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The chemical composition and extraction behaviour of Ranger RP1 sediments

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THE CHEMICAL COMPOSITION AND EXTRACTION BEHAVIOUR OF RANGER RP1 SEDIMENTS

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Abstract

Keywords: Ranger, RP1, sediments, uranium, lead, sulfide, manganese, adsorption, desorption, extraction, mobilisation potential

Ranger Retention Pond 1 (RP1) was excavated as part of mine construction in 1980. Its primary purpose is as a sediment trap, to prevent erosion products from mine rock used in tailings dam construction, and other purposes, leading to unacceptable increases in the suspended load of Coonjimba Creek, and ultimately Magela Creek.

There have been recent observations of increased uranium concentration ([U]) in RP1 water, and the discovery of elevated [U] in RP1 sediments. Therefore, water and hydrochloric acid (HCl) extractions have been performed on sediments acquired from 10 cm cores to asess the likelihood of mobilisation of U from these sediments. If desorption is facile, this may lead to unacceptable increases in [U] in RP1 and hence Magela Creek into which RP1 flows unimpeded during the Wet Season.

Results from three cores lead to the tentative conclusion that uranium, and other relevant chemical constituents, are closely identified with the fine fraction of sediments. These are presumed to primarily constitute alluvium transported from the catchment. Hence the chemical contents of the sediments, at least to 10 cm depth, are probably mostly catchment derived, and only weakly related to chemical processes in the pond itself. An exception to this is the formation of sulfidic mineralisation, which is probably caused by *in situ* reduction of sulfate (SO_4^{2-}) by sulfate-reducing bacteria.

Extractions over 11 days with 1M HCl resulted in significant desorption of Mg, Mn, Pb and U (20%-50%), with mobilisation efficiency inversely dependent on the availability of binding species within the sediment. For water extractions, mobilisation of heavy metals was minimal, even where the pH dropped below 4.0 (presumably due to partial oxidation of sulfide contents). Only a small proportion of the sulfide contents was mobilised, even with 1M HCl. This may explain the the observed retardation in sediment-derived SO_4^{2-} at the onset of the Wet Season.

With the exception of Mg, SO_4^{2-} and possibly some Mn, there is no evidence for the seasonal remobilisation of RP1 sediment constituents under normal conditions. Some U may have been remobilised at the onset of the second Wet Season after abnormal inputs. The attainment of extreme natural acidification events (pH<3) is unlikely in RP1, even if the pond substantially dries, because of the slow and incomplete oxidation of sulfidic components of the sediments, and the significant buffering of pond water at near-neutral pH.

Introduction

Background

RP1 is an excavated impoundment dammed by a weir in the catchment of Coonjimba Creek, downstream from the Ranger tailings dam. The median surface area of RP1 is ~160,000 m^2 although when overflowing, its area is increased by about 50%. The maximum volume of the pond is about 440,000 m^3. RP1 was designed as a sediment trap and was constructed at the same time as the mine (circa 1980). Run-of-mine rock (waste rock) is used extensively for construction in the catchment of RP1, notably for the tailings dam. Much of this rock contains low but measurable amounts of heavy metals, notably uranium and lead. Ranger waste rock typically weathers quickly (exposed schistose rock substantially degrades in less than 10 years-Evans et al. 1995). The dispersal of these erosion products mandates the existence of a settlement pond downstream from weathering sites.

Until about 1986 the water quality of RP1, as determined by electrical conductivity (EC), pH and heavy metal values, was very good, with EC typically below 50 µS/cm and mine-related heavy metal concentrations near detection limits (Ranger Uranium Mines 2000). EC values gradually increased from 1986 to 1990. Since 1990, EC values have shown no long-term upward trend, although a very pronounced annual cycle is evident. The mean value for EC since 1988 is 200 µS/cm (median 194 µS/cm), with a standard deviation of 72 µS/cm (n=653). The source of the elevated conductivity in RP1 is almost entirely $MgSO_4$, which derives mainly from the weathering of magnesite, chlorite and minor sulfides in run-of-mine rock. The value of pH also shows a very evident annual cycle, with this indicator varying predictably between ~6.5 in the mid-Wet Season and 7.5-8.0 immediately before the onset of Wet Season rains. The latter values are probably related to characteristic episodes of SO_4^{2-} reduction during the Dry Season. There has been no long-term temporal trend in pH values in RP1.

Until the beginning of 1999, [U] too was low. For the period June 1980 to December 1998, mean [U] was 1.2 µg/L (median 0.9 µg/L) with a standard deviation of 1.4 µg/L (n=412). During the 1998-99 and 1999-2000 Wet Seasons [U] increased very markedly, as depicted in Figure 1. This increase is very probably identified with the importation of mineralised (but below ore-grade) rock from Ranger Pit 3 to the catchment of RP1. This practice was well established by 1998.

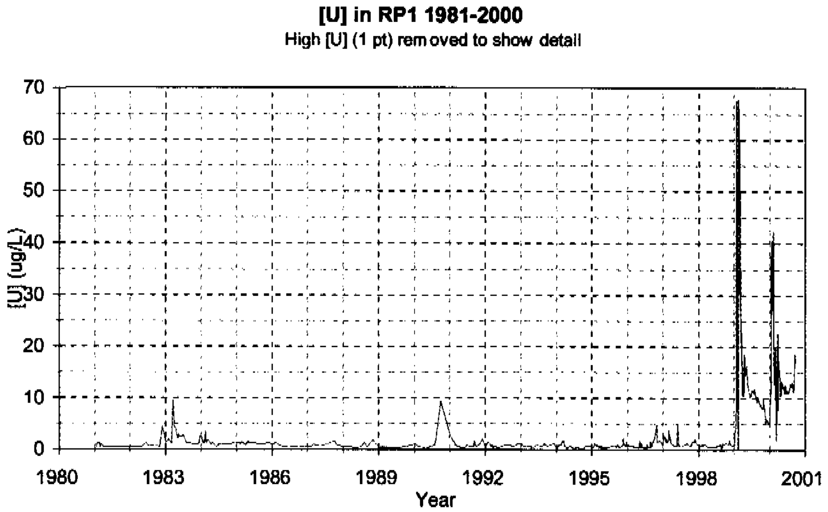

Figure 1. [U] in RP1 from January 1981 to September 2000 (data source footnote 1)

As part of its assessment and remediation program, ERA collected a number of RP1 sediment grab samples in September 1999. These revealed significantly enhanced and fairly uniform U contents in the range ~50-60 mg/kg. As far as we have been able to determine, no U-contents data have previously been reported for RP1 sediments. For a nominal surface area for the pond of 160,000 m², these values translate to ~500 kg of uranium for the top 5 cm of sediment. The contribution to this total from 1998-99 runoff was not estimated at that time.

To assess the potential contribution of catchment-related U to sediments, a calculation of the rate of loss of U from the water column of RP1 during the 1999 Dry Season (when RP1 is an isolated pond) was made. This loss is likely to correspond to adsorption to sediment. During this period, ~4 kg of U was calculated to be lost from the water column, as shown in Figure 2.

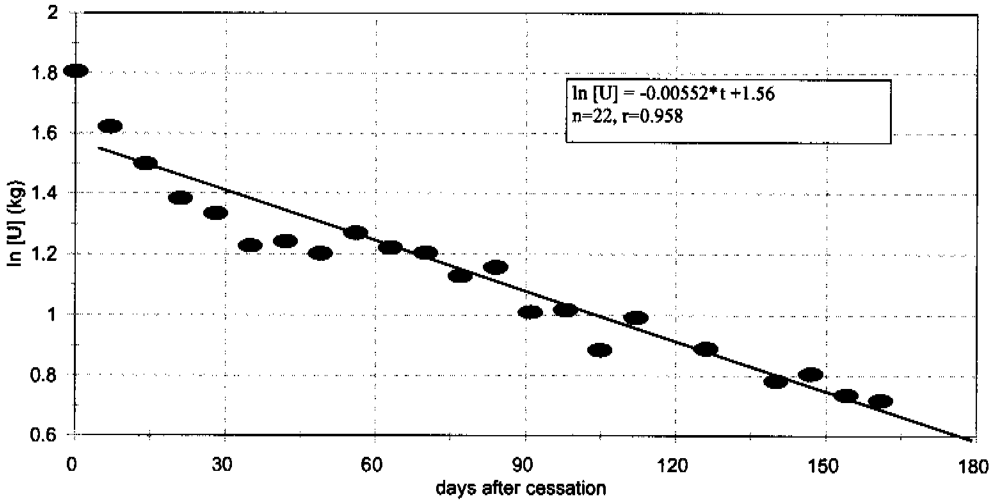

Figure 2. Loss of uranium from the RP1 water column, May-October 1999 (data from RUM 2000)

Extrapolating this value to a full year, the contribution of U to RP1 sediments from the 1998-99 catchment inputs would amount to ~8 kg, or about 2% of the total burden. This assumes that the rate of adsorption, ~17%/month, is the same during the Wet Season (when adsorption cannot be measured independently of U inflow and outflow), as during the time when it can be measured directly. It follows that most of the U contents of RP1 sediments predate the 1998-99 'catchment incident'. Whether this U burden can be mobilised under conditions that may occur naturally is the subject of this report.

Recent investigations on behalf of the Ranger Mine

A recent report by Batterham and Overall (2000), prepared by EWL Sciences Pty Ltd for the Ranger Mine is a detailed investigation into the sources and mechanisms of uranium flux in RP1 during the period 1999-2000. It attempts to explain elevated [U] observed during the 1998-99 and 1999-2000 Wet Seasons. The report proposes three sources of solutes (including U) for RP1:

- catchment inputs;
- dissolution of evaporites associated with readily soluble U, mostly slightly acidic $MgSO_4$ derived from oxidation of seasonally exposed sediments; and
- remobilisation from benthic sediments.

The EWLS report apparently favours the second option as the most important. According to this mechanism, uranium from catchment sources during the 1998-99 Wet Season, and sulfide minerals, deposited in the shallow margins of RP1. As RP1 retreated during the 1999 Dry Season, these sediments were exposed, the sulfide minerals oxidised yielding $MgSO_4$ (with associated acid generation) and mobilised uranium. With the onset of the 1999-2000 Wet Season, these soluble compounds washed into the pond, with a consequent increase in [U]. A subsidiary role for additional catchment inputs is acknowledged. However, the temporal pattern and values of [U] during 1999-2000 do not support the favoured mechanism. There are three main inconsistencies:

1. If the principal source of U in RP1 is washoff from exposed margins as the pond fills, maximum [U] should be observed before overflow. In 2000, $[U]_{max}$ was observed on 7 February. This was about 7 weeks after overflow commenced, by which time about 1.3 pond volumes had spilled over the weir.
2. At the end of the 1998-99 Wet Season, [U] when overflow ceased (and RP1 became an isolated pond) was ~16 µg/L (RUM 2000). An additional burden of U was adsorbed to the sediments which, calculated from extrapolated adsorption data above could contribute the equivalent of an additional ~10 µg/L to a full pond, assuming 100% desorption. Therefore, unless the adsorption rate of U to sediments was much greater during the Wet Season (when it cannot be measured) than during the Dry Season, a supposition for which there is no evidence, $[U]_{max}$ is only about 60% of the $[U]_{max}$ observed.
3. According to data incorporated in the EWLS report, even if all the exposed margins had the lowest pH observed at any margin site it is doubtful whether sufficient U would be mobilised to account for the measured flux.

Conversely, RP1SED (a sediment trap upstream from the RP1 inlet) was overflowing each time it was observed (four times) between 17 December 1999 and 30 March 2000, with flow rates estimated to be 10-30 L/sec. The first date was before RP1 overflowed. Measured [U] in RP1SED was stated to vary between 300-726 µg/L (Batterham & Overall, 2000). If the assumption is made that RP1SED was overflowing at 10 L/sec for the ~100 day period over which observations were made, and using the median [U] concentration in RP1SED (~500 µg/L), the total mass of U entering RP1 from this source is ~43 kg, approximately equal to the estimated U flux during 1999-2000.

Experimental approach

The major identified mechanism for metals desorption from RP1 sediments is acid generation from the oxidation of sulfide minerals within the sediments. The potential severity of any acidification event cannot be determined with certainty. The lowest pH value ever recorded in RP1 was 4.3 (Ranger Uranium Mines, 2000) despite strong evidence that sulfidic sediments partly oxidise under certain conditions (ERA, 1991). The observed low-pH event occurred in February 1991 during pond filling, after RP1 was almost drained (during the 1990 Dry Season) for mine-related purposes. Any significant acidification event is likely to be associated with RP1 drying out, or almost so. This is because the pond is moderately buffered near pH 7 under normal circumstances. In spite of the presumption that severe acidification was unlikely in RP1, a conservative approach demands that extraction conditions more acidic than likely to occur without intervention should be used.

The decision to use 1M HCl as extractant was based on the procedure outlined in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality(ANZECC 1999) for assessing whether the heavy metal contents of sediments are likely to induce a toxic response. Extraction with 1M HCl is the recommended procedure for establishing a reference database for sediment metal concentrations, supplanting the previous criterion of 'total' metal contents. In addition, it is the extractant used for determining the ratio of acid-volatile sulfides to simultaneously extractable metals. When the ratio is greater than one, the sediments are regarded as containing insufficient mobilisable heavy metals to constitute a significant toxic hazard. Although regarded as dilute acid, the use of 1M HCl extraction as the nominal criterion for biological hazard from metals is conservative in that it probably overestimates true bioavailability in most cases.

In addition to acid extractions, control experiments were performed using high-purity water as the extractant. In some cases the pH of water extracts dropped below 4.0, giving some insight into possible metals desorption under conditions that have been observed in RP1.

Experimental

Sample acquisition

Three 10 cm cores were obtained using an Eijkelkamp stainless steel soil-column cylinder auger. Site location was established using a Garmin E-trex Summit global positioning system (GPS). The coring sites were near the southern (inlet) end of the pond. GPS locations and some physical properties of the sediments are recorded in Table 1. The selection of sites was restricted to water sufficiently shallow (approximately 1 m) to permit use of the auger. However, two cores with a fine texture (by visual inspection) and one with a sandy texture were deliberately chosen. The collection cylinder was sealed immediately after extraction of the core to prevent the intrusion of oxygen. In the laboratory, the core was divided into three intervals (0-3.3 cm; 3.3-6.7 cm and 6.7-10 cm) and vacuum dried to constant mass at 60°C. Subsequent experiments showed that RP1 sediments are not very air sensitive. Similar observations were made by Willett et al (1993b) on the oxidation of sulfidic sediments from the Magela floodplain. This may mean that no special precautions are needed to prevent aerial oxidation of cores before return to the laboratory. However, the simple measures adopted during sampling for this project did not impose an unreasonable logistical burden.

Core	1	2	3
Location coordinates (UTM zone 53)	0272396; 8597650	0272382; 8597698	0272296; 8597972
Dry/wet mass	-	0.63	0.81
<63 µm (T; M; B)#	68%; 60%; 64%	74%; 81%; 45%	16%; 10%; 11%

#: T, M, B refer to the top, middle & bottom 3.3 cm intervals

Table 1. Selected properties of sediment cores acquired from RP1

Duplicate samples of approximately 5.0 g were accurately weighed for each interval of each core for both water and 1M HCl extractions. This yielded:

3 cores x 3 intervals x 2 treatments x 2 replicates = 36 extractions

In addition, duplicate unextracted 5 g samples for each interval (18 samples) were reserved for analysis.

Experimental methods

Sediments samples were weighed into 60 mL polyethylene screw-topped bottles that had been previously soaked in 10% v/v HNO_3 and thoroughly rinsed with Super-Q water. To each bottle was added 50 mL of either Millipore Super-Q water or 1M HCl prepared by dilution of

36% BDH Aristar HCl with Super-Q water. The suspensions were agitated using a horizontal platform connected to an electric motor. The platform rocked back and forth at about 100 cycles per minute. Aliquots (1 mL) of each sample were removed using a plunger-driven pipette at intervals of approximately 0, 1, 3, 20, 50, 100, 180 and 240 hours, diluted to 50 mL with Super-Q water and acidified to 1% HNO_3 using BDH Aristar acid. In the case of water extractions, the pH of the undiluted extract was measured using an Orion model 720A pH meter with an Orion Ross combination electrode. The meter was calibrated using pH 4.01 (phthalate) and 6.87 (phosphate) buffers.

Samples were weighed using a Mettler PJ3000 (2 decimal place) or a Mettler AT261 (5 decimal place) balance as appropriate. Wet seiving was performed using a Labtechnics stainless steel 63 μm seive. An accurately weighed sample of approximately 10 g was seived using a constant stream of tap water, with manual comminution of aggregates. The residue in the seive was weighed after air-drying in direct sun to constant mass, and the <63 μm fraction calculated by difference.

All chemical analyses were performed by ChemNorth Pty Ltd (Berrimah, NT). All elements were determined by either inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emission spectrometry (ICP-OES) with the exception of carbon. This was determined by loss on ignition at 550°C after prior drying to 250°C. All sediments samples were dried to 110°C before ICP analysis, and reported element contents refer to samples dried in this way.

A number of aqueous and sediment reference samples were included in each batch for quality control purposes. Results for water samples were very good. For sediment samples, analyses for minor elements were good. Results for major sediment constituents were satisfactory but low in all cases, compared with the accepted values. This probably reflects incomplete mobilisation of matrix contents of Al, Fe and a lesser extent, Mg and Mn using the $HNO_3/HClO_4$ acid mixture (as opposed, for example to HNO_3/HF). In view of a complete digestion not being attempted, and the total contents of matrix elements being of relatively minor importance, sediment recoveries are considered acceptable. Complete data for reference samples are reported in Appendix 3.

Results and Discussion

Sediment analyses and texture

Indicator contents for unextracted, water-extracted and HCl-extracted sediments are reported in Appendix 1. Location and sediment texture are reported in Table 1. Cores 1 and 2 were acquired from near the inlet of RP1, about 50 m from each other. Core 3 was extracted about 300 m from Core 2, the three cores being taken along an approximately SE→NW transect. Core 1 is texturally homogeneous, within the uncertainty of measurement. This suggests that the predominantly fine-grained sediments at this site were derived from the catchment to at least 10 cm. In many respects the sediments from core 2 resemble those of core 1, except the texture of the bottom interval (6.7-10 cm) is coarser, suggesting that less than 10 cm of sediment may have been deposited at this site since RP1 was commissioned in 1980. Core 3 has a texture which is predominantly sandy, and homogeneous to 10 cm within the precision of measurement. This site has evidently not received significant quantities of fine sediments from the catchment, despite its relatively close proximity to the inlet.

Indicator contents

As shown in Figure 3, all measured indicators were significantly correlated with the <63 μm fraction (although Fe was weakly so and Mg and S may follow a power function). This fraction can probably be identified mainly with sediment imported from the catchment. It is likely that the elements measured, with the exceptions of S and perhaps Mg, were mainly adsorbed to the sediment before import. Although the possibility of adsorption and deposition in RP1 cannot be discounted, the high degree of sediment enrichment, and the ratios of indicator contents compared with water-column concentrations, make the former mechanism more likely.

The S contents of these cores can be used to calculate a theoretical pH that may be achieved is the entire sulfide burden were oxidised according to the following equation.

$$2S_2^{2-} + 2H_2O + 7O_2 \Leftrightarrow 4SO_4^{2-} + 4H^+$$

The mean value for [S] from the three cores is 1.6 g/kg. This compares with 0.7 g/kg for the ERA (1991) study, a difference which probably reflects the additional sulfide load deposited in RP1 over the past decade. Complete oxidation of this mass of S to a 10 cm depth over the 16 ha of RP1 'permanently' inundated would yield a pH of ~2.6 in a full (400 000m^3) pond.

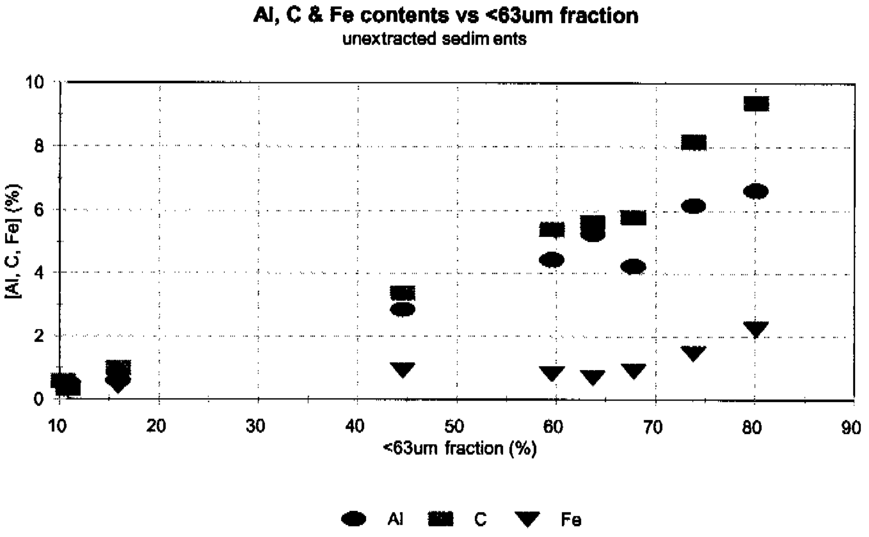

Figure 3a. Aluminium, carbon & iron contents as a function of <63 μm fraction

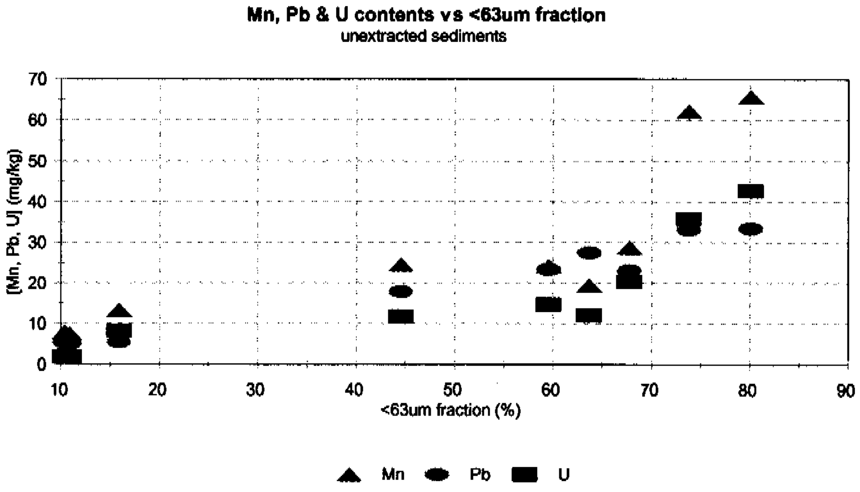

Figure 3b. Manganese, lead & uranium contents as a function of <63 μm fraction

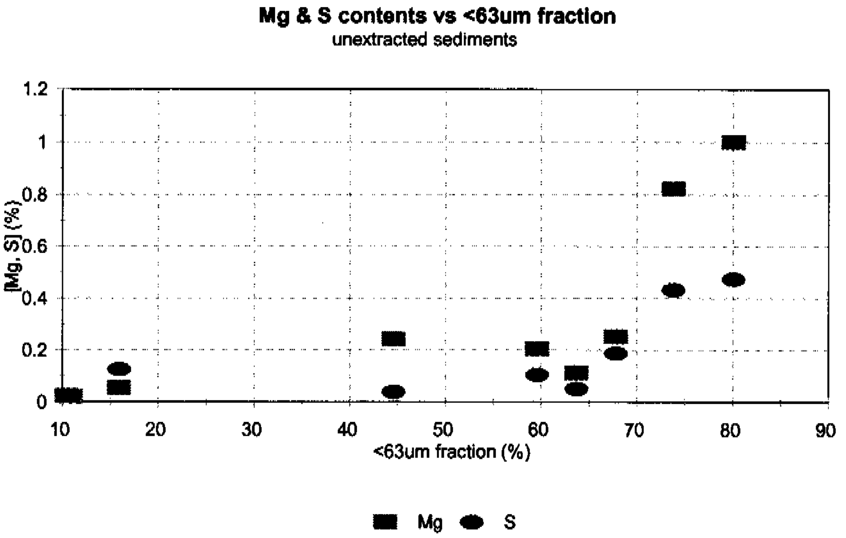

Figure 3c. Magnesium & sulfur contents as a function of <63 μm fraction

Mean extraction efficiencies are recorded in Table 2. The values calculated by difference from sediment analyses are not as precise as values calculated by measurements of indicators directly in extraction supernatants (reported later). There are a number of general sources of imprecision expected for sediment analyses, such as heterogeneity in sediment subsamples, small differences in retained moisture after drying to 110°C and slight inconsistencies in digestion procedures.

Nevertheless, it is evident that, while water is a very poor extractant for most indicators (mean extraction near zero), 1M HCl extracts a significant fraction of all metallic indicators. Neither carbon or sulfur is extracted well by HCl. The low lability of sulfur, confirmed by aqueous concentrations from direct extraction, strongly implies that most of the sulfide contents of the sediments is not 'acid volatile'. This may be due to extensive recrystallisation of sulfide minerals (previously identified as 'pyrite'-ERA 1991) rendering them less susceptible to acid attack. The relative insensitivity of RP1 sediments to oxidation and acid dissolution is the probable explanation for the observation that remobilisation of SO_4^{2-} at the onset of the Wet Season is slow and incomplete. Indeed, permanently submerged sediments may contribute a negligible proportion of mobilised solutes.

The carbon contents of sediments correlates well with a number of important constituents, particularly sulfur and uranium. In the case of sulfur, the presence of suitable organic substrates is necessary as electron donors in the enzymatic reduction of SO_4^{2-} to S^{2-} by sulfate-reducing bacteria. The coincidence of C and S in sediments is therefore not surprising. For carbon, other studies near the Ranger mine have implied or demonstrated a relationship between uranium binding and the presence of natural organic matter (NOM) in sediments (Klessa et al. 1997; leGras & Klessa 1997). The results presented here provide further evidence that carbon compounds are important complexing agents for uranium. Organic uranium complexes do not in general have very large binding constants (Perron 1979), an expectation previously demonstrated for RP1 constructed wetland filter sediments (Klessa et al. 1997).

A good correlation was found between carbon contents and aluminium contents of sediments. The rapid weathering rate of Ranger run-of-mine rock, particularly schistose facies, has been well documented (Milnes 1988; Evans et al. 1995). These weathering schemes usually portray the terminal mineral phase of muscovite/chlorite degradation as kaolinite. However, in acidic, strongly leaching environments, typically tropical areas with rainfall >1500 mm/year or zones of inundation, an additional stage of desilication resulting in aluminium hydroxide (gibbsite) can occur (McBride 1994). Extraction profiles of Al, Fe and Mn with 1M HCl (discussed in detail later) are qualitatively similar, suggesting that the 1M HCl-labile fraction of Al (~5% of total contents) is probably gibbsite or a related mineral. The correlation between C and Al may then imply that fine particulates containing Al, including kaolinite and gibbsite, are the most important adsorbants of NOM in the sediments of RP1, and hence the most important loci of relevant complexation reactions. Regression graphs of carbon with aluminium, sulfur and uranium are presented in Figure 4.

The relationship between extraction behaviour and contents of potential binding species

As might be expected, the efficiency of remobilisation of metals by extraction with 1M HCl for 11 days has a inverse relationship with the contents of potential binding species. For example, for Mn, Pb and U, the percent extraction bears a negative correlation with carbon contents, as shown in Figure 5. The strong relationship between uranium and carbon may imply that NOM is an important binding species for U. This conclusion is supported by other evidence, as discussed previously, and is the expected finding if an equilibrium partitioning (between the aqueous and sediment phase) model for uranium is proposed.

Conversely, Pb mobilisation shows a very weak dependence on carbon contents, lending support to the idea that NOM is not an important binding substrate for this metal. Organic complexes of Pb typically have small stability constants (Perron 1979. Lead extraction shows a better inverse relationship with iron contents, which may mean that Pb is predominantly surface-bound to ferric oxyhydroxide particles.

In apparent contradiction to this was the inverse relationship between Mn extraction and C contents. Mn is known to form very weak complexes with organic ligands (Perron 1979), and under strongly acidic conditions no binding would be expected. A better explanation for Mn

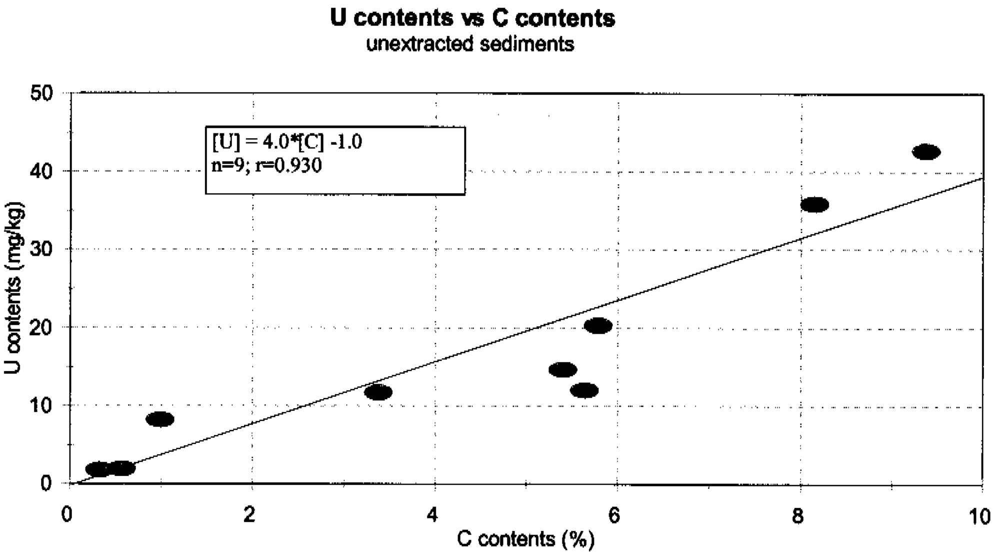

Figure 4a. Regression of U contents with C contents of RP1 sediments

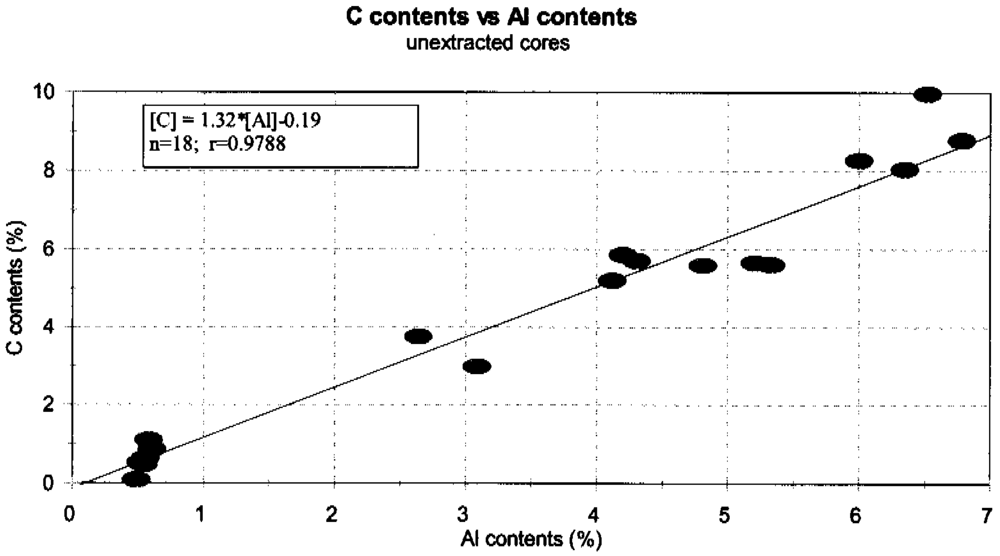

Figure 4b. Regression of C contents with Al contents of RP1 sediments

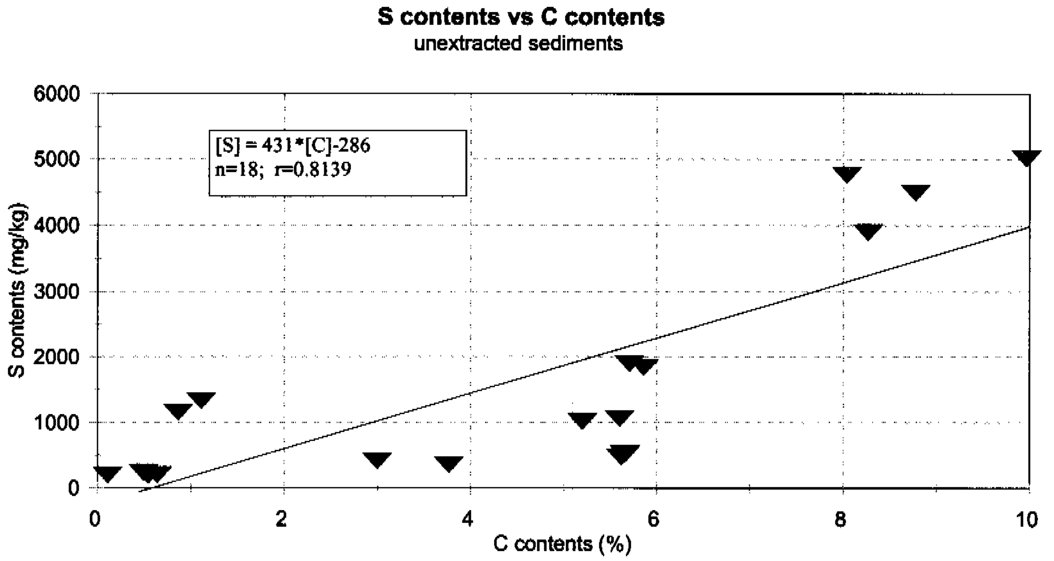

Figure 4c. Regression of S contents with C contents of RP1 sediments

Sample	Extractant	Al	C	Fe	Mg	Mn	Pb	S	U
Core 1 top	Water	6.7	14	3.0	7.0	5.1	-2.9	14	-0.7
Core 1 mid	Water	19	8.6	15	14	13	10.5	23	2.7
Core 1 bottom	Water	-22	-7.8	-12	-15	-12	-1.0	3.2	-2.5
Core 1 top	1M HCl	-7.6	-10.2	22	26	31	32	1.5	41
Core 1 mid	1M HCl	3.3	-13.3	43	28	28	29	16	53
Core 1 bottom	1M HCl	7.3	-2.4	19	32	30	39	13	59
Core 2 top	Water	26	6.9	-66	16	17	2.0	-2.6	-11.1
Core 2 mid	Water	15	4.4	-16	16	14	11.3	9.4	7.8
Core 2 bottom	Water	-15	0.4	-9.1	12	-4.2	-2.4	3.9	7.2
Core 2 top	1M HCl	12	-19	12	24	30	29	-10.2	27
Core 2 mid	1M HCl	29	-1.8	7.5	27	30	39	6.5	48
Core 2 bottom	1M HCl	12	-54	22	41	31	44	22	65
Core 3 top	Water	-3.4	65	9.7	27	24	22	25	17
Core 3 mid	Water	36	39	21	49	47	49	48	49
Core 3 bottom	Water	45	28	28	56	54	32	49	30
Core 3 top	1M HCl	-0.3	-13	7.0	52	53	37	9.8	48
Core 3 mid	1M HCl	32	-17	14	61	59	51	26	67
Core 3 bottom	1M HCl	34	5.3	22	57	60	52	31	67

Table 2. % extraction from sediments (mean of replicates) for water and 1M HCl-calculated from differences in indicator contents of unextracted and extracted sediments

behaviour is the occlusion of MnOx particulates, the presumed major repository for Mn in RP1 sediments, by NOM. If this were the case, then Mn-oxide dissolution would be controlled by diffusion of reactants across the organic sheath, and possibly by removal of organic films from oxide particles by acid hydrolysis. Occlusion of U by organic films may also play a part in the extraction relationship of this metal with carbon contents.

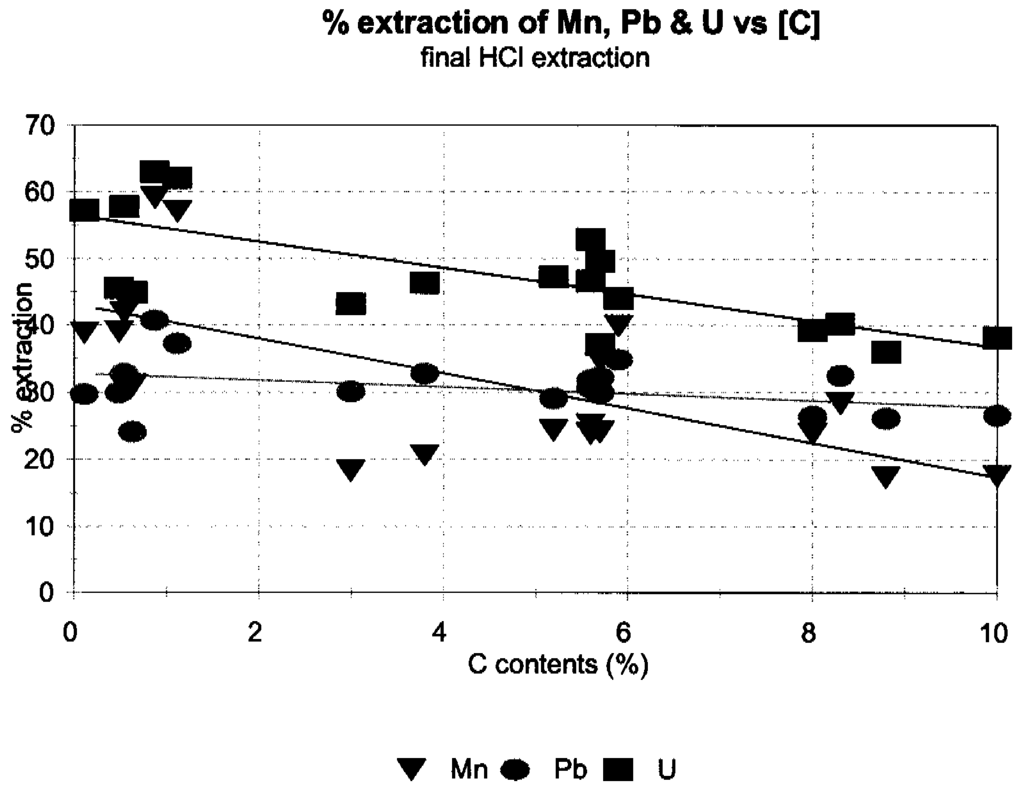

Figure 5. Relationship between metals extraction and the carbon contents of RP1 sediments

An estimate of uranium mobilisation under low-pH conditions

As remarked above, water is not an efficient medium for extracting measured species from RP1 sediments. This is despite the observation that pH dropped significantly in supernatant water for all cores during the approximately 11 days of extraction. The acid-generating properties of the three cores are depicted in Figure 7. This behaviour can be attributed to partial oxidation of sulfide minerals in the sediment. As noted above, the slow rate of oxidation (as measured both by diminution in sulfur contents of sediments and the appearance of SO_4^{2-} in supernatant) is consistent with the observations of Willett et al. (1993b). For Core 2, final pH was approximately 4.0, but this did not result in appreciable mobilisation of relevant species.

An attempt was made to model U mobilisation at pH values in the range 4.0-6.5, to estimate possible [U] in RP1 should an acidification event occur. This was done by fitting a prediction based on literature values of acid dissociation constants for humic acids (Morel 1983) and uranium-humic stability constants (Geisy et al. 1986) with observed [U] as a function of pH. The model prediction and observed values for water extracts is shown in Figure 6.

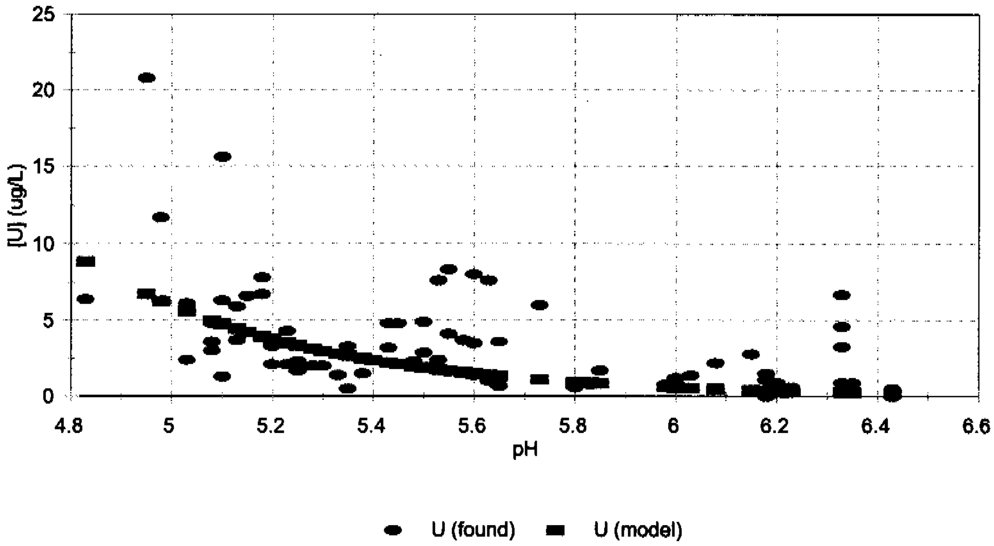

Figure 6. Predicted and observed [U] as a function of pH in RP1

The fit is satisfactory, considering the polydisperse nature of humic materials. The model supports the hypothesis that organic ligands are the most important complexing agents for U in RP1 sediments. Using this model and a pH of 2.6 calculated above, [U] should be ~1.5 mg/L. Based on the U and S contents of the three cores extracted, this situation could theoretically occur if 25% of the entrained sulfides oxidised (in the absence of buffering) in a pond 25% full (~100 000m^3). This is based on an estimate of 1M HCl-labile U in pond sediments of ~150 kg (which would also be desorbed, according to the model, at pH 2.6) and a total sediment S contents of 36 tonnes. This analysis is broadly consistent with the relationship found by Batterham and Overall (2000) between pH and U desorption.

Indicator concentrations in water and 1M HCl supernatants

Table 2 (above) records the percent extraction of indicators by comparing species contents of sediments before and after extraction. An alternative approach is to compare aqueous concentrations at the completion of extraction with original sediment contents. These results are presented in Table 3. In general these results are more consistent, but otherwise present a similar picture of extraction behaviour.

An interesting feature of the extraction experiment is the finding that water mobilises sulfur to a greater extent than 1M HCl. This behaviour is consistent between the cores and supported by both the sediment-depletion and direct measurement approaches to quantifying extraction.

Sample	Extractant	Al	C	Fe	Mg	Mn	Pb	S	U
Core 1 top	Water	0.01	-	0.23	6.9	3.4	0.46	13	0.58
Core 1 mid	Water	0.00	-	0.25	6.1	2.1	0.71	14	1.1
Core 1 bottom	Water	0.01	-	0.26	11.1	2.8	1.1	17	1.7
Core 1 top	1M HCl	4.9	-	39	35	37	33	3.1	40
Core 1 mid	1M HCl	5.1	-	57	28	25	30	4.0	47
Core 1 bottom	1M HCl	4.6	-	24	31	24	30	1.7	51

Sample	Extractant	Al	C	Fe	Mg	Mn	Pb	S	U
Core 2 top	Water	0.01	-	0.14	2.1	1.4	0.00	6.6	0.08
Core 2 mid	Water	0.00	-	0.09	3.0	2.4	0.08	11.6	0.11
Core 2 bottom	Water	0.02	-	0.19	0.0	0.68	0.08	13.2	0.21
Core 2 top	1M HCl	3.4	-	23	20	26	29	2.9	40
Core 2 mid	1M HCl	3.5	-	21	14	18	26	2.6	37
Core 2 bottom	1M HCl	8.5	-	18	13	20	31	2.2	45
Core 3 top	Water	0.10	-	0.16	18	5.8	0.00	18	0.17
Core 3 mid	Water	0.15	-	0.41	0.0	3.4	0.27	38	0.51
Core 3 bottom	Water	0.54	-	0.20	0.0	3.8	0.00	34	0.24
Core 3 top	1M HCl	10.2	-	12	54	58	39	4.7	63
Core 3 mid	1M HCl	10.5	-	15	39	38	29	15.0	47
Core 3 bottom	1M HCl	8.5	-	16	23	40	31	16.9	57

Table 3. % extraction from sediments (mean of replicates) for water and 1M HCl-calculated from aqueous indicator concentrations at the completion of extraction and unextracted sediment contents

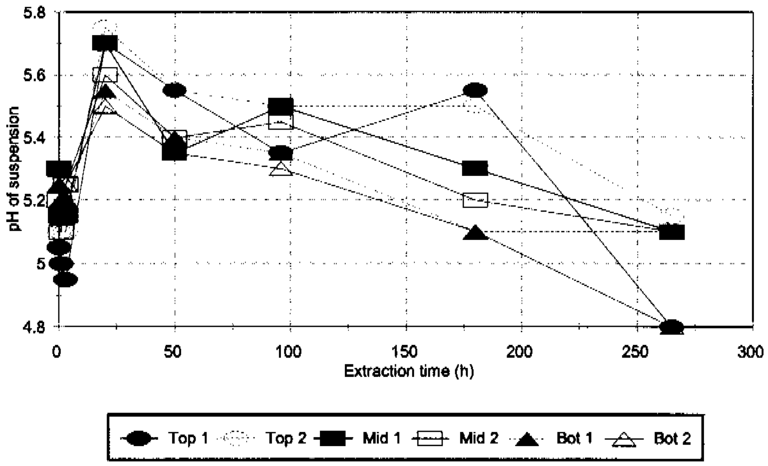

Figure 7a. pH of Core 1 water supernatants as a function of time

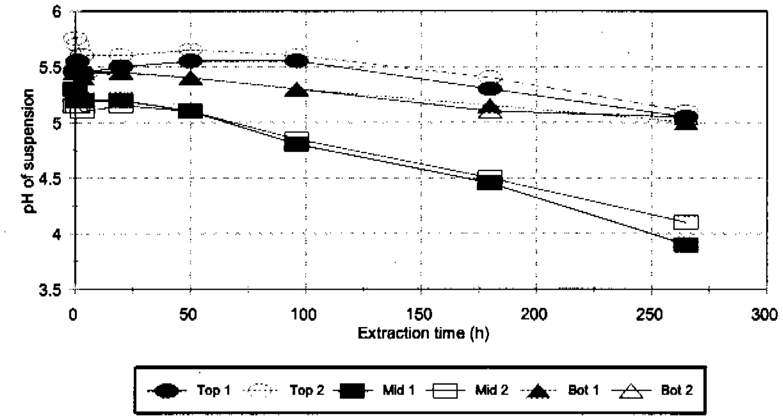

Figure 7b. pH of Core 2 water supernatants as a function of time

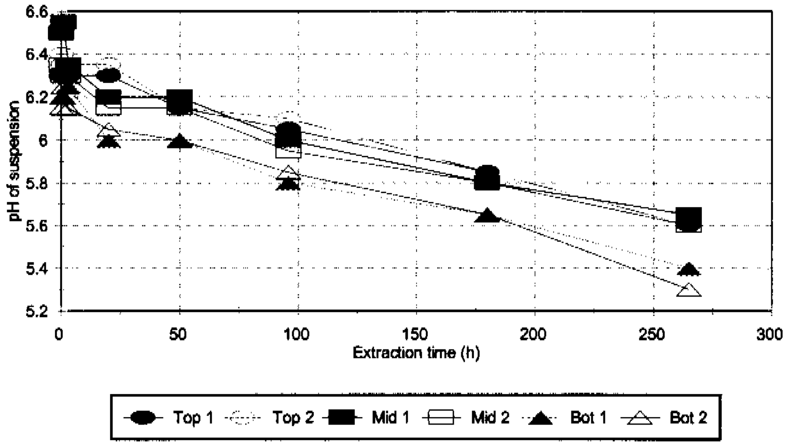

Figure 7c. pH of Core 3 water supernatants as a function of time

The extraction behaviour for water and 1M HCl media is depicted in Figure 8 (top segment only displayed for illustration). It is probable that both the rate and extent of sulfide oxidation is suppressed by acidic extraction conditions. Because the oxidation of sulfides is an acid-generating process, performing the reaction in the presence of excess acid will retard oxidation as a result of mass action. Oxygen is less soluble in 1M HCl than in pure water (Lide 1995), which will result in a slower rate of reaction. For these cores, median $t_{1/2}$ values for sulfide oxidation was 10 weeks and 36 weeks for H_2O and HCl respectively. The apparently low acid lability of RP1 sulfides was remarked on earlier. The extraction experiments do not rule out the possibility of H_2S generation, which subsequently escaped from the reaction vessels before oxidation. However, the small degree to which S was depleted from extracted sediments demonstrates that this mechanism cannot be extensive.

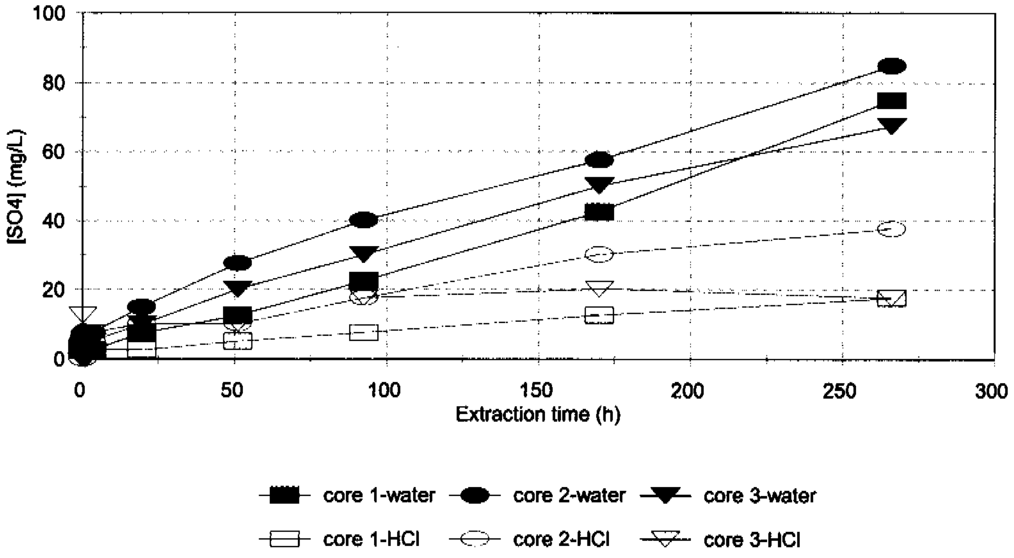

Figure 8. The rate of SO_4^{2-} evolution from RP1 sediments (top segment only)

Temporal extraction of metals from RP1 sediments

For the purpose of discussing the extraction behaviour of heavy-metal indicators with 1M HCl, they have been divided into two groups. The first group comprises metals presumed to be present in extractable form as oxyhydroxides, and therefore act as potential adsorbants or substrates for NOM adsorbants. This group (the 'oxide' group) includes Al, Fe and Mn. The second group comprises metals that once mobilised may participate in detrimental environmental processes. This group (the 'contaminant' group) includes Pb and U, with Mn also included because of possible ecological relevance, and for comparison purposes. Extraction profiles for all core intervals are presented in Figures 10 and 11. Complete extraction data are recorded in Appendix 2.

The extraction behaviour of the members of oxide group are qualitatively similar. The extraction profiles are characterised by initial rapid mobilisation, followed by a period of much slower, almost linear extraction. The period of rapid extraction is probably attributable to mineral surfaces in direct contact with the extractant, which may also be amorphous or poorly crystalline. The period of slower extraction may possibly be identified with occluded mineral surfaces (such as by NOM), as well as recrystallised or otherwise passivated surfaces.

For members of the contaminants group (Pb and U), extraction profiles are different from the oxide group and from each other. For Pb, equilibrium is reached quickly, except perhaps for Core 2, where evidence for a small amount of resorption is present. For U, after a period of rapid mobilisation, significant resorption is evident, particularly for Cores 1 and 2. We believe that resorption is due to the generation of new binding surfaces as a result of acid reaction with substrate components. The strong relationship between this effect and the carbon contents of the sediments (Figure 9) leads us to believe that the dominant effect is chemical reaction between NOM and HCl. For example, hydrolysis of ester and amide substituents of NOM would produce ligands with higher U stability constants than the original functional groups. If this occurred, the equilibrium between sediment and aqueous phases would be altered, with greater partitioning of U (and perhaps Pb) in favour of sediment. The production of greater surface activity on mineral surfaces cannot be discounted as a contributory factor.

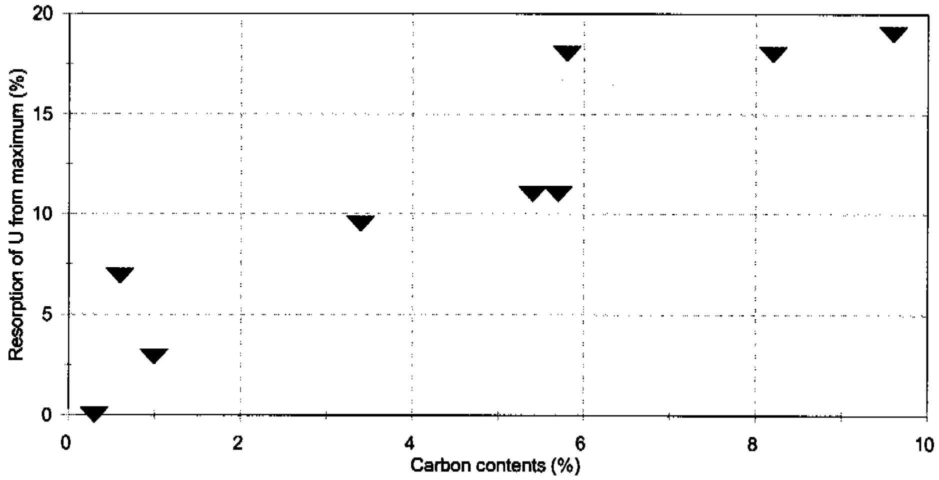

Figure 9. The relationship between C contents of sediments and U resorption

Conclusions

A summary of the findings of this project

The main conclusion of this work is that a substantial fraction of the heavy-metal burden of RP1 sediments can be mobilised by 1M HCl. This extractant was selected because of its status as a quasi-standard for the fraction of total metal contents that is potentially available to the environment. For this purpose it is regarded as a conservative criterion in that in most cases it overestimates the availability of the metal contents of sediments. However, the work of Batterham and Overall (2000), and semiquantitative calculations made in the present work suggest that the 'labile' U fraction in RP1 sediments may be desorbed under much less acid conditions than 1M HCl. This implies that the extraction conditions used may not grossly overestimate the U (and possibly also Pb) desorbed if RP1 dries completely and subsequently refills.

Extractions with water showed that mobilisation is minimal for most indicators under these conditions. Some of the sulfide contents of sediments are mobilised using water extraction. Concomitant reduction in pH suggests that partial oxidation of 'pyritic' contents occurs, but that this process has a halflife of many weeks. In practice this means that sulfide oxidation was incomplete on the time scale of the experiments, an observation consistent with the slow rate of SO_4^{2-} evolution in RP1 at the onset of the Wet Season. In fact, there is no convincing evidence that sulfides in submerged RP1 sediments oxidise to a measurable extent. In some cases, aqueous supernatants had a final pH lower than has ever been observed in RP1, when mobilisation of heavy-metal contents remained minimal.

Potential binding substituents were concentrated in the <63 µm fraction, and the concentration of these potential adsorbants in particular sediments had a material influence on the extraction of heavy metals. We believe that NOM has a major moderating role in sediment processes. It has three major functions:

- It acts as a reductant (electron donor) for SO_4^{2-}, through the agency of appropriate bacteria, for the production of sulfide minerals;
- It acts as the main binding substituent for uranium, and possibly as a minor substituent for lead complexation;

- It acts to occlude mineral surfaces, and therefore modify other adsorption/desorption reactions that might otherwise occur.

Uranium extraction using 1M HCl is more complex than for other metals. After an initial period of rapid extraction, [U] slowly declines for the remainder of the experiment. We believe that the most probable explanation for this is the production of additional U-binding ligands within NOM by acid hydrolysis of substituents with low binding capacity.

Comments on the possibility of a serious acidification event in RP1

During its approximately 20-year existence RP1 has never dried completely except for one instance (1990) when it was deliberately drained for mine-related purposes after an exceptionally dry 1989-90 Wet Season. At this time the sulfide contents of RP1 sediments was estimated to be ~0.7 g/kg, compared with an estimate of 1.6 g/kg from the present work. This difference is explained by additional sulfide deposition since 1990. Only 'permanently' submerged sediments are considered, because seasonally exposed sediments probably do not accumulate S, as they experience annual cycles of deposition and oxidation-driven mobilisation. A mild acidification event occurred during pond filling, in January 1991. The minimum pH measured was 4.3, when the pond was approximately half full. The value for [SO_4^{2-}] at this time was ~150 mg/L (50 mg/L S)-interpolated from Ranger Uranium Mines (2000) data. As the pond was nearly dry immediately before the Wet Season, most of this S would have originated from sulfide oxidation. The mass (10 tonnes of S) corresponded to more than 50% of the estimated S contents of usually submerged sediments (~16 tonnes). While the sediments were undoubtedly well-buffered, the extraction of water, apart from leading to an extended period of pond drying also removed neutralants from the water column, which would contribute to acidification during filling. In this sense the 1990-91 incident constituted a fairly rigorous test of the acidification potential of RP1, except that the sulfide load was approximately 40% of the burden in 2000. At the minimum pH, measured [U] was about 2 μg/L (interpolated).

Unless water is deliberately removed from RP1, it appears unlikely that the extended drying conditions necessary for acidification would be met. One caveat to this assessment is the possibility that significant volumes of water may be diverted from the RP1 catchment in an attempt to control the export of U from waste-rock stockpiles to the pond. In that case insufficient water may enter RP1 during a poor Wet Season to prevent it from drying in the ensuing Dry Season. The avoidance of this possibility is an issue of water management.

If benthic sediments of RP1 were exposed for an extended period (for example, greater than a month), an acidification event would ensue upon refilling. The magnitude of the acidification would be dependent on the area of exposure and the time for which dissication and oxidation continued. Environmentally significant mobilisation of U and Pb could occur under these circumstances. However, the one antecedent incident allows for some optimism that the outcome would be much less severe than is theoretically possible.

There is little evidence that seasonally exposed sediments contribute materially to pond processes. They probably do not accumulate significant sulfidic deposits, and their acid-generating capacity is seemingly too modest to measurably alter the pH of the pond. While they contribute $MgSO_4$ to RP1, the question of U contribution is more uncertain. The evidence of Batterham and Overall (2000) seems to confirm that soluble U is associated with $MgSO_4$ evaporites at the margins of the pond. However, the period of surface flow of water is preceded by wetting of these evaporites by the first rains. This would probably lead to dissolution of $MgSO_4$ and exposure of the U contents to the sediments. Willett et al. (1993a) have demonstrated that U is tightly bound to soils of the Ranger lease, so subsequent surface flow to RP1 may wash soluble components of the evaporites into the pond but substantially retain the U. This may explain the observations of Jones, quoted in Batterham and Overall (2000), that U is apparently more mobile during laboratory experiments than in the field.

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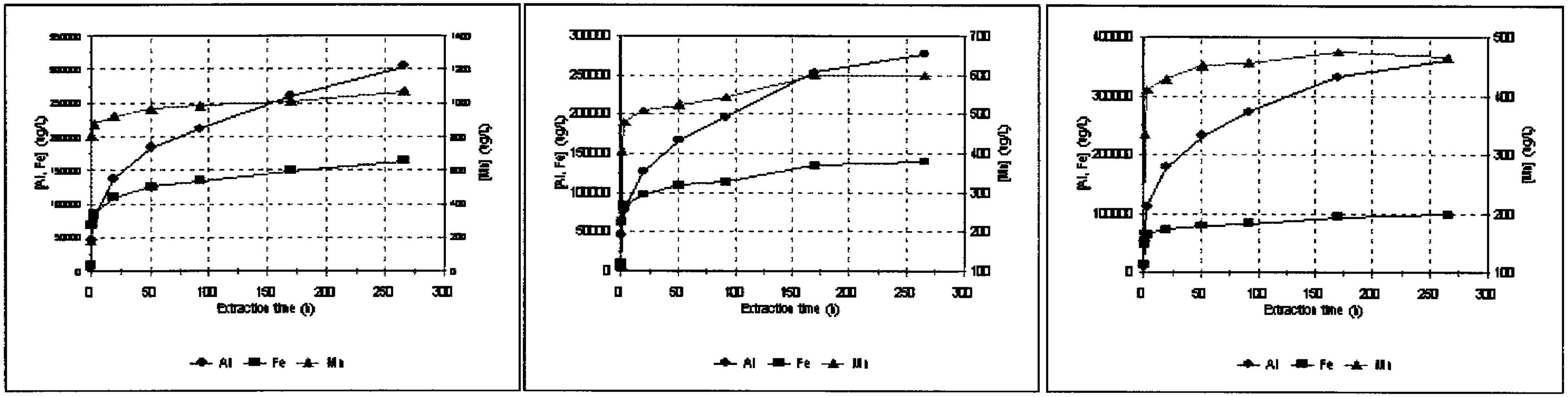

Figure 10a. Extraction profiles for Al, Fe & Mn for Core 1 (top, middle & bottom segments respectively)

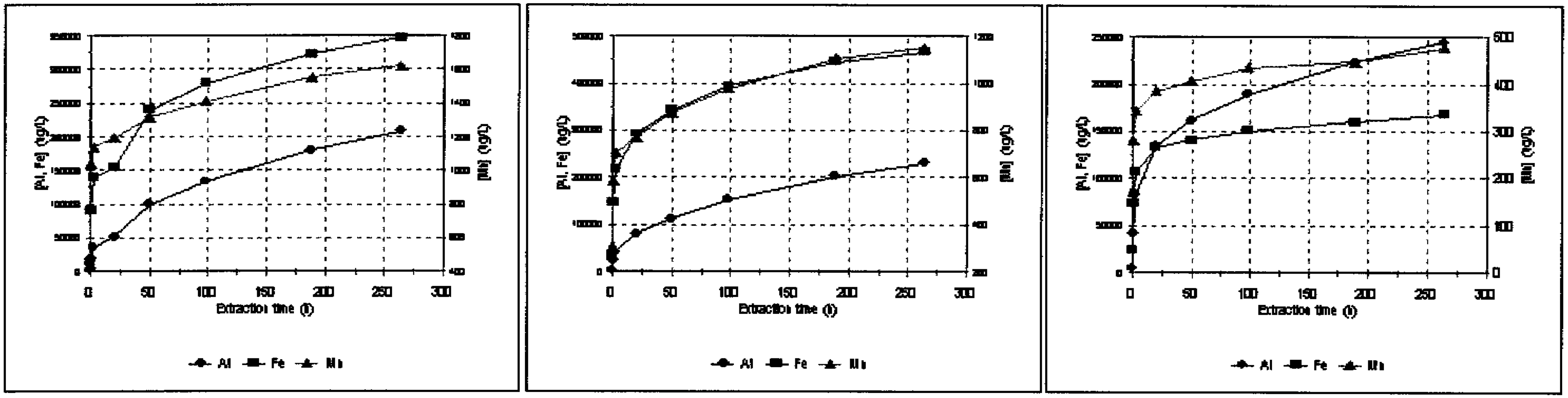

Figure 10b. Extraction profiles for Al, Fe & Mn for Core 2 (top, middle & bottom segments respectively)

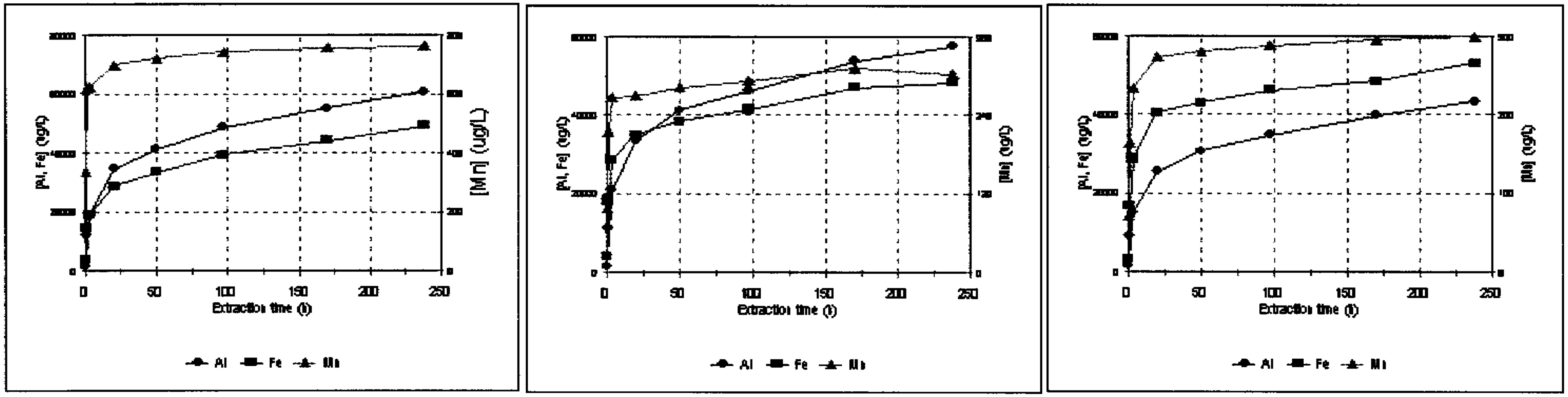

Figure 10c. Extraction profiles for Al, Fe & Mn for Core 3 (top, middle & bottom segments respectively)

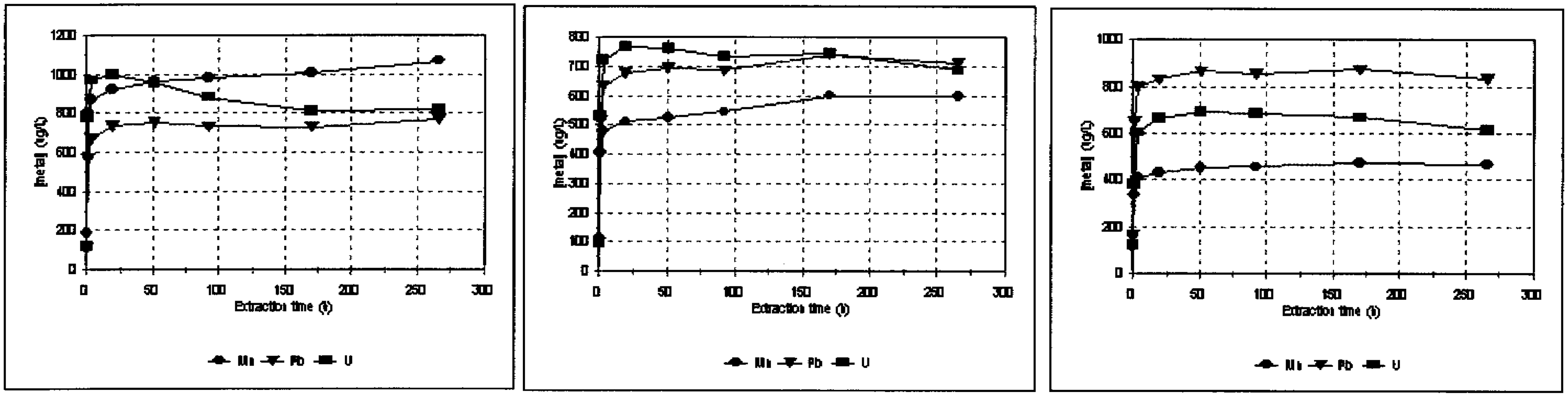

Figure 11a. Extraction profiles for Mn, Pb & U for Core 1 (top, middle & bottom segments respectively)

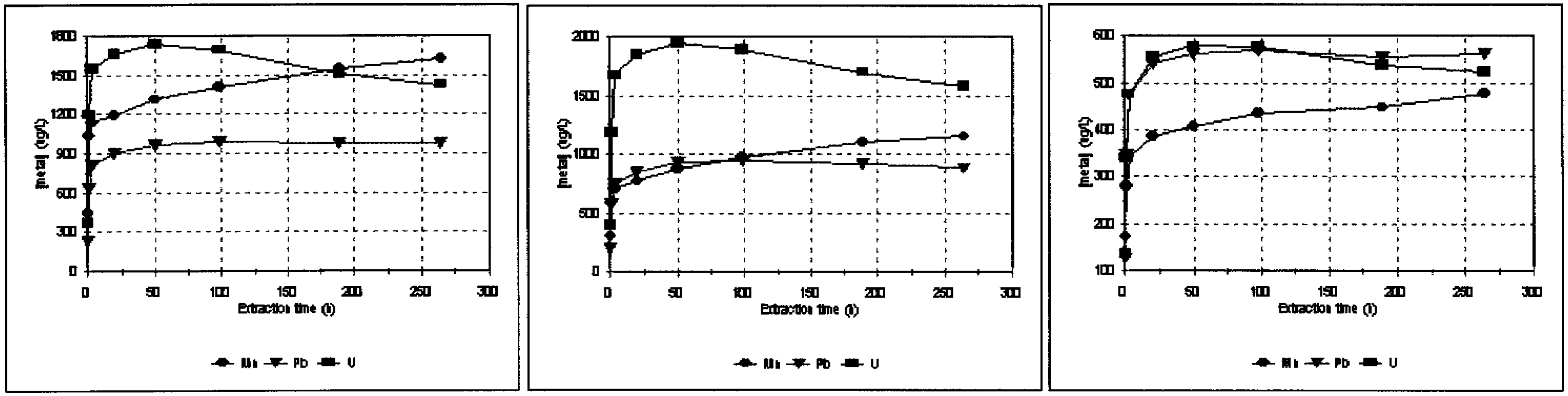

Figure 11b. Extraction profiles for Mn, Pb & U for Core 2 (top, middle & bottom segments respectively)

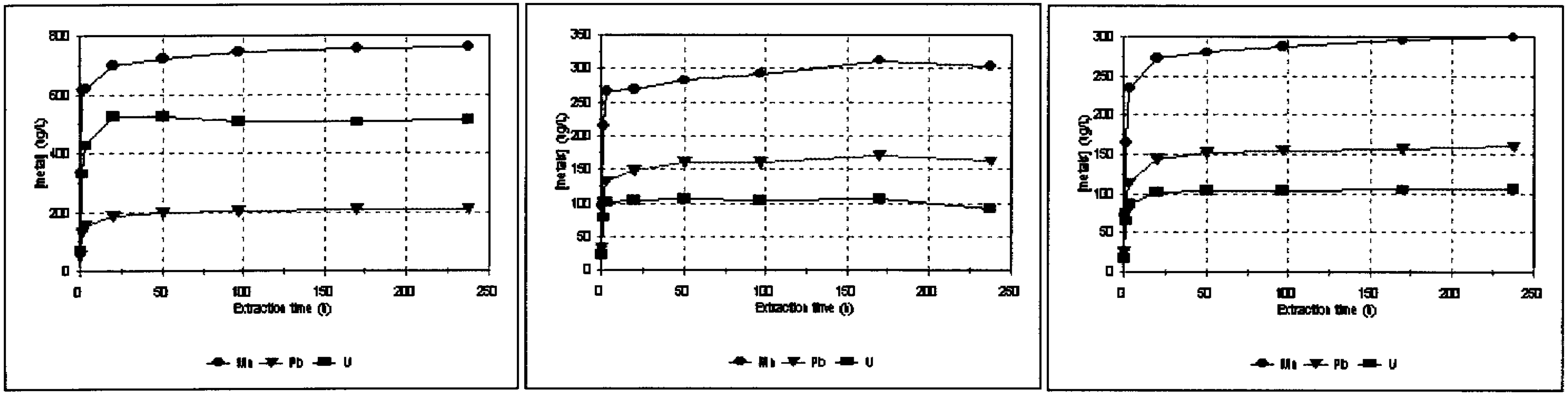

Figure 11c. Extraction profiles for Mn, Pb & U for Core 3 (top, middle & bottom segments respectively)

Interval	Extractant	Al %	C %	Fe %	Mg mg/kg	Mn Mg/kg	Pb mg/kg	S mg/kg	U mg/kg
Top rep. 1	None	4.3	5.7	0.91	2560	29.4	23.2	1898	21.0
Top rep. 2	None	4.2	5.9	0.89	2511	28.1	22.9	1837	19.6
Middle rep.1	None	4.1	5.2	0.77	1936	23.7	23.6	1014	14.0
Middle rep. 2	None	4.8	5.6	0.86	2177	24.5	23.0	1060	15.2
Bottom rep. 1	None	5.3	5.6	0.68	1087	19.3	26.3	476	11.4
Bottom rep. 2	None	5.2	5.7	0.71	1175	19.4	28.6	527	12.6
Top rep. 1	Water	4.2	5.2	0.90	2433	28.0	24.5	1627	20.7
Top rep. 2	Water	3.7	4.8	0.84	2283	26.5	22.9	1571	20.2
Middle rep.1	Water	3.5	4.4	0.68	1781	20.2	19.6	765	13.4
Middle rep. 2	Water	3.7	5.5	0.71	1746	21.7	22.1	839	15.1
Bottom rep. 1	Water	6.1	6.2	0.76	1216	21.2	27.6	505	12.2
Bottom rep. 2	Water	6.8	5.9	0.79	1385	22.1	27.7	461	12.3
Top rep. 1	1M HCl	4.8	6.3	0.81	1936	20.7	16.3	1998	12.2
Top rep. 2	1M HCl	4.4	6.4	0.59	1837	19.0	14.9	1684	11.8
Middle rep.1	1M HCl	3.9	7.0	0.43	1361	16.2	13.0	809	6.3
Middle rep. 2	1M HCl	4.7	5.2	0.50	1616	18.7	20.1	926	7.6
Bottom rep. 1	1M HCl	4.8	5.3	0.54	755	13.3	15.3	384	4.4
Bottom rep. 2	1M HCl	4.9	6.2	0.57	793	13.7	18.3	493	5.4

Appendix 1a. Element contents of core 1

Interval	Extractant	Al %	C %	Fe %	Mg mg/kg	Mn mg/kg	Pb mg/kg	S mg/kg	U mg/kg
Top rep. 1	None	6.4	8.0	2.2	8617	64.4	34.4	4757	33.2
Top rep. 2	None	6.0	8.3	0.8	7871	59.9	31.8	3890	38.5
Middle rep.1	None	6.8	8.8	1.8	10160	66.0	33.3	4489	43.1
Middle rep. 2	None	6.5	10.0	2.8	9893	65.5	33.8	5007	42.3
Bottom rep. 1	None	3.1	3.0	1.1	2432	24.8	18.0	409	11.5
Bottom rep. 2	None	2.6	3.8	0.8	2446	24.2	17.8	349	11.9
Top rep. 1	Water	4.3	7.5	1.8	6603	49.7	29.3	4312	35.5
Top rep. 2	Water	4.9	7.7	1.9	7188	53.6	35.3	4459	44.5
Middle rep.1	Water	6.1	9.1	2.5	8569	56.3	30.4	4299	40.4
Middle rep. 2	Water	5.3	8.7	2.4	8267	56.4	29.1	4282	38.3
Bottom rep. 1	Water	3.3	3.2	1.0	2196	26.6	18.9	387	11.1
Bottom rep. 2	Water	3.2	3.5	1.0	2105	24.4	17.7	340	10.6
Top rep. 1	1M HCl	6.1	9.7	1.9	6802	48.5	25.8	5155	27.7
Top rep. 2	1M HCl	4.7	9.7	1.6	5691	38.4	21.6	4362	23.8

Interval	Extractant	Al %	C %	Fe %	Mg mg/kg	Mn mg/kg	Pb mg/kg	S mg/kg	U mg/kg
Middle rep.1	1M HCl	4.3	9.9	1.9	7431	44.4	20.4	4421	21.9
Middle rep. 2	1M HCl	5.2	9.1	2.1	7190	47.5	20.7	4433	22.3
Bottom rep. 1	1M HCl	2.3	5.2	0.6	1271	15.5	9.3	251	3.7
Bottom rep. 2	1M HCl	2.7	5.1	0.8	1592	18.4	10.9	329	4.6

Appendix 1b. Element contents of core 2

Interval	Extractant	Al %	C %	Fe %	Mg mg/kg	Mn mg/kg	Pb mg/kg	S mg/kg	U mg/kg
Top rep. 1	None	0.61	0.87	0.40	533	12.90	5.1	1154	8.2
Top rep. 2	None	0.59	1.12	0.43	578	13.43	5.8	1323	8.2
Middle rep.1	None	0.56	0.64	0.33	257	8.02	5.6	203	1.9
Middle rep. 2	None	0.55	0.49	0.33	255	7.79	5.4	242	2 0
Bottom rep. 1	None	0.53	0.54	0.33	219	7.24	4.8	195	1.8
Bottom rep. 2	None	0.49	0.11	0.33	220	7.63	5.5	201	1.9
Top rep. 1	Water	0.50	0.20	0.37	386	9.28	4.2	934	6.4
Top rep. 2	Water	0.73	0.51	0.38	426	10.75	4.3	921	7.1
Middle rep.1	Water	0.37	0.26	0.30	145	4.72	2.9	126	1 0
Middle rep. 2	Water	0.33	0.40	0.22	118	3.64	2.7	102	1 0
Bottom rep. 1	Water	0.28	0.39	0.24	93	3.39	2.4	97	1 0
Bottom rep. 2	Water	0.28	0.36	0.24	100	3.48	4.7	104	1.6
Top rep. 1	1M HCl	0.60	1.32	1.19	219	6.52	3.4	861	4.1
Top rep. 2	1M HCl	0.60	0.83	0.40	318	5.79	3.4	1399	4.5
Middle rep.1	1M HCl	0.37	0.64	0.31	99	3.33	2.7	174	0.7
Middle rep. 2	1M HCl	0.39	0.65	0.25	104	3.22	2.7	152	0.6
Bottom rep. 1	1M HCl	0.39	0.51	0.27	108	3.42	2.8	169	0.7
Bottom rep. 2	1M HCl	0.29	0.68	0.25	80	2.47	2.1	103	0.5

Appendix 1c. Element contents of core 3

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	[SO_4^{2-}] mg/L	[U] µg/L
Top H_2O	0	5.08	605	575	2.5	11.3	7.8	2.5	3.6
	1	5.08	520	1675	2.5	10.8	1.8	5.0	4.8
	3	5.03	583	800	2.5	10.3	2.3	2.5	6.1
	19.5	5.73	958	1850	2.5	15.5	1.5	7.5	6.0
	51	5.55	813	1975	2.5	16.0	2.8	12.5	4.1
	92.5	5.43	480	1400	2.5	21.5	1.3	22.5	3.2
	170	5.53	518	1875	7.5	35.0	2.0	42.5	2.4
	266	4.98	4875	4125	17.5	98.5	10.5	75.0	11.7
Middle H_2O	0	5.25	260	1175	2.5	8.5	2.0	2.5	2.3
	1	5.13	253	1975	2.5	9.3	1.5	2.5	3.7
	3	5.20	250	825	2.5	10.5	1.3	2.5	3.3
	19.5	5.65	565	1925	2.5	11.8	1.5	2.5	3.6
	51	5.38	315	1675	2.5	9.8	1.5	2.5	2.5
	92.5	5.48	228	1775	2.5	12.0	1.3	12.5	2.3
	170	5.25	260	1575	2.5	19.5	1.3	22.5	1.7
	266	5.10	9453	5700	12.5	49.8	16.5	42.5	15.6
Bottom H_2O	0	5.28	235	0	2.5	9.5	1.3	2.5	2.0
	1	5.20	195	1675	2.5	8.0	2.0	2.5	2.1
	3	5.23	238	1800	2.5	10.5	1.3	2.5	2.1
	19.5	5.53	395	1650	2.5	10.5	1.8	2.5	1.9
	51	5.38	230	1475	2.5	9.3	1.3	2.5	1.5
	92.5	5.33	260	1575	2.5	12.0	1.5	5.0	1.4
	170	5.10	310	1325	2.5	19.3	1.3	12.5	1.3
	266	4.95	19125	6175	12.5	54.5	31.0	25.0	20.8
Top HCl	0		4038	9250	17.5	189.3	113.0	2.5	122.3
	1		46655	67250	65.0	802.3	569.5	2.5	778.1
	3		79325	85975	72.5	874.8	666.8	2.5	970.2
	19.5		138350	108950	72.5	922.0	737.5	2.5	1000.4
	51		183775	125400	77.5	967.0	751.3	5.0	955.3
	92.5		212275	134650	77.5	984.3	733.8	7.5	883.9
	170		259925	148800	82.5	1009.5	732.3	12.5	815.1
	266		304150	163800	87.5	1070.3	770.8	17.5	820.9
Middle HCl	0		4280	9375	12.5	115.3	99.0	2.5	94.4
	1		45215	62900	42.5	407.8	515.0	2.5	530.3
	3		77225	83225	47.5	481.5	634.5	2.5	722.4
	19.5		127025	97675	52.5	511.3	676.5	2.5	767.3
	51		167525	109275	52.5	525.0	694.5	2.5	762.3
	92.5		196475	113800	52.5	544.5	685.8	2.5	734.8

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	[SO_4^{2-}] mg/L	[U] µg/L
	170	▨	253400	135525	57.5	600.8	741.3	2.5	745.8
	266	▨	277250	139950	57.5	599.8	709.5	12.5	685.9
Bottom HCl	0	▨	11050	12800	17.5	161.8	164.0	2.5	121.2
	1	▨	66225	46025	32.5	336.5	647.3	2.5	383.3
	3	▨	111825	63925	32.5	410.8	798.5	2.5	604.0
	19.5	▨	179125	72275	35.0	430.0	828.8	2.5	665.7
	51	▨	232500	79325	35.0	452.0	864.0	2.5	691.7
	92.5	▨	273425	83450	35.0	456.5	856.0	2.5	684.4
	170	▨	332575	94325	35.0	475.0	871.3	5.0	667.8
	266	▨	361975	97750	35.0	466.5	831.8	2.5	613.5

Appendix 2a. Temporal aqueous indicator concentrations for Core 1

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	[SO_4^{2-}] mg/L	[U] µg/L
Top H_2O	0	5.60	75	675	0	9	3.3	5	3.5
	1	5.63	123	1675	0	15	0.0	8	7.6
	3	5.53	135	1800	0	16	0.0	8	7.6
	20	5.55	170	1200	0	21	0.0	15	8.3
	50	5.60	1373	3025	5	25	5.3	28	8.0
	98	5.58	540	1800	5	26	1.5	40	3.7
	189	5.35	375	1300	10	44	3.8	57	3.3
	264	5.08	383	2050	18	84	0.0	85	3.0
Middle H_2O	0	5.23	78	825	0	9	0.0	5	4.3
	1	5.18	53	1350	0	11	0.0	8	6.7
	3	5.15	130	1950	0	13	0.0	5	6.6
	20	5.18	78	1675	0	18	0.0	10	7.8
	50	5.10	180	1175	0	13	0.0	18	6.3
	98	4.83	233	1825	0	18	5.0	32	6.4
	189	4.48	278	1225	10	54	0.0	80	4.3
	264	4.00	178	2025	30	161	2.5	165	4.8
Bottom H_2O	0	5.50	55	550	0	7	0.0	0	2.9
	1	5.50	90	2425	0	7	1.8	0	4.9
	3	5.43	85	1925	0	7	1.3	0	4.8
	20	5.45	63	750	0	7	0.0	0	4.8
	50	5.40	120	1825	0	9	0.0	0	2.4
	98	5.30	170	1575	0	8	1.5	5	2.0
	189	5.13	325	1000	0	13	0.0	10	5.9
	264	5.03	435	1775	0	17	1.5	15	2.4
Top HCl	0	▨	2025	14100	53	451	235.0	0	366.8

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	$[SO_4^{2-}]$ mg/L	[U] µg/L
	1		20203	91725	110	1034	633.3	3	1201.2
	3		35538	139000	117	1139	816.5	5	1547.7
	20		50960	153325	125	1195	906.5	10	1661.7
	50		99325	240500	127	1316	967.0	10	1736.2
	98		133625	279275	138	1411	991.8	18	1692.9
	189		179325	323175	153	1552	983.8	30	1514.9
	264		207950	347325	165	1623	975.5	38	1427.8
Middle HCl	0		1478	35775	50	308	198.0	0	393.9
	1		23198	147200	83	587	578.8	0	1183.1
	3		41748	215925	95	705	751.8	3	1673.5
	20		80075	292900	95	772	849.0	10	1848.3
	50		112775	342375	102	877	931.7	10	1951.5
	98		153025	394925	115	979	947.0	20	1892.6
	189		201775	446075	127	1104	917.3	32	1698.4
	264		229800	466025	138	1152	885.2	38	1583.2
Bottom HCl	0		5635	23375	15	173	126.8	0	136.5
	1		42085	73050	25	281	348.5	0	341.4
	3		82375	106775	28	343	474.5	0	475.6
	20		134250	132600	30	385	539.5	0	555.2
	50		162200	140550	30	407	561.8	0	578.3
	98		189075	150150	30	434	567.5	0	575.2
	189		223925	160525	32	448	556.0	3	537.4
	264		244375	167725	32	478	562.0	3	523.2

Appendix 2b. Temporal aqueous indicator concentrations for Core 2

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	$[SO_4^{2-}]$ mg/L	[U] µg/L
Top H_2O	0	6.35	190.0	975.0	0.0	8.3	1.3	0.0	0.9
	1	6.33	6070.0	0.0	0.0	10.3	2.3	0.0	3.3
	3	6.33	670.0	0.0	0.0	10.3	0.0	5.0	4.6
	20	6.33	325.0	0.0	0.0	16.8	0.0	10.0	6.7
	50	6.15	382.5	0.0	0.0	21.5	0.0	20.0	2.8
	97	6.08	847.5	0.0	0.0	35.0	0.0	30.0	2.2
	170	5.85	732.5	650.0	5.0	53.8	2.3	50.0	1.7
	238	5.60	592.5	650.0	10.0	75.8	0.0	67.5	1.4
Middle H_2O	0	6.43	207.5	1275.0	0.0	6.8	0.0	0.0	0.0
	1	6.43	172.5	650.0	0.0	7.0	0.0	0.0	0.5
	3	6.33	160.0	0.0	0.0	7.3	0.0	0.0	0.9
	20	6.18	312.5	625.0	0.0	9.0	0.0	2.5	1.5
	50	6.18	697.5	0.0	0.0	11.5	0.0	0.0	1.1

Extract	t (h)	pH	[Al] µg/L	[Fe] µg/L	[Mg] mg/L	[Mn] µg/L	[Pb] µg/L	$[SO_4^{2-}]$ mg/L	[U] µg/L
	97	5.98	237.5	625.0	0.0	16.3	0.0	5.0	0.8
	170	5.80	215.0	1175.0	0.0	20.8	0.0	17.5	0.6
	238	5.63	832.5	1350.0	0.0	27.0	1.5	25.0	1.0
Bottom H_2O	0	6.18	1050.0	0.0	0.0	10.5	0.0	0.0	0.0
	1	6.23	172.5	0.0	0.0	6.0	0.0	0.0	0.6
	3	6.20	14915	0.0	0.0	8.5	0.0	0.0	0.9
	20	6.03	150.0	0.0	0.0	9.0	0.0	0.0	1.4
	50	6.00	1312.5	0.0	0.0	10.5	0.0	0.0	1.2
	97	5.83	175.0	0.0	0.0	14.0	2.5	5.0	0.8
	170	5.65	240.0	525.0	0.0	19.8	0.0	10.0	0.7
	238	5.35	2737.5	675.0	0.0	28.3	0.0	20.0	0.5
Top HCl	0		1790.0	3600.0	15.0	337.0	52.5	12.5	68.1
	1		12442	14750	22.5	617.5	132.0	5.0	331.9
	3		18630	18900	22.5	621.0	152.8	7.5	427.0
	20		34575	28575	25.0	698.8	186.3	10.0	525.0
	50		41312	33425	25.0	720.5	199.3	10.0	525.0
	97		48815	39325	25.0	745.0	205.0	17.5	509.3
	170		55195	44275	27.5	756.8	208.8	20.0	506.3
	238		60820	49250	30.0	764.0	211.8	17.5	513.2
Middle HCl	0		1705.0	3950.0	0.0	97.3	32.0	15.0	22.2
	1		11135	18275	7.5	215.3	101.0	5.0	78.6
	3		20910	28700	10.0	267.3	132.8	2.5	101.7
	20		33650	35000	10.0	269.8	148.0	12.5	104.2
	50		41353	38400	10.0	283.0	160.8	10.0	106.7
	97		46285	41475	10.0	292.5	160.5	7.5	104.4
	170		53795	47175	10.0	312.3	170.3	7.5	107.4
	238		57745	48450	10.0	303.5	162.0	10.0	91.3
Bottom HCl	0		1412.5	3200.0	0.0	72.0	25.8	2.5	17.6
	1		9020.0	16750	2.5	164.5	74.5	5.0	65.2
	3		15055	28775	5.0	234.8	113.5	7.5	86.3
	20		25635	40600	5.0	273.5	143.5	2.5	101.6
	50		30862	43125	5.0	280.5	152.5	5.0	104.7
	97		34895	46200	5.0	287.8	155.5	7.5	103.9
	170		39805	48500	7.5	295.3	156.3	10.0	105.3
	238		43428	53100	5.0	299.8	160.3	10.0	106.3

Appendix 2c. Temporal aqueous indicator concentrations for Core 3

Reference Sample	Al (found)	Al (cert.)	C % (found)	C% (cert.)	Fe (found)	Fe (cert.)	Mg (found)	Mg (cert.)	Mn (found)	Mn (cert.)	Pb (found)	Pb (cert.)	S/SO4 (found)	S/SO4 (cert.)	U (found)	U (cert.)
NBS SRM 1643d	13.9	12.8	n/a	n/c	27	9.12	0.8	0.799	3.95	3.77	1.85	1.82	0	n/c	0	n/c
NBS SRM 1643d	10.5	12.8	n/a	n/c	27	9.12	0.8	0.799	3.78	3.77	1.77	1.82	0.1	n/c	0	n/c
NBS SRM 1643d	14.3	12.8	n/a	n/c	0	9.12	0.8	0.799	3.7	3.8	1.79	1.82	0	n/c	0	n/c
CRC SLRS-3	31.1	31	n/a	n/c	103	100	1.6	1.6	4.48	3.9	0.08	0.068	8.7	n/c	0.042	0.045
CRC SLRS-3	30.8	31	n/a	n/c	104	100	1.6	1.6	4.38	3.9	0.08	0.068	8.5	n/c	0.041	0.045
CRC SLRS-3	31.4	31	n/a	n/c	103	100	1.6	1.6	4.2	3.9	0.09	0.068	9	n/c	0.041	0.045
SPEX MQCS	1.3	n/c	n/a	n/c	0	n/c	2.4	2.51	0.12	n/c	0	n/c	9.6	10	0	n/c
SPEX MQCS	1	n/c	n/a	n/c	0	n/c	2.5	2.51	0.13	n/c	0	n/c	9.5	10	0	n/c
SPEX MQCS	2.8	n/c	n/a	n/c	0	n/c	2.4	2.51	0.12	n/c	0	n/c	9.6	10	0	n/c
PE Pure	0	n/c	n/a	n/c	0	n/c	0	0.01	0	n/c	9.84	10	0	n/c	9.734	10
PE Pure	0	n/c	n/a	n/c	0	n/c	0	0.01	0	n/c	9.7	10	0	n/c	9.702	10
PE Pure	0	n/c	n/a	n/c	0	n/c	0	0.01	0	n/c	9.6	10	0	n/c	10.175	10
CRC TMDA54	436	487	n/a	n/c	319	283	1.6	n/c	217.6	224	507.88	554	6.4	n/c	58.968	68
CRC TMDA54	475.7	487	n/a	n/c	321	283	1.6	n/c	220.2	224	539.8	554	6.4	n/c	59.399	68
CRC TMDA54	487.6	487	n/a	n/c	284	283	1.6	n/c	209.2	224	519.7	554	6.8	n/c	62.546	68
NBS SRM 1645 (river)	0.6	2.26	3.1	10.72	9.94	11.3	7192	7400	745.4	785	755.5	714	14261	11000	0.9	1.11
NBS SRM 1646 (est.)	2.9	6.25	4.4	n/c	3	3.35	8766	7400	288.3	375	29.8	28.2	9661	9600	1.9	n/c
NBS SRM 1646 (est.)	2.38	6.25	2.87	n/c	2.37	3.35	9383	7400	242.0	375	24.6	28.2	6329	9600	1.7	n/c
CRC LKSD 1 (lake)	0.5	n/c	8	12.3	2.12	2.8	6503	n/c	449.2	700	84	82	17799	15700	8.9	9.7
CRC LKSD 1 (lake)	0.6	n/c	8.6	12.3	2.3	2.8	6424	n/c	512	700	90.6	82	16339	15700	9.1	9.7
CRC LKSD 1 (lake)	0.51	n/c	6.99	12.3	1.8	2.8	6943	n/c	462.2	700	86	82	12179	15700	8.8	9.7
CRC LKSD 2 (lake)	1.9	n/c	3.7	4.5	3.49	4.3	6742	n/c	1762.6	2020	44.3	44	1613	1400	6.6	7.6

Reference Sample	Al (found)	Al (cert.)	C % (found)	C% (cert.)	Fe (found)	Fe (cert.)	Mg (found)	Mg (cert.)	Mn (found)	Mn (cert.)	Pb (found)	Pb (cert.)	S/SO4 (found)	S/SO4 (cert.)	U (found)	U (cert.)
CRC LKSD 2 (lake)	2.1	n/c	3.5	4.5	3.8	4.3	6878	n/c	1875.1	2020	42.3	44	1571	1400	6.8	7.6
CRC LKSD 2 (lake)	1.81	n/c	2.73	4.5	3.69	4.3	6672	n/c	1775.0	2020	39.5	44	1433	1400	6.6	7.6
CRC LKSD 3 (lake)	2.1	n/c	3.9	4.5	3.5	4	8947	n/c	1306.8	1440	25.8	29	1693	1400	4.1	4.6
CRC LKSD 3 (lake)	2.1	n/c	3.6	4.5	3.5	4	8460	n/c	1320.9	1440	28.8	29	1588	1400	4	4.6
CRC LKSD 3 (lake)	2.18	n/c	2.73	4.5	3.84	4	9286	n/c	1314.4	1440	26.8	29	1557	1400	4	4.6

Appendix 3. Results for reference samples (all values for waters in µg/L except Mg and SO_4^{2-}; mg/L). Units for sediments are mg/kg except Al, Fe and C (%)