in the surficial environment for heavy metals (Hall et al., 1996a). Scavenging by these secondary oxides occurs by a combination of coprecipitation, adsorption, ion exchange and absorption (penetration of the mineral lattice; Hall et al., 1996a). The importance of Fe and Mn oxides as scavengers will depend upon such conditions as existing pH-pE values, degree of oxide crystallinity, their abundances and presence of organic matter (Hall et al., 1996a).

The element that reports the largest proportion in the reducible fraction of the East Trinity drain sediments is Fe (43 % in the OF). A considerable amount of Fe also occurs in the reducible fraction of the BO (21 %). Reducible Fe hosts identified in the OF drain sediments were goethite and amorphous Fe phases. Though the mineralogy of the BO could not be determined due to oxidation during drying, the large amount of Fe reporting in the reducible fraction of the BO suggests that oxidised Fe forms persist in the BO. Evidence of oxidised Fe phases has been found in black oozes from other locations. Smith and Melville (2004) identified two zones of Fe³⁺ in porewaters from a monosulfidic profile on the Tweed River floodplain. The first Fe³⁺ zone was at the sediment-water interface and was likely a product of oxidation, or sedimentation of oxidised Fe³⁺ phases. The second zone of Fe³⁺ was approximately 0.4 m deeper in the profile and was thought to be from relict Fe³⁺ oxyhydroxides from a previous period of oxidation. These relict Fe-oxyhydroxides were thought to be undergoing reduction to Fe-monosulfides and eventually pyrite. The results from the East Trinity BOs and other BOs indicate that oxidised Fe phases are potentially important hosts in both the OF and BO drain sediments.

Elements other than Fe that report at more than 10 % in the reducible fraction of the drain sediments are (OF %/BO %): Al, (10/11), Co (22/14), Cu (8/5), Mn (14/3), Ni (12/9), Pb (14/31), and Zn (15/15). The large amount of Fe reporting in the reducible fraction from both the BO and OF indicates that the probable hosts for these metals are hydrous Fe oxides, with the greater host being amorphous Fe oxyhydroxides due to it being more chemically reactive than crystalline Fe oxides (Hall, 1998; Hall et al., 1996a). Cobalt, Cu, Ni, Pb, and Zn that report in the reducible fraction are likely to have been strongly sorbed (i.e. form inner-sphere complexes) onto the oxidised Fe phases in the drain sediments. The strength of their sorption prevented release during the AE extraction, but destruction of the oxidised Fe phases during the reducible extraction caused them to be solubilised.

Aluminium and Mn (oxyhydr)oxides may also host trace metals that report in the reducible fraction, but the lower concentrations of these elements in the drain sediments mean they are less important. Aluminium and Mn may themselves be hosted by Fe hydroxides (e.g. appreciable substitution of Al and Mn for Fe is known to occur in goethite; Deer et al., 1992). The proportions of Al in the reducible fraction of the BO and OF were similar, but not the proportion of Mn. Only 2.8 % of Mn reported in the reducible fraction of the BO. The low occurrence in the BO is likely due to Mn mobility under reducing conditions (see Figure 4.3, diagram B).

Extensive, rapid reduction of the drain sediments could lead to the release of significant amounts of Al, Co, Cu, Mn, Ni, Pb and Zn. Any release by reduction would be greater from the OF than the BO drain sediments. The mechanism for the release of these elements during reduction is largely the dissolution of oxidised Fe phases. However, the extensive rapid reduction caused by the reducible fraction extraction of the MBCR-SEP is unlikely to occur in the drains of East Trinity. Instead, reduction of the East Trinity drain sediments is likely to occur at near neutral pH values. This is because the inundating seawater that is critical to generating the reducing conditions has a pH value of ~ 8.2 and a considerable buffering capacity. Furthermore, the SO_4^{2-} and Fe^{3+} reducing reactions consume acidity (see Equations 1.30, 1.31 and 1.32). This suggests that reduction of the drain sediments on East Trinity is likely to occur at circum neutral pH values. Finally, Calmano et al. (1992) identified that low pH (less than 4.5) is the key factor in element mobilisation. Therefore, significant element mobilisation is doubtful in the drains of East Trinity because the pH conditions under which reduction are expected to occur (i.e. circum neutral) are not conducive to extensive element mobilisation.

6.4.2.2.3 *Oxidisable Fraction*

The two major hosts of the oxidisable fraction in the East Trinity drain sediments are expected to be sulfides and organic matter. This study was unable to verify the presence of sulfide minerals in the drain sediments. The non-oxidised mineralogy of the BO could not be identified because dry samples were required for XRD analysis. However, the black colour of the BO drain sediments may be due to Fe-monosulfides. Additionally, considerable organic matter was associated with the drain sediments during sampling, but the quantity of organic matter was not directly determined (e.g. LOI is indicative of structural water as well as organic matter). Elements that report in the oxidisable fraction of the drain sediments at greater than 10 % are (OF %/BO %): Co (10 / 26), , Cu (5/16), Ni (60/58), Sc (30/35) and Zn (12/10). Iron reports in the oxidisable fraction of the OF at 3 % and of the BO at 2 %.

More Co, Cu and Sc report in the oxidisable fraction of the BO than in the OF and the oxidisable fractions of Ni and Zn in the two drain sediment types are comparable. The occurrence of a larger

element proportion in the oxidisable fraction of the BO, compared to the OF, may be indicative of element hosting by sulfide. If this is the case, sulfide is a potentially important host for Co, Cu and Sc in the BO; though it is likely that most of the metals reporting in the oxidisable fraction are hosts to some degree by sulfides.

Assuming that the black colour of the BO is caused by monosulfides, and the monosulfides are an important host of Fe in the oxidisable fraction, the BO results suggest that only a small amount of Fe monosulfide needs to be present to cause a change in the colour of the drain sediments. Furthermore, comparison of the Fe hosting in the OF and BO finds that more Fe reports in the oxidisable fraction of the OF than the BO. The greater amount of Fe in the oxidisable fraction of the OF than in the BO suggests that Fe-monosulfide may not be the only controlling factor on drain sediment colour. Moreover, twice as much Fe occurred in the reducible fraction of the OF compared to the BO. This suggests that the colour of the drain sediments may not simply be due to the presence of Fe-monosulfides, but the result of a combination of Fe-monosulfides and Fe-oxidised phases.

6.4.2.3 Management of Drain Sediments

The element hosting data show that the behaviour of many elements in the drain sediments are sensitive to redox changes. This makes their management of significant importance on East Trinity and in other ASS locations.

In general, the threat posed by the redox sensitivity of the drain sediments is balanced by their generally low trace element content. However, potentially toxic concentrations of As, Cu and Ni were identified in the drain sediments by comparison with the ANZECC and ARMCANZ (2000) sediment quality guidelines. Yet, assessment of toxicity on total element contents is questionable. For example, the results of the MBCR-SEP indicate that the potential toxicity of Cu is likely to be diminished by being hosted largely in the residual fraction where it is unlikely to be available to biota. Comparatively, mitigation of toxic effects by residual hosting is unlikely to be as great for Ni. Oxidising conditions could release up to 50 % of the Ni in the examined drain sediments, making drain sediment oxidation potentially harmful to organisms.

The greatest threat with regard to mobilisation of elements from the drain sediments is oxidation. This is because oxidation will not just cause the release of the elements in the oxidisable fraction, but will also cause the release of the elements in the acid extractable fraction because of acidification during oxidation. Reduction is unlikely to cause a major release of elements because it is expected to occur at near neutral pH conditions.

Oxidation due to drying of the drain sediments could cause the release of Co, Cu, Ni, Sc and Zn from the drain sediments due to a combination of acidification and sulfide mineral dissolution. Furthermore, fluctuations in the watertable resulting in cycles of oxidation/reduction could also cause an increased release of elements. This is because of the poor scavenging of trace elements by the drain sediments. Each event of oxidation would mobilise Co, Cu, Ni, Sc and Zn. Of the elements mobilised, only a portion would be sorbed or coprecipitated during neutralisation/reduction events. Such cycles would lead to a decreased element content in the drain sediments. Redox cycling may explain the low concentration of trace element in the Firewood Creek drains of East Trinity compared with the MBOs reported by Smith and Melville (2004) from the Tweed River floodplain (See Table 6.9).

6.4.3 Geochemistry of Mouth Sediments

Sediments from the mouth of Firewood Creek were investigated for element enrichment and temporal trends in element concentrations. Of particular importance is the identification of the effects of AASS inundation on the elemental composition of the Firewood Creek sediments. Firewood Creek has been exposed to periods of uncontrolled tidal exchange (and subsequently, AASS inundation) since 2000; but since 2002 tidal exchange in the Firewood Creek catchment has been more extensive. Element enrichment in the sediments is identified by comparison with “background” sediments (i.e. sediments from nearby Falls Creek), whereas temporal trends are ascertained by comparison with “baseline” mouth sediments (i.e. earlier sediments collected from Firewood Creek). Four sets of mouth sediments are compared here, they are:

- 1) a set of 13 samples of mouth sediments collected from Firewood Creek in April 2004 (Appendix H, Table H.1);
- 2) a set of 13 samples of mouth sediments collected from Firewood Creek in September 2002 (Appendix H, Table H.2);
- 3) a set of 13 “baseline” samples of mouth sediments collected from Firewood Creek in July 2002 (Appendix H, Table H.3); and
- 4) a set of 14 “background” sediments from Falls Creek in 2002 (Appendix H, Table H.4).

The July 2002 and September 2002 Firewood Creek sediments and the Falls Creek sediments were collected, analysed and described by Hall (2002). Descriptions and sampling details of the sediment sets from Firewood Creek collected in July and September 2002 and the sediments from Falls Creek can be found in Hall (2002). The samples that comprise the 3 Firewood Creek sediment sets were collected from the same 13 locations.

Elemental enrichment in the mouth sediments of Firewood Creek is identified by comparison with the background sediments collected from Falls Creek. Falls Creek is located 3 km south of

Firewood Creek. The Falls Creek catchment is similar in size and geology to Firewood Creek's, but is largely undisturbed (Hall, 2002). The undisturbed state, proximity and similarities to Firewood Creek make Falls Creek suitable for the collection of background sediment samples.

Temporal trends in elemental concentrations in Firewood Creek sediments are identified by comparison with the baseline sediment set collected from Firewood Creek in July 2002 by Hall (2002). The changes in element concentrations with time are identified by comparison of the September 2002 and April 2004 sediments with the July 2002 "baseline" sediment set.

Only As, Fe, Li, Mn, Ni, Pb and Zn are compared in the Firewood Creek sediments because of limited element analysis by Hall (2002) and quality assurance issues with the 2004 sediment sample set (i.e. failed QA for Al and Cu). The sediment datasets are compared using two methods. The first approach is a direct comparison of the sediment geochemistry to identify changes in total element concentration. The second method explores the As, Fe, Mn, Ni, Pb and Zn values normalised to Li concentrations (Loring and Rantala, 1992). In all cases, median concentrations/values of the various datasets are compared.

6.4.3.1 Comparison of Total Element Concentrations

6.4.3.1.1 *Comparison with Background Mouth Sediments*

Comparison of the April 2004 sediments from Firewood Creek with the background sediments (from Falls Creek) shows enrichment of As, Fe, Mn, Ni, Pb and Zn (Figure 6.7). Enrichment values are highest for Fe (129 %), Ni (125 %) and Pb (123 %). Arsenic, Li, Mn and Zn are enriched between 112 and 122 %.

Enrichment in the sediments relative to background indicates that Firewood Creek is transporting and depositing larger loads of As, Fe, Mn, Ni, Pb and Zn than other creeks that drain similar, but undisturbed, areas of ASS. This indicates that the elements released from the oxidised and inundated ASS in the Firewood Creek catchment are reporting in sediments at the mouth of Firewood Creek and are potentially being released into Trinity Inlet.

6.4.3.1.2 *Comparison with Baseline Mouth Sediments*

Temporal trends in the total element concentration of the sediment from the mouth of Firewood Creek indicates enrichment of As, Fe, Ni and Pb and depletion of Li, Mn and Zn in the April 2004 sediments (Figure 6.7). A comparison of median concentrations in the 2004 mouth sediments from Firewood Creek with the 2002 sediments shows that As, Fe, Ni and Pb occur in higher concentrations in the 2004 sediments than in earlier sediments (between 111 - 120 % of 2002 sediment sets). In contrast, the medians for Li, Mn and Zn are lower in the 2004 sediments.

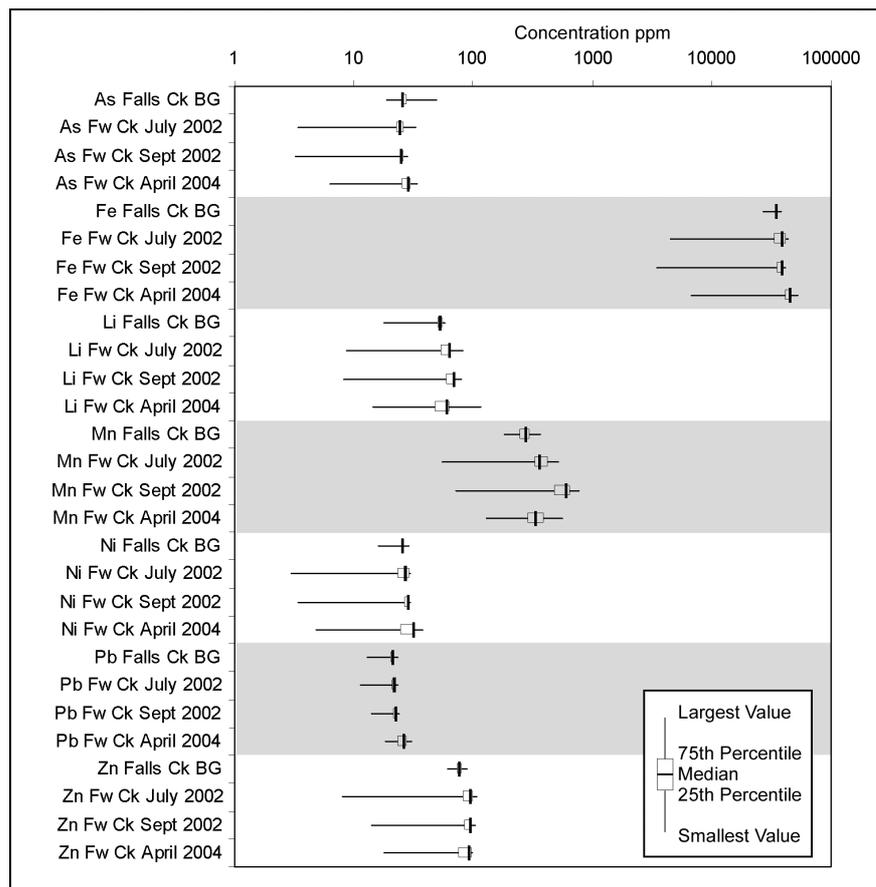


Figure 6.7. Comparison of As, Fe, Li, Mn, Ni, Pb and Zn concentrations in Firewood Creek mouth sediments from July 2002 (“Fw Ck July 2002”), September 2002 (“Fw Ck Sept 2002”), April 2004 (“Fw Ck April 2004”) and Falls Creek (“Falls Ck BG”). Falls Creek is indicative of background values.

The enrichment of As, Fe, Ni and Pb in the 2004 sediments relative to the 2002 sediments demonstrates that these elements are being released from the ASS in the Firewood Creek catchment to the sediments at the mouth of Firewood Creek in larger amounts than in 2002. The potential cause of the increased release of As, Fe, Ni and Pb is the increased seawater inundation of AASS in the Firewood Creek catchment, which has occurred since 2002. However, the lower median concentrations for Li, Mn and Zn in the 2004 Firewood Creek sediments suggests that smaller amounts of these elements have been released since the increased inundation of the Firewood Creek catchment.

6.4.3.2 Lithium Normalised Element Values of Mouth Sediments

Lithium normalisation corrects element concentrations for textural differences in sediments by using Li concentrations as a proxy for clay content (Loring and Rantala, 1992). Normalising sediments to their clay content eliminates grainsize effects and allows for the identification of real trends rather than trends caused by grainsize variations. Lithium can be used as proxy for clay

content because Li is structurally combined in clays and micas. In undisturbed systems, Li is conservative in that it has a uniform flux from crustal rock sources and so compensates for change in the input rates of various diluents or variation in the sedimentation rates (Loring and Rantala, 1992). Element enrichment is calculated from Li normalised values by the enrichment factor, which is the Li normalised element value in the sediment divided by the Li normalised value in the background sediment. An enrichment factor > 1 indicates enrichment of the element relative to the background.

6.4.3.2.1 Recalculation of Lithium Normalised Values from Earlier Studies

Hall's (2002) Li normalised element values were re-calculated because of concerns regarding the representativeness of the method used. Hall (2002) calculated Li normalised values using the median element concentration and median [Li] of the datasets (e.g. Falls Creek and the 2002 Firewood Creek sediment sets). Calculation of Li normalised element values in this way potentially results in element concentrations from different samples being used to calculate the dataset's Li normalised element values. Table 6.13 demonstrates this. The Li normalised values used here have been calculated by first finding the Li normalised element values for all samples in the dataset, then taking the median of the Li normalised values. This provides a valid Li normalised value for the dataset (Appendix H, Table H.5). Recalculation of the Li normalised values for the sediments from Firewood Creek produced different values to those of Hall (2002), but similar trends.

6.4.3.2.2 Lithium Normalised Comparison with Background Sediments

Lithium normalised concentrations of As, Fe, Mn, Ni, Pb and Zn are used to identify grain size corrected element enrichment and temporal trends in the mouth sediments of Firewood Creek. The elemental data for the background sediments (Falls Creek) and the 2002 mouth sediments of Firewood Creek are from Hall (2002).

Lithium normalised values indicate that the April 2004 elements are enriched relative to background in Fe, Mn, Ni, Pb and Zn (Table 6.14). Additionally, a comparison of the July and September 2002 sediments from Firewood Creek with background sediments demonstrates that Mn and Zn are enriched in the July 2002 sediments and that Mn is enriched in the September 2002 sediments. Manganese is the only element examined that is uniformly enriched relative to background in all the Firewood Creek sediments. Furthermore, the greatest enrichment of As, Fe, Ni and Pb occurs in the April 2004 sediments.

Table 6.13. Comparison of Li normalisation method used here and that used by Hall (2002). Data are from the 13 mouth sediments collected September 2002 from Firewood Creek (Hall, 2002). Hall (2002) found the Li normalised element values for the dataset using the median element concentrations in the dataset. The boxed cells indicate the concentrations used by Hall (2002) to calculate the Li normalised value for the dataset. Calculation of Li normalised values in this way potentially results in the value for the dataset being calculated from different samples (see boxed cells). The method used here to calculate the Li normalised element values for the dataset is to first calculate the Li normalised value for each sample, then take the median Li normalised value.

September 2002 Firewood Creek	As	Li	[As]/[Li]
FCT01A	26.2	68.2	0.38
FCT02A	17.3	36.6	0.47
FCT03A	24.7	69.7	0.35
FCT04A	22.8	57.9	0.39
FCT05A	25.2	74	0.34
FCT06A	25.7	79	0.33
FCT07A	27.9	70	0.40
FCT08A	24.9	67.1	0.37
FCT09A	25.3	70.2	0.36
FCT10A	27.2	68.2	0.40
FCT11A	24.5	51	0.48
FCT12A	3.2	8.3	0.39
FCT13A	23.7	61.4	0.39
Median	24.90	68.20	0.39
Median[x]/Median[Li]	0.37	1.00	

Table 6.14. Element enrichment relative to background in mouth sediments of Firewood Creek. Enrichment factors are calculated using Li normalised element values. The background sediments were collected from Falls Creek. Data used to calculate the Li normalised values for the 2002 Firewood Creek and Falls Creek sediments are from Hall (2002). Largest values are in bold.

Li Normalised	Enrichment Factor July 2002 / Background	Enrichment Factor September 2002 / Background	Enrichment Factor April 2004 / Background
Al	0.91	0.93	-
As	0.83	0.81	0.97
Cu	0.82	0.73	-
Fe	0.93	0.86	1.12
Li	1.00	1.00	1.00
Mn	1.15	1.66	1.23
Ni	0.89	0.84	1.05
Pb	0.89	0.84	1.11
Zn	1.04	0.93	1.04

6.4.3.2.3 *Lithium Normalised Comparison with Baseline Sediments*

Temporal trends in element concentrations in the Firewood Creek sediments are identified by comparison of the Li normalised element values from the April 2004 and September 2002 datasets with the July 2002 baseline dataset. The baseline dataset (July 2002) was used to calculate enrichment factors for the April 2004 and September 2002 datasets (Table 6.15).

Table 6.15. Temporal trends in mouth sediments from Firewood Creek. Enrichment factors are relative to baseline data (July 2002 sediments). Lithium normalised values have been used to calculate enrichment factors. Element data for 2002 sediments are from Hall (2002).

Li Normalised	Enrichment Factor Sept 2002 / July 2002	Enrichment Factor April 2004 / July 2002
Al	1.02	-
As	0.98	1.18
Cu	0.88	-
Fe	0.92	1.20
Li	1.00	1.00
Mn	1.44	1.07
Ni	0.94	1.17
Pb	0.94	1.25
Zn	0.89	1.00

Comparison of the Li normalised values of the July 2002 and September 2002 mouth sediments from Firewood Creek shows that As, Cu, Fe, Ni, Pb and Zn all have enrichment factors less than 1. Enrichment factors less than 1 indicates that the element is depleted relative to the baseline (i.e. the July 2002 sediments). The enrichment factors indicate that As is depleted by 2 %, Cu by 12 %, Fe by 8 %, Ni by 6 %, Pb by 6 % and Zn by 11 % in the September 2002 sediments relative to the July 2002 sediments. Aluminium and Mn are the only elements that display an enrichment (+2 % and +44 %, respectively).

Enrichment factors calculated from the Li normalised element values for the April 2004/July 2002 comparison shows that As, Fe, Mn, Ni and Pb are enriched, whereas Zn is comparable. Lead is enriched by 25 %, Fe by 20 %, As by 18 %, Ni by 17 % and Mn by 7 %. This indicates that the increased seawater inundation of the Firewood Creek catchment since 2002 has resulted in an increase in the supply of Pb, Fe, As, Ni and Mn to Creek's mouth sediments.

6.4.3.3 Comparison of Mouth Sediments with Sediment Quality Guidelines

The quality of the sediments from the mouth of Firewood Creek and from Falls Creek was assessed for contamination using the ANZECC and ARMCANZ (2000) sediment quality guidelines

(Tables 6.16 and 6.17, respectively). ANZECC and ARMCANZ (2000) provide quality guidelines for As, Cu, Ni, Pb and Zn in sediments.

None of the ISQG-High guidelines for As, Cu, Ni, Pb and Zn were exceeded by any sediment from either Firewood or Falls Creek. However, more than 25 % of the samples from all the sediment sets (i.e. from Firewood and Falls Creek) exceeded the ISQG-Low value for As and Ni.

Hall (2002) previously identified As and Ni concentrations in excess of the ISQG-Low value. However, Hall (2002) suggested that the anomalous Ni concentrations were contamination introduced during sample crushing with a Cr-steel mill. Calculation of the Cr-Ni correlation coefficient (Spearman's) in Hall's (2002) samples suggests otherwise. As Cr contamination occurs during crushing because of mill abrasion, a high Cr-Ni correlation coefficient will indicate that Ni is also being abraded from the mill and is concurrently contaminating the samples. The Cr-Ni correlation coefficient for the Firewood Creek mouth and Falls Creek sediments samples ($n = 40$) is -0.22; indicating a non-existent statistical relationship. In comparison, Ni correlates strongly with Li (+0.88), likely as a result of Ni associating with clays in the sediments (Loring and Rantala, 1992). The lack of correlation with Cr and the strong correlation with Li, suggests that the Ni concentrations in Firewood and Falls Creeks are not a product of contamination.

The fact that As and Ni were above the guidelines in the Falls Creek sediments, as well as in the Firewood Creek sediments, indicates that As and Ni concentrations are probably naturally high in Trinity Inlet sediments. That is, the similar occurrence of As and Ni in the Falls Creek and Firewood Creek sediments indicates that the high As and Ni values are not necessarily the result of element mobilisation by PASS oxidation or AASS inundation in the Firewood Creek catchment.

6.4.3.4 Impact of Seawater Inundation on Firewood Creek Mouth Sediments

Element enrichment in the mouth sediments relative to background indicates that Firewood Creek is transporting and depositing larger loads of Fe, Mn, Ni, Pb and Zn than other creeks that drain similar, but undisturbed, areas of ASS. Furthermore, enrichment of Fe, Pb and Ni in the April 2004 Firewood Creek sediments relative to July 2002 sediments indicates that seawater inundation is causing an increase in the mobilisation of some elements in the IAASS of East Trinity.

Enrichment in the Firewood Creek mouth sediments relative to background (Falls Creek) is explained by element mobilisation by a combination of PASS oxidation (AASS formation) and AASS inundation (IAASS formation). Chapter 3 demonstrated that Fe, Mn, Ni, Pb and Zn were lost from ASS during oxidation and inundation. A likely source of the enriched elements in the Firewood Creek mouth sediments are elements in the ASS which are mobilised by oxidation (see

Chapter 5), flushed from the AASS by meteoric waters and deposited in the mouth sediments of Firewood Creek. This is the likely cause of the enrichment of Fe, Mn, Ni, Pb and Zn identified in Firewood Creek mouth sediments relative to background sediments.

Table 6.16. Comparison of mouth sediments from Firewood Creek (East Trinity) with the ANZECC and ARMCANZ (2000) quality guidelines for sediments. Values for the mouth sediments in bold exceed the corresponding guideline value.

	Sediment Quality Guidelines		Firewood Creek Mouth Sediments (n = 13 in each set)				
	ISQG-Low ¹	ISQG-High ²	Smallest	25th %tile	Median	75th %tile	Largest
July 2002							
As ppm	20	70	3	22	24	26	34
Cu ppm	65	270	5	19	21	22	23
Ni ppm	21	52	3	23	27	29	30
Pb ppm	50	220	11	21	22	22	23
Zn ppm	200	410	8	80	93	98	108
Sept 2002							
As ppm	20	70	3	24	25	26	28
Cu ppm	65	270	3	19	21	22	23
Ni ppm	21	52	3	26	28	29	30
Pb ppm	50	220	14	21	22	23	24
Zn ppm	200	410	14	82	93	95	104
April 2004							
As ppm	20	70	6	25	28	30	34
Cu ppm	65	270	-	-	-	-	-
Ni ppm	21	52	5	24	31	32	38
Pb ppm	50	220	18	23	26	27	30
Zn ppm	200	410	18	74	91	97	99

¹ Interim Sediment Quality Guideline (ISQG) - Low: “probable-effects concentration” threshold, below which biological effects rarely occur.

² Interim Sediment Quality Guideline (ISQG) - High: “probable-effects concentration” threshold, below which biological effects possibly occur. Concentrations at or above the ISQG-High represent concentrations within which frequent biological effects are expected.

Element enrichment in the April 2004 compared to the July 2002 Firewood Creek sediments is likely due to element mobilisation during AASS inundation. Though the Firewood Creek catchment has been exposed to some seawater inundation since approximately 2000, seawater inundation has been more extensive and occurred for longer periods since 2002. Hence, the influence of element mobilisation by AASS inundation is greater on the April 2004 sediments. The April 2004 sediments display enrichment of As, Fe, Pb and Ni relative to the July 2002. Chapter 3 showed that the IAASS were more extensively depleted in Fe, Pb and Ni than the un-inundated AASS, suggesting that Fe, Pb and Ni were mobilised during AASS inundation. This indicates that seawater inundation has potentially increased the release of Fe, Pb and Ni to sediments at the mouth of Firewood Creek and possibly into Trinity Inlet.

Table 6.17. Comparison of sediments from Falls Creek (background sediments) with the ANZECC and ARMCANZ (2000) quality guidelines for sediments. Values for the mouth sediments in bold exceed the corresponding guideline value.

	Sediment Quality Guidelines		Falls Creek Sediments (n = 14)				
	ISQG-Low ¹	ISQG-High ²	Smallest	25th %tile	Median	75th %tile	Largest
As ppm	20	70	19	24	25	28	49
Cu ppm	65	270	14	21	22	24	28
Ni ppm	21	52	16	25	25	26	29
Pb ppm	50	220	13	20	21	22	23
Zn ppm	200	410	61	73	76	80	89

¹ Interim Sediment Quality Guideline (ISQG) - Low: “probable-effects concentration” threshold, below which biological effects rarely occur.

² Interim Sediment Quality Guideline (ISQG) - High: “probable-effects concentration” threshold, below which biological effects possibly occur. Concentrations at or above the ISQG-High represent concentrations within which frequent biological effects are expected.

In spite of the relative enrichment noted in the Firewood Creek sediments, comparison with the ANZECC and ARMCANZ (2000) sediment quality guidelines does not indicate significant contamination from PASS oxidation of AASS inundation. Arsenic and Ni both exceed the ISQG-Low values in more than 25 % of the sample from the four sediment sets examined (3 from Firewood Creek and 1 from Falls Creek). The fact that As and Ni concentrations are higher than the ISQG-Low value in the background sediments, as well as the Firewood Creek sediments, suggests that Trinity Inlet Creek sediments contain naturally high As and Ni levels.

6.5 Conclusions

The fate of the elements lost from AASS in the Firewood Creek catchment during seawater inundation was examined by investigating the geochemistry of drain and creek mouth sediments. The objectives were: 1) to describe the mineralogy, geochemistry and element hosting of the drain sediments; 2) to investigate the drain sediments for enrichment in the elements mobilised from IAASS; and 3) to investigate the mouth sediments of Firewood Creek for element enrichment: a) relative to background creek systems; and b) from seawater inundation of AASS.

Few elements mobilised from AASS during inundation were found in the drain sediments of the Firewood Creek catchment. Iron was a major exception to this. However, in the sediments from the mouth of Firewood Creek, concentrations of As, Fe, Ni and Pb increased over a period of more extensive seawater inundation (between July 2002 and April 2004).

Investigation into the drain sediments focussed on their formation, their potential as element sinks for elements mobilised from the ASS and the hosting of elements. The geochemistry of the drain sediments suggested that they form from flocculation of Fe-rich suspended particles. The Fe-rich suspended particles precipitate in egressing ASS soil-waters and consist largely of amorphous and crystalline Fe-oxyhydroxides. The Fe normalised element values of the drain sediments were similar to values for suspended particles reported from Firewood Creek by Hall (2002). This similarity supported the field observation that the OF drain sediments form from flocculation of suspended Fe-rich particles in the drain waters. The field association and similar elemental composition of the OF with the BO further supported the hypothesis of a common origin. The obvious difference in colour was attributed to the BO being a reduced form of the OF. Reduction of the OF occurs when low or non-flow conditions in the drains combines with organic matter and SO_4^{2-} bring about sulfidisation. The reducing condition causes the partial decomposition of the Fe oxyhydroxides and the sulfide formed by sulfidisation combines with metals to form monosulfides. Production of black monosulfide and destruction of Fe-oxyhydroxides combines to transform the OF to BO.

The drain sediments were not found to be effective sinks for the elements released from ASS, with the possible exception of Fe and As. Poor incorporation of elements lost from the ASS into the drain sediments was demonstrated using Fe normalised element values. An estimate of the elements lost from the ASS was calculated by subtracting the PASS element concentration from the oxidised ASS concentration. These element values were normalised to the lost Fe concentration. The Fe normalised lost values were then compared to the Fe normalised drain sediment values. The Fe normalised value comparison showed that, with the exception of As, only a very small proportion of the ASS mobilised elements were incorporated into the drain sediments.

Element hosting in the drain sediments was determined using the MBCR-SEP. The fractions in which the elements reported their largest proportion (other than the residual fraction) were: Co, Mn and Na in the acid extractable fraction; Al, Fe, Pb and Zn in the reducible fraction; and Cu, Ni and Sc in the oxidisable fraction. Elements that did not report significantly in any fraction except the residual fraction were: As, Ba, Ga, Nb and Ti.

Iron did not occur significantly in the oxidisable fraction of either drain sediment type. However, Fe did report in significant amounts in the reducible fraction of both the OFs and BOs. Iron occurrence in the reducible fraction of both the OF and BO drain sediments demonstrated that Fe occurs largely in oxidised phases in both drain sediment types, despite their distinct colour difference. This indicates that oxidised Fe phases are important element hosts, especially for the AE and reducible element fractions, in both types of drain sediment.

Assessment of the drain sediments using sediment quality guidelines indicates potentially toxic concentrations of As, Cu, Ni and V. However, the MBCR-SEP data suggested that only Ni had the potential to become available to biota, as the vast major of Cu was hosted by the residual fraction of the drain sediments. The MBCR-SEP did not provide valid data on As or V.

The MBCR-SEP results indicate that the greatest threat with regard to element mobilisation from the drain sediments is oxidation. This is because oxidation will not just cause the release of the elements in the oxidisable fraction, but will also cause the release of the elements in the acid extractable fraction due to acidification during oxidation. Reduction is unlikely to cause a major release of elements because it is expected to occur at near neutral pH conditions. Finally, though the drain sediments were found to contain a large proportion of their elements in labile fractions, their low trace element content offsets the risk posed by their reactivity. It is important to note that the reducible fraction extraction of the MBCR-SEP was found to be of limited effectiveness with ASS samples (see Chapter 5). Therefore, conclusions drawn from the MBCR-SEP results include considerable uncertainty.

Sediments from the mouth of Firewood Creek were examined to identify whether: 1) element concentrations in the sediments from Firewood Creek were higher than from creeks with undisturbed catchments; or 2) seawater inundation of AASS in the Firewood Creek catchment had increased sediment element concentrations. The first aim was addressed by comparison of Firewood Creek sediments with background sediments collected from Falls Creek. Comparison of element concentrations in Firewood Creek sediments with the background sediments shows enrichment of As, Fe, Mn, Ni, Pb and Zn. This suggests that elements mobilised from the AASS in Firewood Creek are being released to the sediments at rates slightly greater than background.

The second aim was addressed by comparison of April 2004 sediments from Firewood Creek with sediments from July 2002. The period between July 2002 and April 2004 was significant because the extent of seawater inundation increased during the period relative to before July 2002. Arsenic, Fe, Ni and Pb were enriched in the April 2004 sediments relative to the earlier sediments. The enrichment indicated that there had been an increase in the release of As, Fe, Ni and Pb to the sediments of Firewood Creek since July 2002. The observed increase in As, Fe, Ni and Pb was likely because of the increased seawater inundation of the Firewood Creek catchment. The enrichment of Fe, Ni and Pb in the sediments was consistent with the elements that were identified as mobilised from IAASS in Chapter 3.

It is therefore probable that seawater inundation has caused the increased release of Fe, Ni and Pb from ASS in the Firewood Creek catchment. The source of As to the mouth sediments during this period remains unidentified. In spite of the increased element release, comparison with sediment quality guidelines indicates that no ecologically significant contamination could be attributed to element mobilisation by seawater inundation of the Firewood Creek catchment.

7. PHYTOAVAILABILITY AND BIOACCUMULATION OF ELEMENTS BY PLANTS IN INUNDATED AASS

7.1 Introduction

The bioavailability of elements in soils is of major concern because of the potential for elements to enter the food chain in toxic concentrations (Reichman, 2002). An important pathway by which elements in the soil can enter the food chain is via accumulation by plants. Plants are able to take up nutrients and elements from the soil and accumulate them in edible tissue (Siegel, 2002). Plants that accumulate elements, particularly in their leaves and stems, can contribute to increased element concentration in organisms that feed on them (e.g. insects, birds and mammals; Vandecasteele et al., 2005). Excessive accumulation of elements may lead to toxic effects in plants and animals (Meharg and Hartley-Whitaker, 2002; Reichman, 2002; Rout et al., 2001; National Research Council, 1980).

The portion of an element in soil that can be readily taken up by plant roots is the phytoavailable fraction (Intawongse and Dean, 2006). The phytoavailable fraction generally consists of the elements that are exchangeable and water-soluble (Intawongse and Dean, 2006; Rayment and Higginson, 1992). Element phytoavailability is influenced by the physical and chemical factors of the soil, e.g. pH, pE, texture and moisture content. As a result, changes in the soil environment (such as inundation) may alter an element's phytoavailability and hence alter the uptake of the element by plants.

Soil inundation with water has been shown to reduce the uptake of some elements by plants. Kashem and Singh (2001a, b) examined the effects of soil inundation on the phytoavailability of Cd, Ni and Zn to rice plants (*Oryza sativa* L.). The authors found that soil inundation reduced the amount of Cd, Ni and Zn in the soil solution and a corresponding reduction of the elements was found in the plant tissue. Vandecasteele et al. (2005) measured the uptake of Cd, Mn and Zn using the indicator species *Salix cinerea* (a willow) that was growing under different degrees of soil inundation. Extended periods of soil inundation were found to reduce the availability of Cd, Mn and Zn to the plants.

Plant responses to phytoavailable element fractions are strongly dependent on the characteristics of the species (Hund-Rinke and Kordel, 2003). Baker (1981) classified plants as accumulators, indicators, or excluders based on how they responded to the bioavailable element fraction. Accumulators concentrate elements from the soil in their above-ground tissues (for brevity, the term 'stems' is used herein to describe the entire above ground tissue, e.g. leaves, stems and shoots). Accumulators are of environmental concern because of their potential to transfer elements from the soil into the food chain (i.e. by being eaten by animals), as well as into the wider environment

(Stoltz and Greger, 2002). Indicator species regulate the transfer of elements from the soil to their stems so that stem concentrations reflect the soil phytoavailable concentrations. This makes indicator species of special importance to remediation studies, as their stems can be used to indicate the phytoavailability of elements in the soil. Excluders restrict the uptake of the element from the soil and/or the translocation of the element from their roots to their stems. Excluders are preferred for the stabilisation of contaminated soils/tailings because they do not transfer elements from the substrate to their stems.

At East Trinity, the phytoavailability of Al, As, Co, Cr, Cu, Ni, Pb and Zn in the IAASS was investigated. In conjunction, the accumulation of these elements by the two dominant re-colonising plant species, *Acrostichum speciosum* (mangrove fern) and *Paspalum vaginatum* (seashore paspalum, a grass), of the IAASS was also investigated. The chapter objectives were: 1) to assess elements for increased phytoavailability under inundated soil conditions; 2) to determine the responses of the sampled plant species to the phytoavailable element pool; and 3) to identify if plants growing in the IAASS contained higher element concentrations than background samples or toxicity guidelines.

An additional objective of the chapter was to compare the extractive properties of three chelating agents. The three chelating agents were EDTA, DTPA and EDDS. EDDS is a chelating agent that has recently been examined as a replacement for EDTA in metal extraction and phytoextraction activities (e.g. Tandy et al., 2006a, b; Finzgar et al., 2005; Hauser et al., 2005; Tandy et al., 2004; Kos and Lestan, 2003; Vandevivere et al., 2001). EDDS has similar chelating characteristics to EDTA, but unlike EDTA, EDDS is biodegradable.

The data and interpretations provided insight into the phytoavailability of elements in IAASS and the accumulation of elements by plants colonising IAASS. Additionally, the identification of *Acrostichum speciosum* and *Paspalum vaginatum* as potential indicator species for the conditions on East Trinity will assist future biomonitoring programs.

7.2 Methods

Examined in this chapter were plants and associated 'plant soil', and ASS material from the dry and wet ASS profiles collected from East Trinity. The plant samples were used to identify element bioavailability in the IAASS. The ASS from the soil profiles were used to compare the extractive properties of EDTA, DTPA and EDDS.

7.2.1 Sampling

7.2.1.1 Plant Samples

Element bioavailability in the IAASS of East Trinity was investigated with plant and ‘plant soil’ samples. Two plant species were collected for elemental analysis: the fern *Acrostichum speciosum* and the grass *Paspalum vaginatum*. *Acrostichum speciosum* and *Paspalum vaginatum* were sampled because they were the dominant vegetative species in the areas of IAASS on East Trinity, apart from the dead *Melaleuca leucadendra* (Figure 7.1). The identities of the plant species were confirmed by the Queensland Herbarium (2007a, b). Sixteen samples of each species were collected (Table A.5, Appendix A); eight of each species from IAASS and eight from background locations (i.e. taken from undisturbed or non- ASS sites). The locations from where the plants and associated soils were collected are shown in Figure 2.9.

The background samples of *Acrostichum speciosum* (n = 8) were collected from the outside edge of the East Trinity bundwall. These specimens were growing in near-undisturbed mangrove muds that were frequently inundated by seawater. The background samples provide an indication of the element concentrations in plants growing in near-undisturbed mangrove systems.

The *Paspalum vaginatum* background samples were collected from the top of the Firewood Creek catchment within the East Trinity property, from the samphire flats between the bundwall and coastline, and along the outside of East Trinity’s bundwall. The sample from the top of the Firewood Creek catchment (MF4) was selected because it was growing in imported road ballast and was inundated with saltwater at the time of sampling. The remaining seven background samples were growing in undisturbed mangrove/samphire muds.

7.2.1.2 Plant Soil Samples

Soil was collected from the roots of seven samples of each plant species (samples MF1 - MF7 and PV1-PV7) for extraction with EDTA. This sample material is referred to as ‘plant soil’. The plant soil was stored in airtight containers at -18 °C to prevent redox changes.

The importance of the redox state of the plant soils is demonstrated by Figure 7.2, which shows the difference in colour between the soil in the root mass (black) and the material exposed to the atmosphere (orange). The black material in the root mass was typically saturated with brackish water. A similar pattern of colour (i.e. orange flocculants on the surface, underlain by black ooze) was reported in the drain sediments (Figure 2.12). The black coloured material in the root mass is probably caused by reductive processes (i.e. SO_4 and Fe^{3+} reduction) that have been initiated by inundation. This is further supported by the noted odour of H_2S from the black material during sample preparation and by many of the black soil samples turning brown/orange during drying.

The change in colour of the black plant soil samples is likely because of Fe sulfide oxidation/Fe oxide formation during drying. The fact that many of the plants were found growing in the black soil suggests that it offers some benefit to the plant. A possible plant benefit is decreased phytoavailability of some elements due to reducing conditions in the black substrate.

7.2.1.3 ASS Samples

The ASS samples came from the top 0.7 m of the dry and wet ASS profile. Seven samples were taken from each ASS profile (DP2-1 to DP2-7 from the dry ASS profile and WP2-1 to WP2-7 from the wet ASS profile). Sampling locations are plotted on Figure 2.9 and given in Table A.1 of Appendix A. Sample information is provided in Table A.2 of Appendix A.

7.2.2 **Sample Processing**

7.2.2.1 Plant Processing

Plant samples were processed as described in Section 2.6.3. Both stem and root tissue of each sample were analysed for their element content.

7.2.2.2 Plant Soil Processing

To test if elements were less phytoavailable in the “reduced” black soil than in the “oxidised” oven dried soil, EDTA extractions were conducted on both reduced and oxidised substrate. The reduced samples of plant soils were centrifuged at 3000 g for 20 minutes before being extracted using EDTA. The oxidised samples were also centrifuged at 3000 g for 20 minutes, but were then oxidised by drying for approximately 5 days at 75 °C before being extracted using EDTA.

7.2.2.3 ASS Processing

The ASS samples were processed for extraction by removing free water (by centrifuge). The samples were not ground. A full description of the ASS sample processing for extraction is given in Section 2.8.1.

7.2.3 **Analyses**

7.2.3.1 Biogeochemical Analysis (Plants)

Section 2.6.3 describes the plant sample processing and analysis. The element concentrations determined in the plant samples are given in summary in Tables I.1 and I.2 for the *Acrostichum speciosum* and *Paspalum vaginatum* samples, respectively. The individual data are given in Table I.3 for

the *Acrostichum speciosum*, and Table I.4 for the *Paspalum vaginatum* samples. These tables are located in Appendix I.



Figure 7.1. Vegetation in the inundated areas of East Trinity. The dead trees are *Melaleuca leucadendra*. The grass is *Paspalum vaginatum*. The mangrove ferns are *Acrostichum speciosum*. Photo was taken at GR 372450/8126650.

Accuracy of the plant element analysis could not be assessed because of the lack of a suitable reference material. Reproducibility was measured by inclusion of replicate samples (see Appendix B Tables B.9 and B.10). The method used to assess the reproducibility of the analytical data is provided in Sections 2.9.3. Nickel was the only element that failed reproducibility assessment. The plant element dataset therefore consisted of Al, As, Co, Cr, Cu, Pb and Zn.

7.2.3.2 EDTA Extraction of Plant Soil

Element phytoavailability in the 14 plant soil samples was determined using EDTA extractions. The EDTA extraction method is detailed in Section 2.7.9. Two EDTA extractions were conducted on the plant soils. The first extraction used the wet “reduced” soil and the second used dried “oxidised” soil. Both extractions used 3.3 g of wet plant soil that had been centrifuged twice at 3000 g for 20 minutes with the supernatant water decanted. The reduced soil extraction used the 3.3 g of centrifuged soil directly. The oxidised soil EDTA extraction used 3.3 g of centrifuged soil after it had been dried at 75 °C to a constant weight (approximately 5 days). In both cases, the soil was leached with 15 mL of 0.01 M EDTA (wet soil to solution ratio of 1.1 g : 5 mL). The same mass of centrifuged soil was used in the reduced and oxidised soil extractions to maintain comparability between the extraction results. Element concentrations in the extractions were back calculated to 1 g of dry soil. The concentrations of the elements extracted with EDTA from the plant soils are given in Table I.5 of Appendix I.

Aluminium, As, Co, Cu, Ni, Pb and Zn were determined in the plant soil EDTA leachates. The leachates were analysed at the AAC (Townsville). Analytical data quality was assessed by the inclusion of an aliquot of the SLRS-4 SRM and a replicate sample. The methods used to measure the accuracy and reproducibility of the analytical data are given in Sections 2.9.2 and 2.9.3, respectively. Chromium and Pb were not determined accurately in the plant soil EDTA solutions (Appendix B, Table B.10). The reproducibility of all elements was acceptable (Appendix B, Table B.11). Hence, the plant soil EDTA extraction dataset consisted of Al, As, Co, Cu, Ni and Zn.

7.2.3.3 DTPA, EDTA and EDDS Leaches of ASS Samples

Element concentrations extracted with EDTA were compared to DTPA and EDDS extractions. EDTA and DTPA are frequently used to extract the phytoavailable element fraction from soil. EDDS is a structural isomer of EDTA, but unlike EDTA, it is readily biodegradable (Tandy et al., 2006b). The biodegradability of EDDS has instigated studies for its use as an environmentally friendly chelating agent for the removal of metals from soils (e.g. Tandy et al., 2006b; Hauser et al., 2005; Tandy et al., 2004; Vandevivere et al., 2001). The DTPA, EDTA and EDDS extraction procedures are given in Sections 2.7.8, 2.7.9, and 2.7.10, respectively. Element concentrations in

the extractions were back calculated to 1 g of dry soil. The EDTA, DTPA and EDDS data are given in Table J.1 of Appendix J.

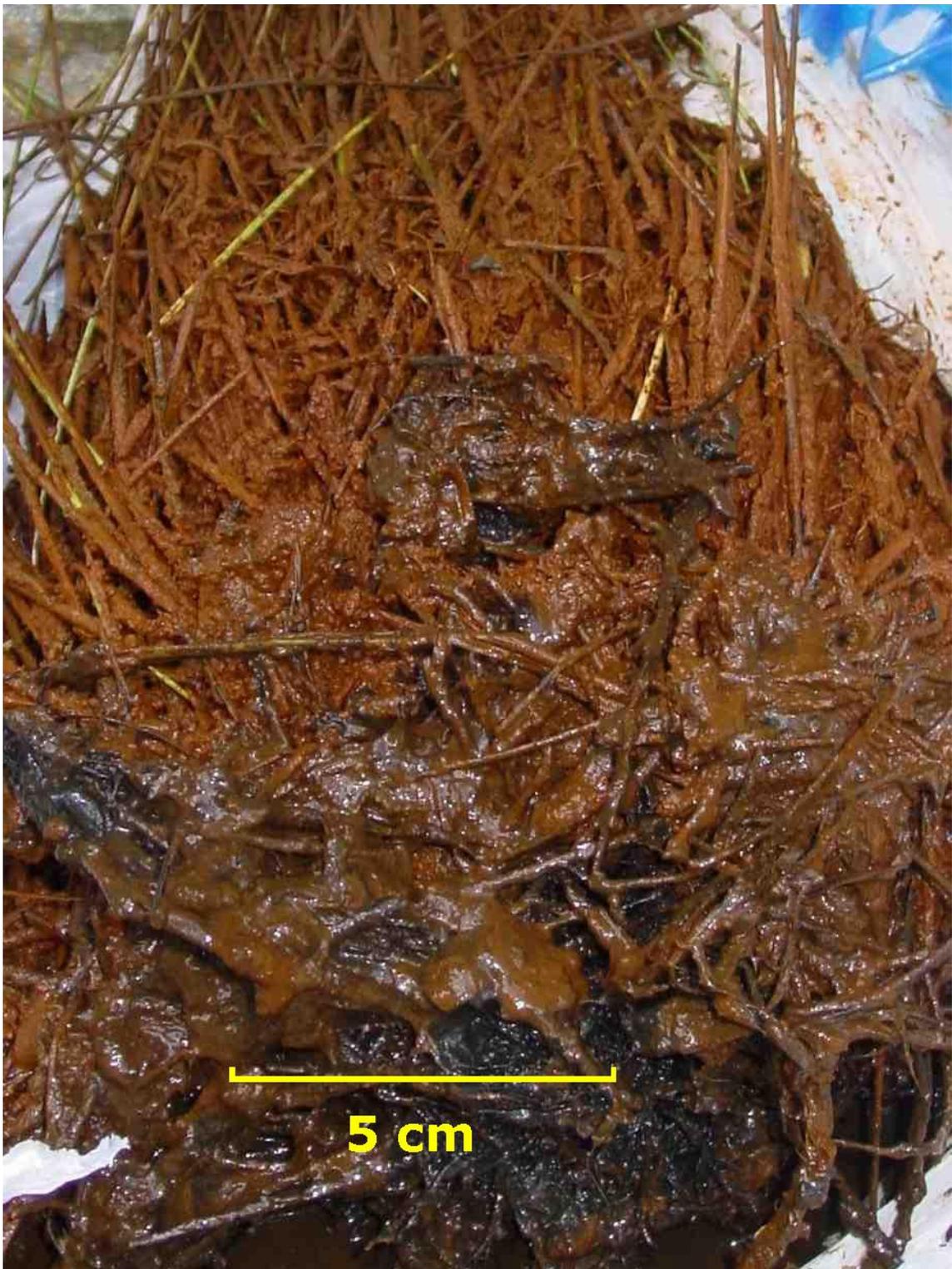


Figure 7.2. Root mass of sample PV6 (*Paspalum vaginatum*) showing distinct colour difference between soil in the root mass and the soil exposed to the atmosphere.

The ASS DTPA, EDDS, and EDTA leachates were analysed with the SEP extracts for Al, As, Co, Cr, Cu, Ni, Pb, and Zn. An aliquot of the SLRS-4 SRM was included to assess the accuracy of the elemental determination (Appendix B, Table B.5). A replicate sample was included to measure reproducibility (Appendix B, Table B.6). Accuracy and reproducibility of the analytical data were determined as detailed in Sections 2.9.2 and 2.9.3, respectively. The accuracy assessment is discussed in Section 5.2. Chromium was not determined accurately and the reproducibility for As was not acceptable. Therefore, the ASS DTPA, EDDS, and EDTA extraction dataset consisted of Al, Co, Cu, Ni, Pb, and Zn.

7.3 Results

7.3.1 Element Concentrations in Plants

Samples of both *Acrostichum speciosum* (n = 16) and *Paspalum vaginatum* (n = 16) were analysed for element concentrations. Eight samples of each species were collected from background locations. The plants collected from IAASS were compared with the background samples and with the NRC (1980) guidelines for element toxicity in animal feed.

7.3.1.1 Acrostichum Speciosum

In the stems of *Acrostichum speciosum* from IAASS, the order of the median concentrations was Al > Zn > Cu > Cr > As > Co > Pb (Figure 7.3) and in the roots Al > Zn > Cu > As > Cr > Pb > Co (Figure 7.4). The order of median concentrations in the background samples of *Acrostichum speciosum* was Al > Zn > Cu > As > Pb > Cr > Co in the stems, and in the roots Al > Zn > Cu > Pb > As > Cr > Co (Figure 7.4).

Comparison of the two sample groups identified that the median concentrations of Co, Cr and Zn were larger in the stems of the samples from IAASS than in the background samples (Figure 7.3). With respect to the roots, the median concentrations were greater in the IAASS samples for As, Co, Cr and Cu than in the background samples (Figure 7.4). This demonstrates that *Acrostichum speciosum* growing in IAASS frequently contain more Co, Cr and Zn in their stems, and more As, Co, Cr and Cu in their roots, than specimens growing in undisturbed areas. The data suggests that seawater inundation of AASS may increase the availability of As, Co, Cr, Cu and Zn to *Acrostichum speciosum*.

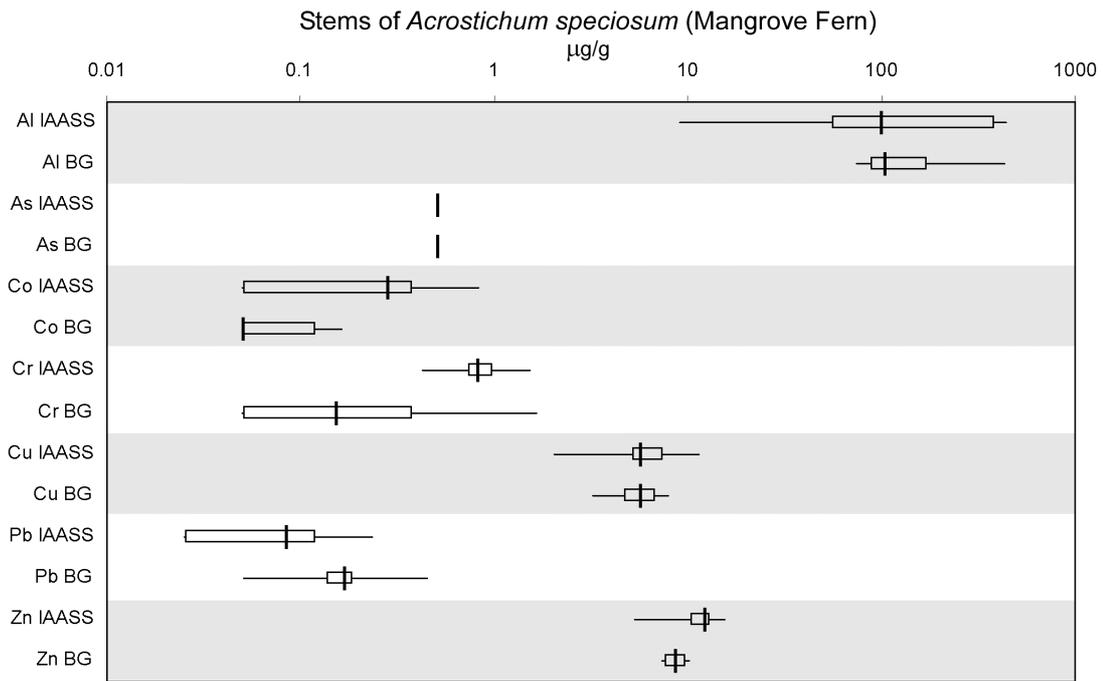


Figure 7.3. Comparison of element distributions in the stems of the *Acrostichum speciosum* samples collected from IAASS and background locations. Concentrations are described by smallest, 25th percentile, median, 75th percentile and largest values. Sample population for both groups is 8.

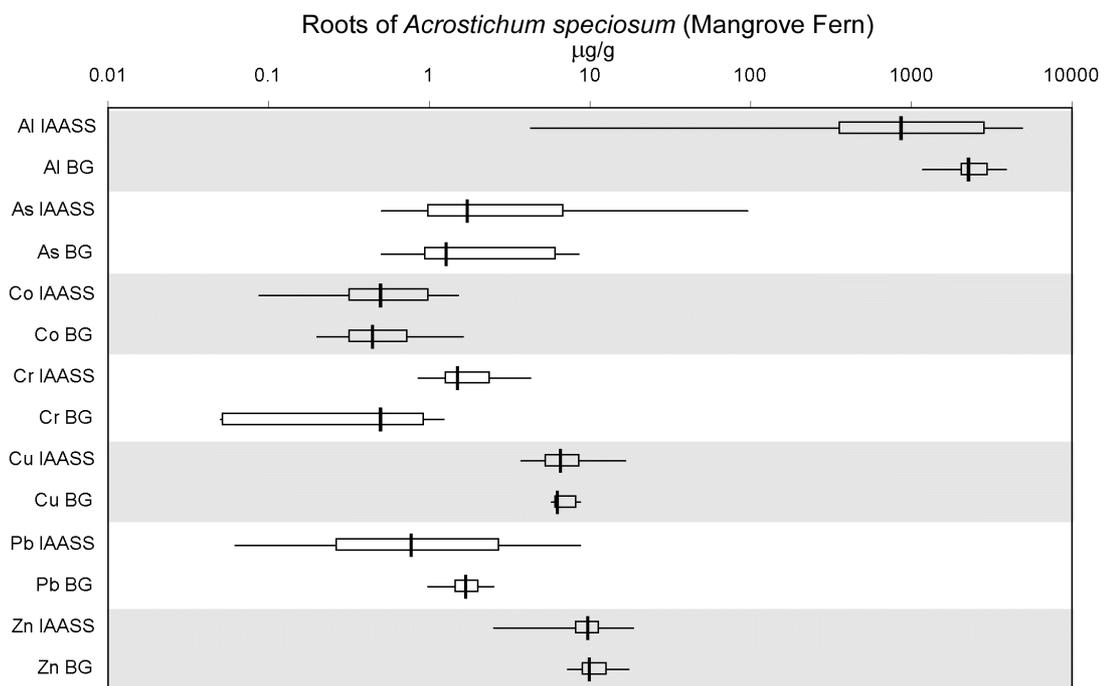


Figure 7.4. Comparison of element distributions in the roots of the *Acrostichum speciosum* samples collected from IAASS and background locations. Concentrations are described by smallest, 25th percentile, median, 75th percentile and largest values. Sample population for both groups is 8.

7.3.1.2 Paspalum vaginatum

The order of the median element concentrations in the stems of the *Paspalum vaginatum* samples collected from IAASS was Al > Zn > Cu > Cr > As > Pb > Co. In the roots, the order was Al > Zn > Cu > As > Cr = Pb > Co. For the background samples of *Paspalum vaginatum*, descending order of the element median concentrations was Al > Zn > Cu > Cr > Pb > As > Co in the stems, and Al > Zn > Cu > As > Cr > Pb > Co in the roots.

Copper and Zn occurred in higher median concentrations in the stems of *Paspalum vaginatum* samples collected from IAASS compared to the background samples (Figure 7.5). This trend was minored in the roots of the *Paspalum vaginatum* samples, where the median concentrations of Cu and Zn were again higher in the samples from IAASS than in the background samples (Figure 7.6).

The analysis of *Paspalum vaginatum* demonstrates that samples from IAASS contain more Cu and Zn in their stems and roots than samples not growing in IAASS. This suggests that the seawater inundation of AASS has caused *Paspalum vaginatum* to accumulate increased concentrations of Cu and Zn.

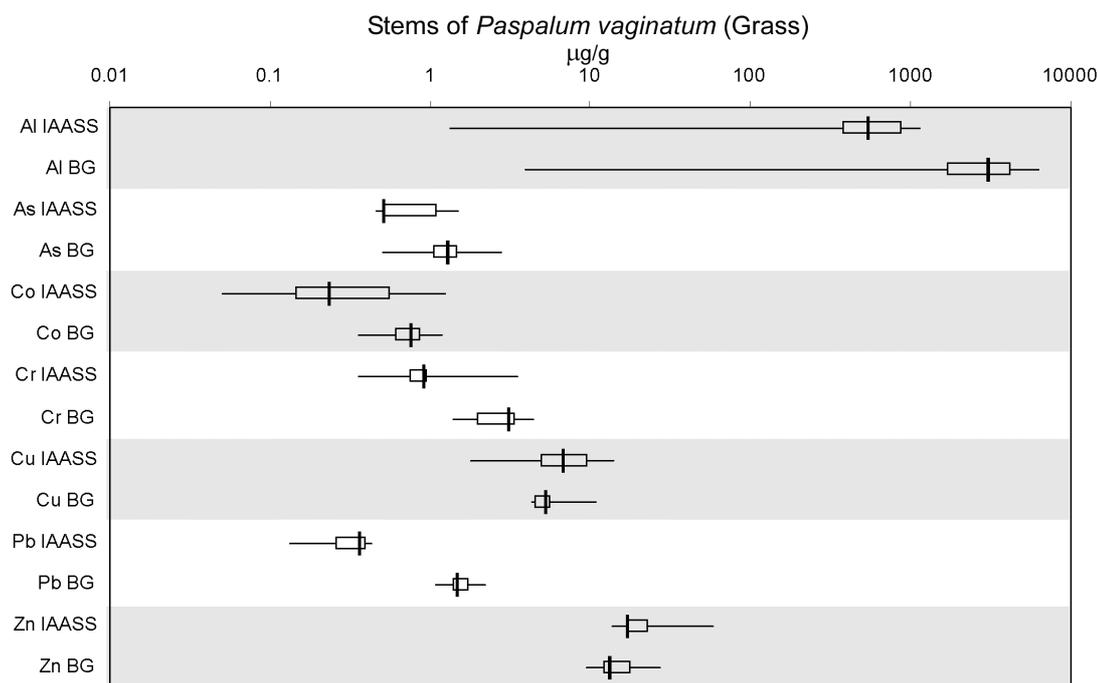


Figure 7.5. Comparison of element distributions in the stems of the *Paspalum vaginatum* samples collected from IAASS and background locations. Concentrations are described by smallest, 25th percentile, median, 75th percentile and largest values. Sample population for both groups is 8.

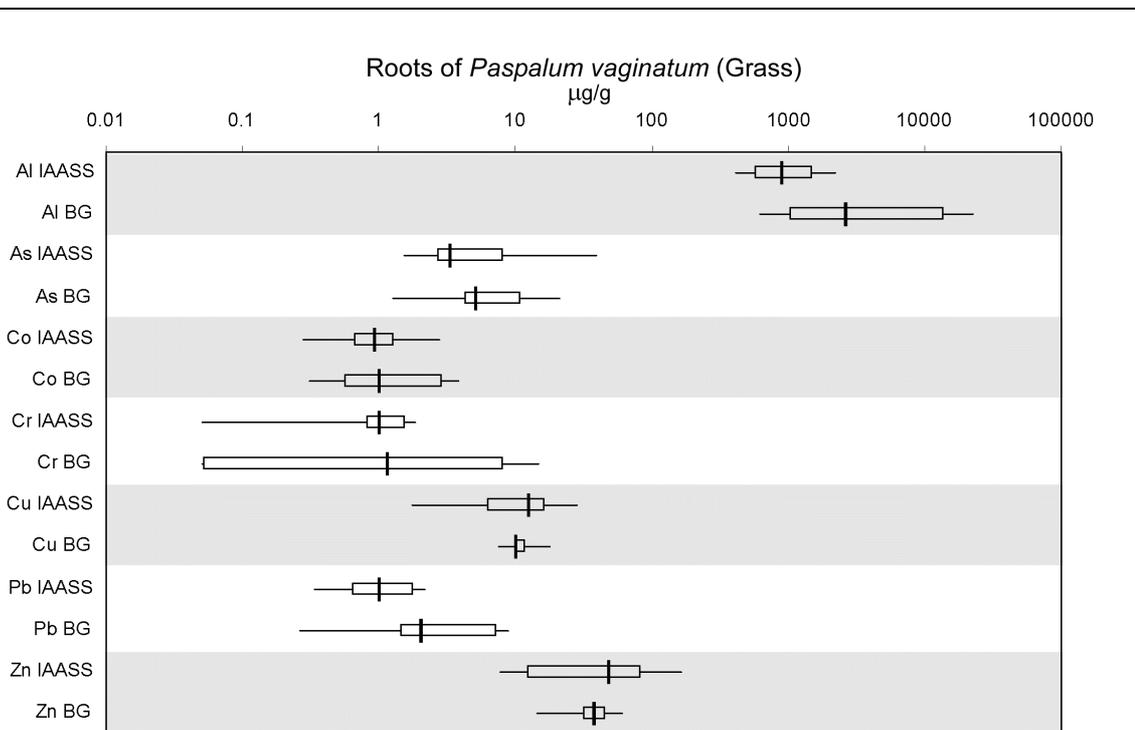


Figure 7.6. Comparison of element distributions in the roots of the *Paspalum vaginatum* samples collected from IAASS and background locations. Concentrations are described by smallest, 25th percentile, median, 75th percentile and largest values. Sample population for both groups is 8.

7.3.1.3 Potential Toxicity to Grazing Animals

Accumulation of toxic element concentrations in the stems of the plants from East Trinity were identified by comparing plant element concentrations with NRC (1980) guidelines on the tolerable element values in domestic animal diets (Table 7.1). The comparison indicated only one instance of toxic element concentrations (Table 7.2). Aluminium occurred in concentrations toxic to cattle and sheep in 12.5 % of the *Paspalum vaginatum* samples from IAASS and 75 % of samples from background locations. The comparison also identified that Al in the stems of *Paspalum vaginatum* was toxic to pigs, poultry, horses and rabbits in 75 % of the samples from both IAASS and background locations.

The stems of *Acrostichum speciosum* also reported Al concentrations toxic to pigs, poultry, horses and rabbits in 37.5 % of samples from IAASS and 12.5 % of samples from background locations. However, the validity of the comparison is doubtful, as it is unclear if *Acrostichum speciosum* would likely to be consumed by pigs, poultry, horses or rabbits. No other elements exceeded the NRC (1980) guidelines in either of the plant species examined.

Aluminium concentrations in the stems of *Paspalum vaginatum* from East Trinity (i.e. IAASS and background samples) ranged from between 1.33 to 6,260 ppm with a median of 849 ppm. In the

samples of *Paspalum vaginatum* from IAASS, Al ranges between 1.33 - 1,140 ppm with a median of 540 ppm. The NRC (1980) guideline for Al toxicity in dry feed is 1,000 ppm for cattle and sheep, and 200 ppm for pigs, poultry and horses. This indicates that Al is readily available to grazing animals and birds in potentially toxic concentrations from grasses not just growing in the IAASS, but also from those growing in the undisturbed locations around East Trinity. The accumulation of Al by *Paspalum vaginatum* growing on East Trinity poses a significant risk to wild and domestic animals that may feed on it, but this risk can only be partially attributed to the grass growing in IAASS.

Table 7.1. Maximum tolerable concentrations of selected elements in the diet of domestic animals (NRC (1980)). All values are µg/g of dry feed.

Element	Cattle	Sheep	Swine	Poultry	Horse	Rabbit
Al ¹	1,000	1,000	200 ³	200	200 ³	200 ³
As (organic)	100	100	100	100	100 ³	100 ³
Co	10	10	10	10	10 ³	10 ³
Cr (chloride)	1,000 ³	1,000 ³	1,000 ³	1,000	1,000	1,000 ³
Cr (oxide)	3,000 ³	3,000 ³	3,000 ³	3,000	3,000 ³	3,000 ³
Cu	100	25	250	300	800	200
Pb ²	30	30	30	30	30	30 ³
Zn	500	300	1,000	1,000	500 ³	500 ³

¹ In highly bioavailable salts.

² Values are based on residue in human food.

³ Values in parentheses were derived by interspecific extrapolation.

7.3.2 EDTA Extraction of Reduced and Oxidised Plant Soil

Extractions using EDTA were conducted on samples of the reduced and oxidised plant soils collected from East Trinity (Table I.5, Appendix I). The EDTA extractions were used to assess the phytoavailability of Al, As, Co, Cu, Ni and Zn. The plant soils from the IAASS and the background samples were assessed separately. All samples (including the background samples) were collected from areas influenced by seawater inundation (i.e. all the plant soils were potentially reduced).

Comparison of the concentrations in EDTA leaches of the reduced and oxidised plant soils from IAASS showed that all the elements were extracted in larger amounts from the oxidised samples (Table 7.3). Arsenic and Cu were the only elements that had concentrations in the oxidised and reduced soil leachate that differed more than 10 %. The percentage of As and Cu extracted from the oxidised soil that report in the reduced soil leachates was 74 % and 72 %, respectively. The results suggest that at East Trinity, saltwater inundation of IAASS reduces the phytoavailability of Al, As, Cu, Ni and Zn.

Similar trends in element phytoavailability to those of the IAASS samples were found for the background samples (Table 7.4). Less Al, As, Co and Cu were extracted with EDTA from both of the reduced background samples than the oxidised samples. The only case where an element was extracted in a larger amount from the oxidised sample than the reduced sample was Ni in MF4. Otherwise, the background samples indicate that, like the in the IAASS samples, saltwater inundation reduces element phytoavailability.

Table 7.2. Comparison of element concentrations in the stems of *Acrostichum speciosum* and *Paspalum vaginatum* samples collected from IAASS and background locations. Comparison is made by identifying the percentage of samples in the IAASS and background populations that exceeded the toxic value. See Table 7.1 for details of element forms used to set toxic levels. Element concentrations are $\mu\text{g/g}$ of dry plant mass.

Element	Animal	Value	% of samples in population greater than toxic level			
			<i>Paspalum vaginatum</i>		<i>Acrostichum speciosum</i>	
			IAASS	BG	IAASS	BG
Al	Cattle, Sheep	1000	12.5	75	0	0
	Swine, Poultry, Horse, Rabbit	200	75	75	37.5	12.5
As (organic)	All ¹	100	0	0	0	0
Co	All ¹	10	0	0	0	0
Cr (chloride)	All ¹	1000	0	0	0	0
Cr (oxide)	All ¹	3000	0	0	0	0
Cu	Horse	800	0	0	0	0
	Poultry	300	0	0	0	0
	Swine	250	0	0	0	0
	Rabbit	200	0	0	0	0
	Cattle	100	0	0	0	0
	Sheep	25	0	0	0	0
Pb	All ¹	30	0	0	0	0
Zn	Swine, Poultry	1000	0	0	0	0
	Cattle, Horse, Rabbit	500	0	0	0	0
	Sheep	300	0	0	0	0

¹ All refers to cattle, horse, poultry, rabbit, sheep and swine.

7.3.3 Plant Responses to Phytoavailable Elements

Three responses of *Acrostichum speciosum* and *Paspalum vaginatum* to the phytoavailable element pool were investigated. Each species was assessed for: 1) its ability to take up available elements; 2) the degree to which elements are transferred from its roots to its stems; and 3) its ability to act as an indicator of phytoavailable element concentrations in the soil. The plant responses to the phytoavailable element pool were expected to be species specific and not relate to the growing substrate. Hence, the seven samples from each species from which soil was extracted using EDTA

(i.e. the 12 IAASS and 2 background samples) were used to examine the responses of *Acrostichum speciosum* and *Paspalum vaginatum* to phytoavailable elements.

Table 7.3. Ratio of EDTA extractable elements in reduced and oxidised samples of the plant soils from the IAASS of East Trinity (reduced soil:oxidised soil = Red:Ox). Element concentrations used to calculate ratios were in units of $\mu\text{g/g}$ of dry soil.

	Al Red:Ox	As Red:Ox	Co Red:Ox	Cu Red:Ox	Ni Red:Ox
MF1	0.13	1.39	0.60	0.46	0.20
MF2	0.77	1.00	1.39	0.94	1.20
MF3	-	0.70	1.68	1.17	1.22
MF5	0.63	0.72	1.00	0.56	0.88
MF6	1.45	0.73	1.63	1.06	0.99
MF7	4.76	0.20	1.51	0.88	4.14
PV1	0.99	0.73	1.32	0.88	0.99
PV2	1.04	1.27	0.99	0.44	0.85
PV4	0.96	0.75	0.98	0.94	1.00
PV5	0.55	0.71	0.62	0.53	0.78
PV6	-	0.96	0.84	0.13	0.81
PV7	-	1.39	0.56	0.04	0.46
IAASS Median	0.96	0.74	0.99	0.72	0.94
<i>n</i>	11	12	12	12	12

Table 7.4. Ratio of EDTA extractable elements in reduced and oxidised samples of the background plant soils from East Trinity (reduced soil:oxidised soil). Element concentrations used to calculate ratios were in units of $\mu\text{g/g}$ of dry soil.

	Al Red:Ox	As Red:Ox	Co Red:Ox	Cu Red:Ox	Ni Red:Ox
MF4 (BG)	0.62	0.55	0.54	0.95	1.23
PV3 (BG)	0.67	0.99	0.92	0.76	0.81

7.3.3.1 Uptake of Phytoavailable Elements

Comparisons of the element concentrations in the roots, stems and EDTA leachates of the reduced and oxidised soils are used to identify the responses of the plant species to the phytoavailable element pool (Figure 7.7). The data used to construct the graphs in Figure 7.7 are given in Table I.3 (samples MF1 - MF7 and PV1 - PV7) of Appendix I.

The higher concentrations of Al, Co, Cu and Zn in the roots and stems compared to the EDTA extractions indicated that *Acrostichum speciosum* accumulated those elements (Figure 7.7). Arsenic was also accumulated by *Acrostichum speciosum*, but only in its roots.

In *Paspalum vaginatum*, Al, Cu and Zn were accumulated in the roots and stems, whereas As and Co accumulated only in the roots. The results indicate that relative to the elements extracted in the EDTA leaches, all the elements examined (Al, As, Co, Cu and Zn) accumulate in either, or both, the roots and stems of *Acrostichum speciosum* and *Paspalum vaginatum*.

7.3.3.2 Element Transfer from Root to Stem

The concentration ratio of Al, As, Co, Cr, Cu, Pb and Zn between the stems and roots of *Acrostichum speciosum* and *Paspalum vaginatum* were calculated to identify if any elements accumulated in the above ground tissue (stems). All the plant samples were used to calculate the median element [stem]:[root] ratio.

In the samples of *Acrostichum speciosum*, no element reported a median [stem]:[root] greater than one (Table 7.5). The median ratio for Zn was the highest (0.99) and Al the lowest (0.06). No elements reported a [stem]:[root] median greater than one in the samples of *Paspalum vaginatum* (Table 7.6). The decreasing order of the [stem]:[root] medians for the elements was Cr > Cu > Al > Zn > Co > Pb > As. Comparison of root and stem element concentrations in the two plant species indicated that *Acrostichum speciosum* and *Paspalum vaginatum* were not preferentially transferring Al, As, Co, Cr, Cu, Pb or Zn to their stems and leaves.

Table 7.5. Root to stem transfer factor for Al, As, Co, Cr, Cu, Pb and Zn in the mangrove fern *Acrostichum speciosum*. Transfer factor is the ratio of

Sample Type	$\frac{[\text{element}]_{\text{stem}}}{[\text{element}]_{\text{root}}}$																
	MF1 IAASS	MF2 IAASS	MF3 IAASS	MF5 IAASS	MF6 IAASS	MF7 IAASS	MF15 IAASS	MF16 IAASS	MF4 BG	MF8 BG	MF9 BG	MF10 BG	MF11 BG	MF12 BG	MF13 BG	MF14 BG	Median
Al	0.01	0.12	0.08	0.55	92.09 ¹	1.25	0.00	0.04	0.15	0.12	0.03	0.05	0.06	0.03	0.04	0.04	0.06
As	1.00	0.17	0.45	1.00	0.30	0.25	0.03	0.01	1.00	0.39	0.08	0.08	0.47	1.00	0.30	0.06	0.30
Co	0.19	0.33	0.57	0.89	0.77	1.30	0.03	0.10	0.51	0.51	0.04	0.08	0.30	0.25	0.11	0.03	0.28
Cr	0.33	0.35	0.47	0.94	0.23	0.97	0.66	0.36	0.62	1.00	0.06	4.78	0.10	33.00	0.22	0.16	0.41
Cu	0.49	0.77	0.72	0.44	0.86	0.55	1.75	1.70	0.70	0.74	1.37	0.91	0.59	1.06	0.72	0.56	0.73
Pb	0.05	0.05	0.08	0.26	0.11	0.41	0.03	0.04	0.05	0.18	0.08	0.08	0.07	0.12	0.10	0.10	0.08
Zn	0.64	1.11	0.95	1.32	4.80	1.46	1.25	0.61	0.89	1.10	1.04	0.56	0.70	1.06	0.75	0.53	0.99

¹ The large ratio for MF6 is due to a very small [Al] in the root sample (4.3 µg/g).

Table 7.6. Root to stem transfer factor for Al, As, Co, Cr, Cu, Pb and Zn in the grass *Paspalum vaginatum*. Transfer factor is the ratio of

Sample Type	$\frac{[\text{element}]_{\text{stem}}}{[\text{element}]_{\text{root}}}$																
	PV1 IAASS	PV2 IAASS	PV4 IAASS	PV5 IAASS	PV6 IAASS	PV7 IAASS	PV15 IAASS	PV16 IAASS	PV3 BG	PV8 BG	PV9 BG	PV10 BG	PV11 BG	PV12 BG	PV13 BG	PV14 BG	Median
Al	0.63	2.19	0.24	1.11	0.00	2.68	0.16	0.25	3.59	0.00	7.25	2.75	1.06	0.00	0.17	0.26	0.45
As	0.16	0.19	0.33	0.10	0.15	0.16	0.21	0.03	1.09	0.55	0.41	0.10	0.31	0.05	0.14	0.06	0.16
Co	0.15	1.91	0.23	0.79	0.08	0.82	0.05	0.18	2.65	2.62	1.09	0.47	0.56	0.16	0.23	0.19	0.35
Cr	0.83	0.74	0.48	0.84	0.60	0.53	69.60	0.46	1.20	88.00	61.40	41.20	1.11	0.26	0.21	0.22	0.78
Cu	0.50	0.75	0.58	0.78	0.89	1.04	0.45	0.49	0.61	0.74	0.44	0.49	0.51	0.43	0.53	0.38	0.52
Pb	0.13	0.79	0.20	0.21	0.36	0.56	0.26	0.24	5.33	1.11	1.57	0.70	0.74	0.22	0.18	0.14	0.31
Zn	0.19	1.78	0.43	0.39	1.35	1.47	0.33	0.35	1.88	0.43	0.38	0.43	0.29	0.39	0.22	0.24	0.39

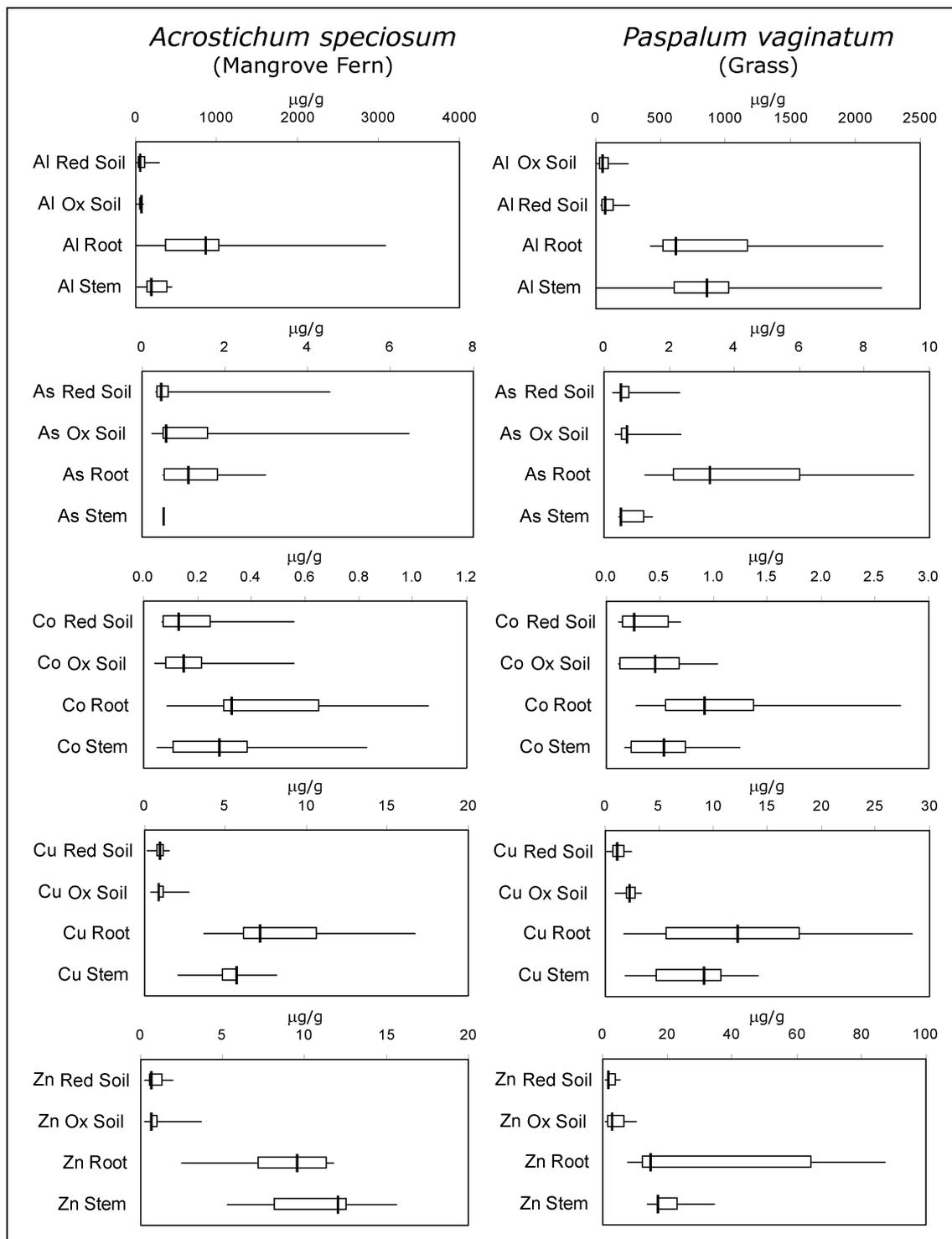


Figure 7.7. Comparisons of Al, As, Co, Cu and Zn concentrations in the above ground tissues (stems), below ground tissues (roots) and EDTA leachates of the plant soil, of all the *Acrostichum speciosum* (n = 7) and *Paspalum vaginatum* (n = 7) samples. Data are compared using the smallest, 25th percentile, median, 75th percentile and largest values. “Red Soil” and “Ox Soil” refers to the EDTA extractions using reduced and oxidised soil, respectively (see Section 7.2.3).

7.3.3.3 Potential Indicator Species

Correlation coefficients were calculated for the element concentrations in the EDTA extractions of the reduced and oxidised soils and the stems of the two plant species. Significant correlations between the concentrations in the plant stems and soil EDTA extractions were used to identify if either of the plant species were indicators for phytoavailable elements. For a plant to be considered an indicator, a significant linear relationship between the element concentrations in the soil and the plant must exist (Bunzl et al., 2000; Sheppard and Evenden, 1988).

Element concentrations in the EDTA extractions of the reduced soils generally correlated more strongly than those of the oxidised soil with the plant stem concentrations (Tables 7.7 and 7.8). The only exception to this was Co in the *Paspalum vaginatum* samples, which correlated more strongly with the EDTA extractions of the oxidised soils. The correlation results indicate that the EDTA extraction using reduced soil is generally a better indicator for element phytoavailability than when oxidised soil is used.

Pearson's correlation coefficient was calculated on untransformed and log₁₀ normalised data (Tables 7.7 and 7.8). The highest significant correlation coefficients for the stems of *Acrostichum speciosum* were with Al (reduced soil, untransformed data), Co (reduced soil, untransformed data) and Zn (reduced soil, log normalised data) (Figure 7.8). *Paspalum vaginatum* stems correlated significantly with Co (oxidised soil, untransformed data), As (reduced soil, log normalised data) and Cu (reduced soil, log normalised data) (Figure 7.8). The significant correlation coefficients indicate that *Acrostichum speciosum* is a potential indicator for Al, Co and Zn, whereas *Paspalum vaginatum* is a potential indicator for Co, As and Cu.

Table 7.7. Comparison of Pearson's correlation coefficients calculated with untransformed and log normalised data between the concentrations of Al, As, Co, Cu and Zn in the oxidised and reduced soil EDTA leaches and the stems of *Acrostichum speciosum*. Values in bold are the largest of the EDTA soil extraction pair. Values in italic are statistically significant (n = 7; see table notes).

Element/ Plant Tissue	Pearson's Correlation Coefficient		Pearson's Correlation Coefficient on Log Normalised Data	
	[Oxidised Soil EDTA]	[Reduced Soil EDTA]	[Oxidised Soil EDTA]	[Reduced Soil EDTA]
Al Stem	0.501	<i>0.810</i> ¹	-0.017	0.681
As Stem	NV	NV	NV	NV
Co Stem	<i>0.850</i> ¹	<i>0.955</i> ²	0.618	<i>0.840</i> ¹
Cu Stem	-0.288	-0.668	-0.451	-0.625
Zn Stem	0.706	<i>0.767</i> ¹	<i>0.775</i>	<i>0.853</i> ¹

¹ Statistically significant at the 0.05 level (0.755, n = 7).

² Statistically significant at the 0.01 level (0.875, n = 7).

Table 7.8. Comparison of Pearson’s correlation coefficients calculated with untransformed and log normalised data between the concentrations of Al, As, Co, Cu and Zn in the oxidised and reduced soil EDTA leaches and the stems of *Paspalum vaginatum*. Values in bold are the largest of the EDTA soil extraction pair. Values in italic are statistically significant (n = 7; see table notes).

Element/ Plant Tissue	Pearson’s Correlation Coefficient		Pearson’s Correlation Coefficient on Log Normalised Data	
	[Oxidised Soil EDTA]	[Reduced Soil EDTA]	[Oxidised Soil EDTA]	[Reduced Soil EDTA]
Al Stem	-0.213	-0.163	0.335	<i>-0.770</i> ¹
As Stem	0.577	0.707	0.618	<i>0.807</i> ¹
Co Stem	<i>0.800</i> ¹	0.666	0.679	0.579
Cu Stem	-0.167	0.640	-0.165	<i>0.854</i> ¹
Zn Stem	-0.053	0.097	0.052	0.114

¹ Statistically significant at the 0.05 level (0.755, n = 7).

² Statistically significant at the 0.01 level (0.875, n = 7).

7.3.4 Element Phytoavailability in AASS and IAASS

Two comparisons were made using the DTPA, EDDS and EDTA extraction data from the ASS samples. The first was a direct comparison of the elements extracted from AASS and IAASS. The second was a comparison of the elements extracted using EDDS against the more commonly employed EDTA and DTPA.

7.3.4.1 Element Phytoavailability in AASS and IAASS

Larger median concentrations were reported by the DTPA, EDDS and EDTA extractions of IAASS than AASS for all the elements examined (Table 7.9). This indicates that Al, Co, Cu, Ni, Pb and Zn are more phytoavailable in IAASS than in AASS. A likely reason for the increased element availability in IAASS is the near neutral pH of the soil. Chelating agents extract elements from the water-soluble and portions of the sorbed fraction (Intawongse and Dean, 2006; Rayment and Higginson, 1992). Aluminium, Co, Cu, Ni, Pb and Zn are readily sorbed onto charged surfaces in neutral soil conditions, but are desorbed under acidic conditions. The acidic conditions in the AASS prevent sorption and limit the size of the element fraction available to be extracted. In comparison, the neutral soil pH of the IAASS promotes element sorption, hence increasing size of the sorbed fraction.

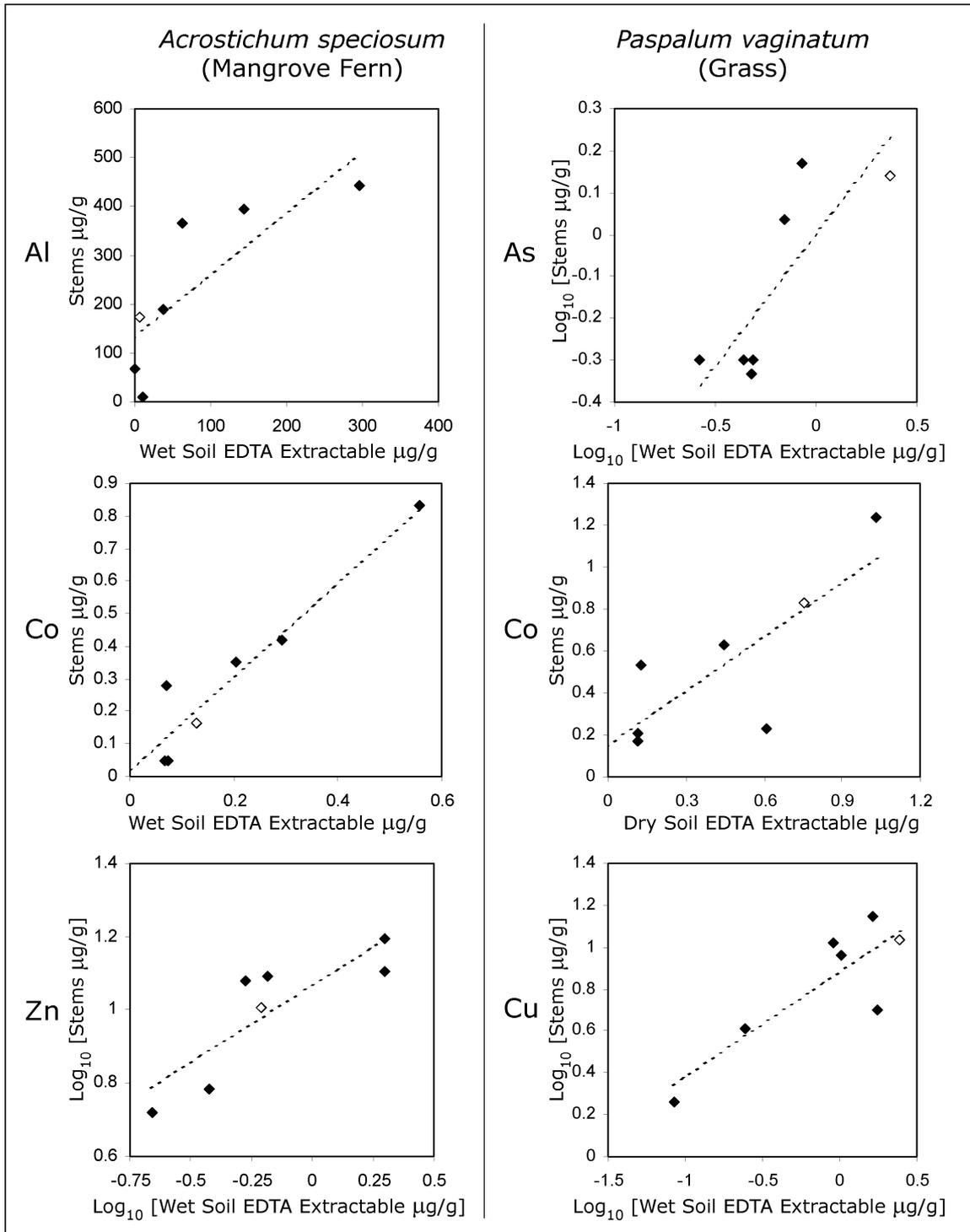


Figure 7.8. Scatter plots and regression lines for elements that reported significant correlation coefficients between EDTA leach and stem concentrations. Graphs are drawn using either untransformed, or log_{10} normalised data depending on the highest correlation coefficient. See Tables 7.7 and 7.8 for correlation coefficients for *Acrostichum speciosum* and *Paspalum vaginatum*, respectively. Closed diamonds are samples from IAASS and open diamonds are background samples.

Table 7.9. Median, minimum and maximum element concentrations in EDTA, EDDS and DTPA extractions of AASS and IAASS. AASS samples (n = 7) were from the dry ASS profile and IAASS samples (n = 7) were from the wet ASS profile.

	AASS (Dry ASS Profile)			IAASS (Wet ASS Profile)		
	EDTA	EDDS	DTPA	EDTA	EDDS	DTPA
Al µg/g	19 (3 - 127)	34 (3 - 261)	25 (4 - 59)	52 (17 - 64)	99 (32 - 133)	111 (17 - 198)
Co µg/g	0.07 (0.06 - 1.24)	0.09 (0.06 - 1.48)	0.08 (0.05 - 1.14)	0.29 (0.05 - 0.38)	0.39 (0.05 - 0.45)	0.29 (0.04 - 0.81)
Cu µg/g	2.47 (1.38 - 3.99)	2.75 (1.33 - 4.03)	0.8 (0.27 - 2.27)	0.66 (0.36 - 1.43)	1.03 (0.78 - 2.33)	0.26 (0.01 - 0.43)
Ni µg/g	0.20 (0.15 - 0.83)	0.22 (0.15 - 0.94)	0.16 (0.12 - 0.51)	0.54 (0.33 - 0.73)	0.77 (0.35 - 0.92)	0.36 (0.14 - 0.72)
Pb µg/g	0.43 (0.06 - 2.72)	0.2 (0.03 - 1.83)	0.03 (0.01 - 0.62)	4.46 (3.02 - 5.94)	3.05 (1.96 - 4.12)	3.08 (0.27 - 5.03)
Zn µg/g	0.51 (0.28 - 1.04)	0.49 (0.35 - 1.03)	0.64 (0.38 - 1.44)	0.91 (0.49 - 1.21)	0.94 (0.44 - 1.29)	0.72 (0.2 - 1.35)

7.3.4.2 Comparison of EDTA, DTPA, and EDDS Phytoavailability Extractions

Comparison of element concentrations in the EDDS leachates with the EDTA and DTPA leachates were made using element concentration ratios. The aim of the comparison was to identify similarities in the extractive properties of the three chelating agents. The ratios were calculated using the element concentrations extracted from each ASS sample with EDDS as the numerator and those extracted with either DTPA or EDTA as the denominators. Elements extracted in similar amounts were identified by a median ratio within $\pm 15\%$ of 1 (i.e. between 0.85 and 1.15).

The median element concentrations extracted using EDDS were generally more similar to EDTA than DTPA. Compared to EDTA, EDDS extracted similar amounts ($\pm 15\%$) of Co, Ni and Zn, but more Al and Cu and less Pb (Table 7.10). By contrast, the EDDS leach removed a similar amount of Al to the DTPA extraction, but more than 15% Co, Cu, Ni, Pb and Zn (Table 7.11).

The concentrations of Cu, Ni, Pb and Zn in the EDTA leachates were more similar to those of the EDDS than the DTPA leaches. The concentrations of Al in the EDDS and DTPA extractions were similar. This indicates that the EDDS extraction removes Co, Ni and Zn in similar amounts to the EDTA extraction. Additionally, the EDDS extraction removes similar amounts of Al to the DTPA extraction.

Table 7.10. Ratios of element concentrations in 0.01 M EDDS and 0.01 M EDTA extractions (EDDS:EDTA). Samples are from the dry and wet ASS profile (n = 7 for each profile). Ratio medians that are between 0.85 - 1.15 are in bold.

	[Median Element] in EDDS:							[Median Element] in EDTA							
	DP2-1	DP2-2	DP2-3	DP2-4	DP2-5	DP2-6	DP2-7	WP2-1	WP2-2	WP2-3	WP2-4	WP2-5	WP2-6	WP2-7	Median
Al	2.06	0.59	1.21	1.36	1.01	3.41	2.41	2.75	1.87	1.57	1.54	2.09	2.21	2.26	1.96
Co	1.00	0.96	1.36	0.99	1.00	1.11	1.19	1.39	1.00	1.00	1.14	1.20	1.19	1.07	1.09
Cu	1.06	0.93	1.36	0.96	0.96	1.01	1.12	2.30	1.38	1.95	1.52	1.73	2.44	2.27	1.37
Ni	1.11	1.02	1.59	0.95	1.01	0.92	1.13	1.64	1.06	1.10	1.14	1.25	1.36	1.16	1.12
Pb	0.46	0.38	0.80	0.57	0.67	0.69	0.68	0.92	0.46	0.58	0.92	0.86	0.66	0.64	0.67
Zn	0.98	0.97	1.67	0.79	0.76	0.92	0.88	1.39	1.11	0.88	1.06	0.98	1.05	0.99	0.98

Table 7.11. Ratios of element concentration in 0.01 M EDDS and 0.005 M DTPA extraction (EDDS:DTPA). Samples are AASS and IAASS from the dry and wet ASS profiles, respectively (n = 7 for each profile). Ratio medians that are between 0.85 - 1.15 are in bold.

	[Median Element] in EDDS:							[Median Element] in DTPA							
	DP2-1	DP2-2	DP2-3	DP2-4	DP2-5	DP2-6	DP2-7	WP2-1	WP2-2	WP2-3	WP2-4	WP2-5	WP2-6	WP2-7	Median
Al	5.35	1.03	0.57	0.14	0.22	1.50	10.82	4.20	1.97	2.59	0.51	1.15	0.86	0.67	1.09
Co	2.19	1.10	1.11	1.29	1.06	1.24	1.30	1.39	1.23	1.35	1.15	1.27	0.56	1.07	1.24
Cu	9.90	2.37	2.52	4.95	1.60	1.90	5.79	11.09	7.61	143.07	3.70	3.80	2.05	2.87	3.75
Ni	2.51	1.38	1.44	1.01	1.28	1.48	1.85	2.69	2.56	2.50	1.69	1.83	1.28	1.59	1.64
Pb	9.00	2.05	3.39	4.51	1.25	1.66	7.55	7.41	8.11	7.15	1.05	0.99	0.81	0.76	2.72
Zn	2.19	0.68	0.45	0.97	0.24	1.05	1.67	2.13	2.76	2.19	0.95	1.25	1.25	1.19	1.22

7.4 Discussion

7.4.1 Assessment of Element Phytoavailability Using EDTA

In soils, the portion of an element which can be readily taken up by plant roots is considered the phytoavailable fraction (Intawongse and Dean, 2006). Phytoavailable elements generally occur in the exchangeable (i.e. adsorbed) and water-soluble fractions (Intawongse and Dean, 2006; Rayment and Higginson, 1992). As the pool of elements available to plants is composed of the water-soluble and exchangeable fractions, element phytoavailability is frequently assessed using chemical extractants that target these fractions. Extractions using chelating agents remove cations adsorbed on solid phases together with water-soluble constituents, effectively simulating the action of plant roots (Rayment and Higginson, 1992). One such chelating agent is EDTA, which has commonly been used to determine plant-available elements, particularly Cu, Fe, Mn and Zn (Chao, 1984; Borggaard, 1976). EDTA is a weak organic acid that is able to complex and chelate divalent and trivalent cations (Borggaard, 1976). In soils, EDTA extracts these cations from exchange sites on both inorganic and organic complexes without dissolving aluminosilicates (Aoyama et al., 1982).

The EDTA extraction used in this study was developed to assess Cu and Zn availability to crop plants (Rayment and Higginson, 1992), but EDTA extractions have been used to measure the phytoavailability of a much wider range of elements. EDTA has also frequently been shown to be superior to other chelating agents (e.g. DTPA) at indicating element phytoavailability. Hooda et al. (1997) tested the effectiveness of a range of chemicals (DTPA, EDTA, NH_4NO_3 and CaCl_2) to measure the phytoavailability of Cd, Cu, Ni, Pb and Zn. Of the extractions used, Hooda et al. (1997) reports that EDTA proved to be the most reliable and consistent in predicting the accumulation of metals in plants. Matúš et al. (2006) examined EDTA and other chemical extractions for their ability to correlate Al extracted from soil with the Al content of grasses growing in the tested soil. The authors concluded that the Al extracted from the soils using EDTA correlated well with Al in the grass. Yaman and Akdeniz (2006) used EDTA to extract phytoavailable Al from the soil in which fruit trees were growing. Aluminium concentrations in the soil EDTA extraction were compared to that of the fruit on the trees, but a significant statistical relationship was not found. Yaman and Akdeniz (2006) did not report the Al content of other plant tissues, preventing comparison of the amount of Al extracted from the soils with the actual plant tissues. Blake et al. (1994) used EDTA to extract Al from soils in which grass for hay was growing. Though no correlation coefficients were calculated, a relationship between the EDTA extractable Al in the soil and Al in the grass was identified. Chojnacka et al. (2005) correlated concentrations of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn extracted from polluted soil using EDTA (amongst other extractants) with whole plants that were growing in the polluted soil. Correlation coefficients were only reported for As, Cd, Cr, Hg and Pb. For these elements, significant correlations were reported between the EDTA soil extractions and plants. However, the EDTA soil extraction-plant correlations were not pursued by Chojnacka et al. (2005) because of stronger correlations between the plants and other extractants (i.e. NH_4 -citrate). Though these studies established the effectiveness of EDTA as an indicator of phytoavailable element concentrations in a range of soil types and conditions, none of the studies examined ASS or ASS like soils.

In this study, significant correlations occur between element concentration in the EDTA extractions and plant stems for all element examined (i.e. Al, As, Co, Cu and Zn). This suggests that EDTA is an effective indicator of element phytoavailability in IAASS. Moreover, stronger and more frequent correlations were found between element concentrations in plant stems and EDTA extractions with reduced (wet) soil than with oxidised (dried) soil. This indicates that EDTA extraction of water-logged soil generally provides a better assessment of element phytoavailability than if the soils were allowed to oxidise (as occurred during sample drying).

7.4.2 Effects of Soil Inundation on Element Phytoavailability

Hund-Rinke and Kordel (2003) identify a range of factors that influence element bioavailability in soils. These factors include sorption of elements to soil constituents (e.g. clays, organic matter and oxides), physical and chemical conditions in the soil (e.g. redox conditions, pH value, moisture content), and the composition of pore waters (pH value, dissolved organic matter content, presence of complexing agents and ionic strength).

In the plant soils from East Trinity, element phytoavailability was compared in reduced (wet) and oxidised (dried) soils. Drying the plant soils (for 5 to 7 days at 65°C) removed soil-waters and likely oxidised any labile sulfides (i.e. monosulfides; Bush et al., 2004; Berner, 1964). Element phytoavailability was identified using EDTA leaches. Comparison of the element concentrations extracted from the reduced and oxidised plant soils showed that larger amounts of all the studied elements were leached from the oxidised samples. As the EDTA extraction used was strongly buffered at pH 8.6 (with 1 M NH_4HCO_3), the effect of soil pH was large negated. The results (section 7.3.2) indicate that at East Trinity, inundation with seawater reduced the phytoavailability of the elements in both the IAASS and background samples.

Diminished element phytoavailability in inundated soils was also found by Vandecasteele et al. (2007; 2005). Vandecasteele et al. (2005) report the results of “wetland” and “upland” hydrological regimes on the uptake of Cd and Zn by willow trees (*Salix cinerea*). The willow trees were growing in soils derived from contaminated dredge sediment that were inundated with freshwater. The wetland hydrological regime, which consisted of extended periods of soil inundation, resulted in lower Cd and Zn concentrations in the leaves of the willow trees than the upland regime. Vandecasteele et al. (2007) further examined the uptake of Cd, Zn and Mn by willow trees (*Salix cinerea*) growing in soils derived from polluted sediments. The 2007 study involved comparing metal concentrations in willow tree tissue over two growing seasons. In the first season, the soils were inundated with freshwater, in the second the soils were not inundated. Vandecasteele et al. (2007) report that the concentration of Cd, Mn and Zn in the leaves and stems of the willows trees was greater from the season when the soils had dried than when the soils were inundated. This indicates that soil inundation decreased the availability of Cd, Mn, and Cd to the willow trees.

At East Trinity, the lower element concentrations in EDTA extractions of the reduced soils relative the oxidised soil are comparable to the findings of Kashem and Singh (2001a;b) and Vandecasteele et al. (2007; 2005). Aluminium, As, Co, Cu, Ni and Zn are likely to be less phytoavailable in the IAASS generated by seawater inundation than if the AASS were excluded from inundation (i.e. allowed to dry).

7.4.3 Plant Responses to Phytoavailable Elements

Plant responses to phytoavailable element fractions are variable and strongly species dependent (Hund-Rinke and Kordel, 2003). Using the Baker (1981) classification, the examined East Trinity species are identified as: a) *Acrostichum speciosum* excluder of Al, As, Co, Cr, Cu, Pb and Zn and an indicator of Al, Co and Zn; and b) *Paspalum vaginatum* excluder of Al, As, Co, Cr, Cu, Pb and Zn; and indicator of As, Co and Cu.

Neither of the species displayed ‘accumulator behaviour’, though studies have identified other ferns that display element accumulating behaviour. Nishizono et al. (1987) reported that the fern *Athyrium yokoscense* accumulated Cd, Pb and Zn. Ma et al. (2001) identified the Chinese brake fern *Pteris vittata* as an As hyperaccumulator.

The response of grasses to phytoavailable elements has been investigated more extensively (e.g. Matúš et al., 2006; Shahandeh and Hossner, 2000; Blake et al., 1994; Pfeiffer et al., 1982), but only two such studies examined *Paspalum vaginatum*. Shahandeh and Hossner (2000) assessed *Paspalum vaginatum* for its ability to accumulate Cr. *Paspalum vaginatum* was found to accumulate Cr⁵⁺, but died as a result of the Cr⁵⁺ accumulation. Accumulation of Cr by *Paspalum vaginatum*, as reported by Shahandeh and Hossner (2000), was not found at East Trinity. Pfeiffer et al. (1982) examined *Paspalum vaginatum* for Cr accumulation in the Irajá River estuary, Brazil. *Paspalum vaginatum* was found to contain higher Cr concentrations than surrounding waters, but lower concentration than in the substrate. Direct comparison of the data from Pfeiffer et al. (1982) with those from this project cannot be made because Pfeiffer et al. (1982) only examined total Cr concentrations in the substrate. However, the Cr concentrations reported for *Paspalum vaginatum* from the Irajá River (mean [Cr] in above ground tissue of 12.28 ppm and below ground tissue of 49.79 ppm) were considerably higher than those from East Trinity.

Indicator species regulate the transfer of elements from the soil to their stems so that stem concentrations reflect the phytoavailable concentration in the soil. Indicator species are important because of their potential use as biomonitors of environmental systems (e.g. Vandecasteele et al., 2002). For a plant to be considered an indicator, a significant linear relationship between the element concentrations in the soil and the plant must exist (Bunzl et al., 2000; Sheppard and Evenden, 1988). Furthermore, Baker (1981) identifies that plants may act as accumulators, indicators and/or excluders over different ranges of phytoavailable element concentrations. This clearly establishes the need for site-specific element phytoavailability assessment.

Both plant species collected from East Trinity displayed linear accumulation of elements in their stems with EDTA extractable element concentrations from their respective soils, i.e. *Acrostichum*

speciosum (Al, Co and Zn) and *Paspalum vaginatum* (Co, As and Cu). The ability to accumulate an element in their stems proportionally to phytoavailable concentrations in the soil identifies that both species have the potential to be used as indicators of element phytoavailability in the inundated areas of East Trinity. However, the indicator response of the plants is only valid over the range of concentrations in the soil extraction that were used to establish the relationship (cf. Bunzl et al., 2000).

7.5 Conclusions

Three objectives were set for this chapter. They were: 1) to assess elements for increased phytoavailability under inundated soil conditions; 2) to determine the responses of the sampled plant species to the phytoavailable element pool; and 3) to identify if plants growing in the IAASS contained higher element concentrations than background samples or toxicity guidelines. The extractive properties of three chelating agents (DTPA, EDDS and EDTA) were also compared using ASS material from East Trinity.

To assess whether elements were more phytoavailable in inundated soil than in dried soils, element concentrations extracted using EDTA from reduced “field condition” soil samples and dried (oxidised) soil samples were compared. The results indicated that less Al, As, Co, Cu, Ni and Zn were extracted using EDTA from reduced soils than oxidised soils. This suggests that Al, As, Co, Cu, Ni and Zn are less phytoavailable in wet soils found in the seawater inundated AASS of the Firewood Creek catchment, than if the soils were not inundated.

The two dominant plant species in the area of inundated AASS at East Trinity were examined for their responses to the phytoavailable element pool. These plant species were the mangrove fern *Acrostichum speciosum* and the grass *Paspalum vaginatum*. Both species were found to be excluders of Al, As, Co, Cr, Cu, Pb and Zn. The plants were also identified as potential indicator species for phytoavailable elements in the IAASS of East Trinity. *Acrostichum speciosum* was a potential indicator for Al, Co and Zn, and *Paspalum vaginatum* a potential indicator for As, Co and Cu.

Samples of *Acrostichum speciosum* and *Paspalum vaginatum* growing in IAASS were compared with samples from background locations to identify if seawater inundation increased element concentrations in plants. Samples of *Acrostichum speciosum* from IAASS were found to have higher median concentrations of Co, Cr and Zn in their stems and As, Co, Cr and Cu in their roots than samples from background locations. In the *Paspalum vaginatum* samples, the IAASS group had larger Cu and Zn medians in both the stems and roots than the background group. This indicated that plants colonising areas of inundated AASS had increased concentrations of Co, Cr, Cu and Zn.

The plants were next investigated for element toxicity to grazing animals using the NRC (1980) guidelines for the maximum tolerable levels in animal diets. Comparison of stem concentrations with NRC (1980) guidelines identified Al in potentially toxic concentrations in samples of *Paspalum vaginatum*. However, the background samples of *Paspalum vaginatum* contained Al concentrations in higher concentrations than the IAASS samples. This indicates that *Paspalum vaginatum* may accumulate toxic concentration of Al naturally in coastal lowland environments.

The extraction of phytoavailable elements from AASS and IAASS samples from the dry and wet ASS profile (respectively) showed that the IAASS contained larger concentrations of phytoavailable elements. The likely reason for the larger phytoavailable element pool in the IAASS was the near neutral soil conditions, which are conducive to element sorption on charged surfaces. The acidic soil conditions of the AASS desorb elements from charged surfaces, causing a reduction in the size of the phytoavailable fraction.

Finally, comparison of the biodegradable chelating agent EDDS with EDTA and DTPA identified that EDDS extracted similar ($\pm 15\%$) Co, Ni and Zn concentrations from ASS samples as EDTA, but more Al and Cu and less Pb. Only the amount of Al extracted by the EDDS leach was within 15 % of the element concentration in the DTPA leach. Generally, the median element concentrations extracted using EDDS were more similar to those of EDTA than DTPA. The comparison showed that EDDS extracted Co, Cu, Ni, Pb and Zn from the ASS in amounts that were more similar to the EDTA extraction than the DTPA extraction. This indicates that EDDS is a feasible biodegradable alternative to EDTA for the extraction of Co, Cu, Ni, Pb and Zn.

8. SUMMARY AND CONCLUSIONS

8.1 Project Summary

The project investigated Acid Sulfate Soils (ASS) in the Firewood Creek catchment, East Trinity, for: 1) element distribution in Actual Acid Sulfate Soils (AASS), Inundated AASS (IAASS) and Potential Acid Sulfate Soils (PASS); 2) element mobilisation during AASS inundation; 3) the fate of elements mobilised during AASS inundation; and 4) element bioavailability in IAASS. These four areas of investigation were encompassed by the key research question:

What are the effects of seawater inundation on the distribution, hosting, fate and bioavailability of elements in actual acid sulfate soils?

The elements examined by the project were: Al, As, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, Sc, V and Zn. Barium, Ga, Nb, S, Ti, and Zr were also frequently determined to assist with interpretation of geochemical processes in the ASS. Other elements were described where relevant. It was envisaged that the research would contribute to understanding element behaviour during PASS oxidation and AASS inundation, as well as assist with the assessment of AASS remediation using seawater inundation. The key project findings and how the research has added to the understanding of geochemical processes in ASS environments are discussed below.

8.1.1 Identification of IAASS

Chapter 3 provided a method for the identification of IAASS. This was critical as IAASS had not been previously defined or discussed in the scientific literature. The method for IAASS identification was based on the expected geochemical outcomes of seawater inundation of AASS. The expected geochemical properties of IAASS were: 1) a near neutral soil pH value (because of acid neutralisation by seawater); 2) Na enrichment (from increased exposure to seawater); and 3) depletion in elements mobilised during PASS oxidation (i.e. Co, Mn and Zn). Using the IAASS identification method, the upper part of the wet ASS profile was found to consist of IAASS.

The method developed to identify IAASS was further supported the by Isocon Analysis (IA) and the Sequential Extraction Procedure (SEP) data. IA showed strong enrichment of Na in the IAASS, whereas Na was depleted in the AASS. The Modified Bureau Communautaire de Référence (MBCR) SEP data reported that Na was largely hosted by the WS and AE fractions in both the AASS and IAASS. However, twice as much Na was hosted by the IAASS compared to the AASS. Hosting by these two fractions indicated that the likely source of the Na in the ASS was

seawater. This confirmed that the wet ASS profile (which contained the IAASS) has been more extensively inundated with seawater than the dry ASS profile (which contained the AASS).

8.1.2 Element Behaviour

Few investigations have been conducted on the behaviour (i.e. mobility/immobility) of elements during seawater inundation of AASS. As a result, element behaviour during seawater inundation of AASS is largely unknown. Element behaviour is of major concern to the success of AASS rehabilitation using seawater inundation. This is because the effectiveness of seawater inundation is highly dependent on it suppressing the mobility and preventing the release off-site of potentially toxic elements. Elements are known to display a range of behaviours during PASS oxidation (AASS formation; Åström, 1998). The research presented here used data from the novel application of IA as well as two SEPs to investigate element behaviour in both AASS-PASS profiles (i.e. the dry ASS profile) and IAASS-PASS profiles (i.e. the wet ASS profile).

The behaviour of Al, Ba, Co, Ga, Mn, Nb, Ni, Ti and Zn were largely unaffected by seawater inundation of AASS. This was demonstrated by the similar IA and SEP data from each of the AASS and IAASS sample groups.

IA showed that both the dry and wet ASS profiles were generally depleted in Co, Mn, Ni and Zn in their upper sections and enriched in their lower sections in Co, Ni and Zn. A similar occurrence of these elements was found in ASS profiles by Åström (1998). The likely mechanism for the depletion of Co, Mn, Ni and Zn in the upper profile was oxidation and soil acidification. This was supported by the SEP data, which indicated very small oxidisable fractions for these elements in the upper parts of the ASS profiles. By contrast, the Geological Survey of Canada (GSC) SEP data indicated that enrichment of Co, Ni and Zn in the lower parts of the profiles was due to immobilisation by either precipitation as sulfides or adsorption on exchange sites.

Aluminium, Ba, Ga, Nb and Ti were found to be largely immobile (i.e. hosted by the residual fraction) in the ASS of East Trinity. However, some Al was being mobilised from the AASS, likely because of extremely acidic soil conditions.

Unlike Al, Ba, Co, Ga, Mn, Nb, Ni, Ti and Zn, the hosting of the Cu, Fe, Na and Pb had been affected to some degree by seawater inundation of AASS. This was indicated by differences in their hosting or occurrence between the AASS and IAASS.

IA indicated that Cu and Pb were depleted from just below the surface to the middle of the ASS profiles, though the depletion was not as extensive as for Co, Mn, Ni and Zn. Copper depletion

was greater in the dry ASS profile, whereas Pb depletion was greater in the wet ASS profile. The pattern of enrichment displayed by Cu and Pb in the IA results was similar to that of Fe, suggesting that Cu and Pb may be associated with Fe in the ASS profiles.

The GSC-SEP data showed that Cu was hosted by the reducible fraction in the AASS and the oxidisable fraction in the IAASS. The much larger concentrations of Cu in the IAASS implied either that the oxidisable Cu had been preserved in the IAASS, or that inundation had caused the transfer of Cu to the oxidisable fraction (by reductive processes, e.g. sulfide formation).

Lead hosting in the AASS and IAASS was generally similar in the AASS and IAASS, but slightly more Pb was hosted by the reducible fraction in the AASS than the IAASS. This suggests that some Pb that is sorbed on Fe oxides may have been released by seawater inundation.

The results of IA showed that Fe was enriched in the upper parts of the dry ASS profile and depleted from the middle of both ASS profiles. The wet ASS profile displayed greater Fe depletion than the dry ASS profile. The GSC-SEP indicated that Fe was hosted largely by the reducible fraction in the AASS and IAASS. This fits with Fe being immobilised in the AASS as Fe³⁺ solid phases. Åström (1998) identified similar Fe behaviour in ASS profiles. However, the size of the reducible fraction in the IAASS was smaller by approximately two thirds that of the AASS. The zone of Fe depletion in the IAASS corresponded with a zone of high Na concentrations in the WS and AE fractions. This suggested that the likely cause of the Fe depletion in the IAASS was reductive dissolution of oxidised Fe phases caused by prolonged seawater inundation. Translocation of Fe in oxidised ASS profiles by reduction induced inundation has previously been reported by Harmsen and van Breemen (1975). However, the extensive loss of Fe from the IAASS was of concern because oxidised Fe phases are scavengers of many elements and may be important in minimising the release of mobilised metals from the AASS. Iron mobilisation from the IAASS is evident from the Fe-rich sediments/flocculants that occur in the drains servicing the areas of IAASS. Lead also showed increased depletion in the wet ASS profile, suggesting that it may be mobilised by the dissolution of oxidised Fe phase hosts.

8.1.3 Drain Sediments

The research in Chapter 6 advanced the understanding of drain sediment formation as well as the role of the drain sediments as element hosts. The geochemistry of the drain sediments was dominated by Fe (as fine-grained amorphous and crystalline oxyhydroxides) and LOI. This indicated that the drain sediments formed from the precipitation of Fe³⁺ phases in soil waters exiting IAASS. The precipitation of the Fe³⁺ phases in the exiting soil-waters was likely due to

oxidation of dissolved Fe^{2+} on exposure of the soil waters to the atmosphere. The Orange Flocculant (OF) drain sediments formed by the flocculation of the Fe^{3+} precipitates.

Comparison MBCR-SEP data from the OF and Black Ooze (BO) samples showed that BO samples had larger oxidisable, and smaller reducible fractions than the OF drain sediments. Furthermore, the OF and BO samples had very similar geochemistries. This suggests that the BOs were formed by reduction of the OFs. Reduction of the OF drain sediments likely occurred due to the formation of reducing conditions in the drains because of near stagnant water movement and available organic matter. The reducing conditions caused the reduction of Fe^{3+} and SO_4^{2-} to form the BO drain sediments.

Hicks and Fitzpatrick (2003) assertion that the drain sediments act as major sinks for heavy metals and metalloids mobilised from ASS was not supported by this research. The drain sediments were not found to be effective sinks for elements released from ASS, with the possible exception of Fe and As. Poor incorporation of elements lost from the ASS into the drain sediments was demonstrated using Fe normalised element values. The source of Fe to the drain sediments was likely the reductive dissolution of Fe oxides in the IAASS. The source of the As remained unresolved.

Hicks and Fitzpatrick (2003) also identified that reduction of the drain sediments may cause the release of heavy metals and metalloids, making the elements available to sediment-dwelling biota. This research showed that the reducible fraction (found using the MBCR-SEP) was greater than 10 % (of total mass) for Al, Co, Fe, Mn, Ni, Pb and Zn in the drain sediments. This indicates that a significant amount of Al, Co, Fe, Mn, Ni, Pb and Zn could be released during reduction of the drain sediments. However, mobilisation of the elements released from the reduced fraction is unlikely to occur because reduction of the drain sediments is expected to occur at neutral pH conditions. This is because the seawater movement into the drains during tidal exchange will neutralise acidity, and element mobilisation is limited above pH values of 4.5 (Calmano et al., 1992).

The research in Chapter 6 clarified the environmental risk posed by the drain sediments. Smith et al. (2003c) identified that the concentrations of metals and metalloids in the drain sediment may prevent re-occupation by benthic biota. Clarification of the issue identified by Smith et al. (2003c) was made by assessing the geochemistry of the drain sediments against the ANZECC and ARMCANZ (2000) sediment quality guidelines. The assessment with the ANZECC and ARMCANZ (2000) sediment quality guidelines also further demonstrated the limited capacity of the drain sediments to act as sinks for elements mobilised from ASS. Comparison with the ANZECC and ARMCANZ (2000) sediment quality guidelines indicated that the only elements that occurred in potentially toxic concentrations in more than 25 % of the drain sediment samples were

As and Ni. Nickel was identified as a potential problem because the MBCR-SEP data indicated that Ni was hosted largely by labile fraction. Hence, Ni had potential to become available to biota. The MBCR-SEP did not provide valid data on As hosting. However, the reducible fraction extraction of the MBCR-SEP was found to be of limited effectiveness with ASS samples in Chapter 5. Therefore, conclusions drawn from the MBCR-SEP results included considerable uncertainty.

Further clarification of the environmental risk posed by the drain sediments was made using the pH_F/pH_{FOx} values and MBCR-SEP data. The pH_F/pH_{FOx} values and MBCR-SEP results indicated that the greatest threat with regard to element mobilisation from the drain sediments was oxidation. This was because oxidation would not just cause the release of the elements in the oxidisable fraction, but also cause the release of the elements in the acid extractable fraction due to acidification during oxidation. Reduction was unlikely to cause a major release of elements because it was expected to occur at near neutral pH conditions. Finally, though the drain sediments were found to contain a large proportion of their elements in labile fractions, their low trace element content offset the risk posed by their reactivity.

8.1.4 Mouth Sediments

Chapter 6 established that seawater inundation of AASS in the Firewood-Magazine Creek was impacting on the geochemistry of sediments from the mouth of the creek. Hall (2002) identified an increase in the concentrations of Mn, Ni and Pb in mouth sediments of Firewood Creek during a three-month period of seawater inundation. The work of Hall (2002) was extended by examination of a third set of mouth sediments from Firewood Creek.

Comparison of element concentrations in Firewood Creek sediments with background sediments showed enrichment of As, Fe, Mn, Ni, Pb and Zn. This identified that elements mobilised by both oxidation and inundation of the ASS in the Firewood Creek catchment were released to the mouth sediment of Firewood Creek at rates greater than background creek systems.

Increased element concentrations from seawater inundation of AASS were identified by comparison of April 2004 sediments from Firewood Creek with sediments from July 2002. The period between July 2002 and April 2004 was significant because seawater inundation was more extensive during the period than before July 2002. Arsenic, Fe, Ni and Pb were enriched in the April 2004 sediments relative to the earlier sediments, indicating an increase in the release of As, Fe, Ni and Pb to the sediments since July 2002. The observed increase in As, Fe, Ni and Pb was likely because of the increased seawater inundation of the Firewood Creek catchment. The enrichment of Fe and Pb in the sediments was consistent with the elements that were identified as mobilised from IAASS in Chapter 4. It is therefore probable that seawater inundation has caused the

increased release of Fe and Pb from AASS in the Firewood Creek catchment. The source of As to the mouth sediments during this period remains unidentified, though IA (Chapter 4) did identify zones of As depletion in both the dry and wet ASS profiles. In spite of the increased element release, comparison with sediment quality guidelines (ANZECC and ARMCANZ, 2000) indicated that no ecologically significant contamination could be attributed to element mobilisation caused by seawater inundation of the Firewood Creek catchment.

8.1.5 Element Phytoavailability in IAASS

Element phytoavailability was investigated by Chapter 7. The phytoavailability of elements in IAASS was unknown and no work had previously been conducted on element phytoavailability in AASS, generally because the wide-scale vegetation death that accompanies AASS formation limits sampling opportunities. However, plants have colonised the IAASS of the Firewood-Magazine Creek system. Furthermore, wild, feral and domestic animals graze on vegetation in the inundated areas.

To assess whether elements were more phytoavailable in inundated than non-inundated soil, element concentrations extracted using ethylenediaminetetraacetic acid (EDTA) from reduced soil (field condition) samples and oxidised soil (dried) samples were compared. The results indicated that less Al, As, Co, Cu, Ni and Zn were extracted using EDTA from reduced soils than oxidised soils. This suggests that soil inundation limits the phytoavailability of Al, As, Co, Cu, Ni and Zn in East Trinity AASS.

The two dominant plant species colonising the IAASS at East Trinity were examined for their responses to the phytoavailable element pool. These plant species were the mangrove fern *Acrostichum speciosum* and the grass *Paspalum vaginatum*. Both species were found to be excluders of Al, As, Co, Cr, Cu, Pb and Zn. *Acrostichum speciosum* and *Paspalum vaginatum* indicated element bioavailability of Al, Co and Zn, and As, Co and Cu, respectively.

Samples of *Acrostichum speciosum* and *Paspalum vaginatum* growing in IAASS were compared with samples from background locations to identify if seawater inundation increased element concentrations in plants. Samples of *Acrostichum speciosum* from IAASS were found to have higher median concentrations of Co, Cr and Zn in their stems and As, Co, Cr and Cu in their roots than samples from background locations. In the *Paspalum vaginatum* samples, the IAASS group had larger Cu and Zn medians in both the stems and roots than the background group. This indicated that plants colonising areas of IAASS had increased concentrations of As, Co, Cr, Cu and Zn compared to plants from background locations.

The plant samples were assessed for element toxicity using the NRC (1980) guidelines for the maximum tolerable levels in animal diets. Comparison of stem concentrations with NRC (1980) guidelines identified Al in potentially toxic concentrations in samples of *Paspalum vaginatum*. However, the background samples of *Paspalum vaginatum* contained Al concentrations in higher concentrations than the IAASS samples. This indicates that *Paspalum vaginatum* may accumulate toxic concentration of Al naturally in coastal lowland environments.

The extraction of phytoavailable elements from AASS and IAASS samples from the dry and wet ASS profile (respectively) showed that the IAASS contained larger concentrations of phytoavailable elements. The likely reason for the larger phytoavailable element pool in the IAASS was the near neutral soil conditions, which are conducive to element sorption on charged surfaces. Acidic soil conditions, such as those in AASS, desorb elements from charged surfaces, causing a corresponding reduction in the size of the phytoavailable fraction.

8.1.6 Technical Advancements

The research presented in Chapter 5 identified that the GSC-SEP was more suitable than the MBCR-SEP for the determination of element hosting in ASS. A particular deficiency identified with the MBCR-SEP was the poor effectiveness of the reducible fraction extraction to dissolve Fe oxides in the ASS. This issue had previously been identified by Davidson et al. (2004), who suggest replacing the current reducible fraction extraction with one that used NH₄-oxalate. The poor effectiveness of the MBCR-SEP reducible extraction led to it reporting undersized reducible and oversized oxidisable element fractions. For this reason, the GSC-SEP is recommended over the MBCR-SEP for future investigations of element hosting in ASS.

The comparison of the biodegradable chelating agent Ethylenediamine-N,N'-disuccinic acid (EDDS) with EDTA and diethylenetriaminepentaacetic acid (DTPA) identified that EDDS extracted similar ($\pm 15\%$) Co, Ni and Zn concentration from ASS samples as EDTA, but more Al and Cu, and less Pb. Only the amount of Al extracted by the EDDS leach was within 15% of the element concentration in the DTPA leach. The data indicates that EDDS is a possible alternative to EDTA for the assessment of Co, Cu, Ni, Pb and Zn phytoavailability.

8.1.7 Answering the Research Question

The research showed that seawater inundation rehabilitated AASS by neutralising soil acidity. However, seawater inundation of AASS also caused a secondary release of elements. The elements most extensively mobilised from IAASS were Fe and Pb. The mechanism of the Fe and Pb mobilisation was reductive dissolution of oxidised Fe phases.

The elements mobilised from IAASS were an additional source of environmental risk. Iron lost from the IAASS formed Fe-rich drain sediments. The formation mechanism of drain sediments was Fe flocculation in egressing soil-water. The reduced soil-waters carried Fe²⁺ that transformed to Fe³⁺ in the oxidising conditions of the drains and precipitated as Fe oxyhydroxides, forming the OF drain sediments. In the drains, the OF undergoes reduction because of SO₄ and organic matter availability, forming BO. The partly reduced drain sediments were extremely sensitive to oxidation, but found to be poor element sinks, except for Fe and As.

The mouth sediments of Firewood Creek displayed an increase in Fe and Pb during a period of increased seawater inundation of the Firewood Creek catchment (between 2002 and 2004). The increase in the elements identified as being mobilised during AASS inundation indicated that some of the mobilised elements report in the mouth sediment, but also that a portion of the mobilised elements were released to Trinity Inlet.

Elements were less phytoavailable in IAASS in their partly reduced “field” condition than after having been dried (oxidised). Plants growing in the IAASS were found to be accumulating elements beyond background. Of particular concern were the toxic concentrations of Al in samples of *Paspalum vaginatum*, though this was not necessarily due to seawater inundation of AASS.

8.2 Limitations and Future Research

A major limitation of the project was that it examined only two ASS profiles. Although these ASS profiles were carefully selected to represent inundated and non-inundated conditions in the Firewood Creek catchment, they may not be representative of the wider geochemical system of East Trinity. A follow up soil survey that examines a larger population of ASS profiles would assist greatly in confirming the findings of this project.

Element hosting in the drain sediments was investigated with the ineffective MBCR-SEP. The drain sediments are environmentally important materials in the Firewood Creek catchment because they can rapidly acidify and release elements in potentially toxic concentrations. In particular, the hosting of As requires clarification. Arsenic and V were identified in toxic concentrations in many of the drain sediment samples. The SEPs solutions failed QA for As and V and therefore did not identify how these two elements were hosted. Element hosting in the drain sediments requires re-investigation using an effective SEP (e.g. the GSC-SEP) to clarify the risk posed by As and V.

8.3 Implications of the Research

Seawater inundation was found to be remediating AASS on East Trinity. This was demonstrated by the near neutral soil pH values of IAASS. However, a number of concerns were identified with seawater inundation of AASS, which were:

- Iron and Pb were mobilised during AASS inundation. The mobilised Fe contributed to the formation of chemical sediments in the drains servicing areas of IAASS. Furthermore, Fe and Pb concentrations increased in mouth sediments of Firewood Creek during a period of more frequent seawater inundation of the Firewood Creek catchment (between July 2002 and April 2004).
- The drain sediments were shown to be able to rapidly oxidise and acidify. This is a potential source of rapid acidification and element release in the Firewood Creek catchment. The drain sediments form by the flocculation of Fe in egressing soil-waters. Seawater inundation may be increasing the occurrence of the drain sediments because of: 1) the generation of reducing conditions in the AASS leading to increased solubility of Fe (i.e. as Fe²⁺); and 2) the increased volume of waters moving through the AASS. The reactivity of the drain sediments suggests that they have the potential to acidify on oxidation, which may occur during drying. However, with the exception of some samples reporting environmentally significant As, Cu and Ni, the drain sediments generally contained low concentrations of potentially toxic elements.
- Plants growing in the IAASS were found to contain higher element concentrations than background samples. This suggests that elements are more phytoavailable in IAASS than in un-impacted areas.
- The grass species *Paspalum vaginatum* collected from East Trinity contained Al concentrations toxic to many grazing animals. The toxic Al concentrations in the stems of *Paspalum vaginatum* did not appear to be related to seawater inundation of AASS, but they nevertheless poses a risk to animals being grazed on the property or eating the grass.

8.4 Recommendations

Based on the findings of the project, it is recommended that controlled seawater inundation of Firewood Creek, similar to that occurring in Hills Creek, be started as soon as possible. Inundating the AASS of the Firewood Creek catchment to a constant elevation will continue the rehabilitation of the AASS, as well as mitigate the risk of oxidation to the drain sediments.

The mouth sediments of Firewood Creek showed increased concentrations of elements mobilised during seawater inundation of AASS. Monitoring of the sediments of Firewood Creek should be conducted to assess the changes in element loads being discharged from the Firewood Creek catchment. Organisms should also be investigated for increased element loads.

Plants growing in the IAASS contained element concentrations (Al) greater than background plants. For this reason, the monitoring of plants colonising the IAASS is recommended.

Samples of the grass *Paspalum vaginatum* from East Trinity were found to have concentrations of Al in their stems that are toxic to grazing animals. Until the risk posed by the Al in the grasses can be quantified, domestic animals should be excluded from the areas of IAASS and grazing wildlife monitored for symptoms of Al toxicity.