

Effects of sample drying on phase distribution of elements in lake-sediment cores

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Abstract: The application of a sequential extraction scheme provides information on the phase association of elements in a sample, such phases being described, for example, as 'exchangeable/adsorbed', 'amorphous Fe/Al oxides', and 'soluble organics'. It is therefore critical to maintain the chemistry of a sample from the time of collection to its analysis and during its preparation for analysis. This paper focuses on the redistribution of elements amongst five operationally defined phases that occurs on air drying of the sample. Two lake-sediment cores ('Green' and 'Gravel Pit' lakes) were sampled at 1 cm intervals and divided into two sets immediately prior to sequential leach analysis of the 'wet' sample; the other set was air dried. Most of the 39 elements determined in the 'Green' Lake sediment showed, on drying, a redistribution to more labile forms, such as Fe where increases in the oxide phases were observed with a concomitant decrease in the crystalline forms of Fe reporting to the final aqua regia digestion. These changes are generally small in magnitude, but they can change the shape of the element profile down the core for an affected leach, which in turn could lead to misinterpretation of the sequential leach data. Surprisingly, S did not show any changes on drying, suggesting that the kinetics of oxidation are reasonably slow and that storage of the sample is more important to avoid than drying. The different behaviour shown by the two cores indicates that redistribution of elements on sample drying is both element- and matrix-dependent.

Résumé : L'utilisation de l'extraction séquentielle renseigne sur l'association des phases des éléments dans un échantillon donné, ces phases étant regroupées, par exemple, par «matières organiques solubles», par «éléments échangeables/adsorbés» et par «oxydes de fer/d'aluminium amorphes». Il est donc crucial que la composition chimique de l'échantillon demeure la même depuis son prélèvement jusqu'à son analyse, en passant par sa préparation. Le présent article porte principalement sur la redistribution d'éléments pendant les cinq phases (définies dans un but pratique) du séchage à l'air de l'échantillon. Deux carottes de sédiments lacustres (lacs «Green» et «Gravel Pit») ont été échantillonnées à 1 cm d'intervalle et subdivisées en deux ensembles juste avant l'analyse par lixiviation séquentielle de l'échantillon «humide»; l'autre ensemble a été séché à l'air. Pendant leur séchage à l'air, la plupart des 39 éléments identifiés dans les sédiments du lac «Green» présentaient une forme plus labile, ce qui fut notamment le cas du fer, qui présentait une augmentation des phases oxydées conjuguée à une diminution des formes cristallines se rattachant à la dissolution finale dans l'eau régale. Ces changements sont généralement petits, mais ils peuvent changer la forme du profil des éléments le long de la carotte dans le cas de la lixiviation visée et, par conséquent, entraîner une fausse interprétation des données sur la lixiviation séquentielle. Fait surprenant, le soufre ne présentait aucun changement attribuable au séchage, ce qui laisse supposer que la cinétique d'oxydation est assez faible et qu'il est plus important d'éviter l'entreposage de l'échantillon que son séchage. Les différentes réactions des deux carottes indiquent que la redistribution des éléments pendant le séchage des échantillons varie selon l'élément et la matrice.

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INTRODUCTION

Sequential extraction techniques are used to provide information on the phase distribution of elements in sediments and soils, often to aid in the interpretation of element sources, diagenesis and mobility (e.g. Kersten and Forstner, 1986, 1989; Howe et al., 2002; Lazareva et al., 2002). An extraction scheme consists of a series of successive chemical leaches of a sample, each being more drastic in action or of a different nature than the previous one (e.g. from mildly reducing through strongly reducing to oxidizing). The order in which the extractants are used is critical and may well depend upon sample type and overall composition, and the objectives of the project. It must be recognized that the results obtained are 'operationally defined', i.e. selectivity is not 100% and is dependent upon such factors as the chemicals employed, the time and nature of contact, and sample to volume ratio. Results will also be predicated on the grain-size fraction chosen for analysis and whether coarser grains have been made finer by ball milling, thus increasing exposure to attack. Resorption of an element back onto the sample during leaching is a recognized problem for some elements (Kheboian and Bauer, 1987; Hall et al., 1995; Kelley et al., 2003). Notwithstanding these limitations, insightful information has been obtained by application of such schemes as those of Gatehouse et al. (1977), Filipek and Theobald (1981), Chao (1984), and Wang (1998), in exploration geochemistry, and those based on the original paper of Tessier et al. (1979), in environmental studies. Sequential schemes designed at the GSC (Hall et al., 1996; Hall and Pelchat, 1999) have been employed in both exploration (Simonetti et al., 1996; Kelley et al., 2003; Gilliss et al., 2004) and environmental (Henderson et al., 1997; Pichler et al., 2001) geochemistry studies. In a typical GSC scheme (Hall et al., 1996), phases nominally separated by the sequential extraction include 'adsorbed/exchangeable/carbonate' ('AEC'); soluble organics ('ORG'); amorphous Fe/Al oxides ('amFeox'); crystalline Fe/Al oxides ('cryFeox'); and sulphides and residual organics (+some silicates, oxides) by aqua regia digestion ('AR').

The growing application of sequential extractions has led the European Commission's Measurements and Testing Programme to harmonize these schemes into one protocol and to certify soil and sediment reference materials for specific classifications of elements (Quevauviller, 1994; Fiedler et al., 1994). Although adequate agreement amongst laboratories can be obtained by adhering strictly to the recommended protocol, the three phases therein defined are vague (1, exchangeable, water and acid soluble; 2, reducible; 3, oxidizable) and therefore limited in their usefulness for interpretative purposes. Difficulty in achieving good agreement amongst the participating laboratories was the driving force in simplifying the extraction scheme. The original disparate results were probably caused in part by lack of optimization of the leaches used and hence problems such as resorption or element instability were encountered.

Although much effort has been focused on designing the conditions of each leach for maximum selectivity and hence 'accuracy', the best method by which to maintain the

integrity of the sample prior to analysis is often overlooked. In their excellent review of the speciation of trace elements in sediments, Kersten and Forstner (1989) discussed the effects of different sample storage and preparation techniques on results of a sequential extraction analysis. They drew upon the findings of two such studies, those of Bartlett and James (1980) and Thomson et al. (1980). The former work found that air and oven drying led to increased solubility of organic matter and manganese. The amount of Mn leached by pH 5 ammonium acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$, commonly used to dissolve the 'AEC' phase) solution increased about threefold (to about 35 ppm Mn) over nine weeks for a loamy sandy soil allowed to dry in air, whereas the same sample kept moist at 22°C from collection maintained a constant leachable Mn concentration of about 6 ppm. The moist frozen sample also showed an increase in extractable Mn but to a lesser degree than the air-dried counterpart. They concluded that aerobic samples should be kept at approximately 4°C as close to their original moisture content as possible (i.e. not dried). Prolonged storage of wet oxidized sediments or soils will lead to a microbially induced shift from oxidizing to reducing conditions with obvious changes in element phase distribution (e.g. more element reporting to the sulphide phase). Thomson et al. (1980) found that the effect on Fe of drying was to reduce the quantity of element reporting to the amorphous oxide phase, with a concomitant increase in Fe in the crystalline oxide phase. Changes in the extractability of trace elements were found to be mostly consistent with their partitioning between iron and manganese oxides and organic matter. Clearly the redox state of the sample presents different challenges: anaerobic samples must not be exposed to atmospheric oxygen.

Saeki et al. (1993) studied the effects of progressive drying of a surface sediment from Lake Teganuma, Japan. As oxidation led to an increase in Eh, from about 0 to 400 mV, and a decrease in pH, from 6.9 to 6.5, the forms of Cd, present originally overwhelmingly in the sulphide-organic phase, changed dramatically to report to the exchangeable and reducible fractions. Although Cu, Pb, and Zn also moved to more labile phases from the sulphide-organic and residual fractions, the changes were of much lower magnitude than for Cd. More recently, Bunzl et al. (1999) studied the effect of sample drying and storage time (up to 30 weeks) on the results obtained by applying the Tessier extraction scheme to two soils for the determination of the fallout radionuclides ^{137}Cs and $^{239+240}\text{Pu}$ and the corresponding stable elements, Cs and Pb. Although no effect on the radionuclides was evident, a significant increase in 'exchangeable' Mn (using 1M pH 8.2 $\text{CH}_3\text{CO}_2\text{NH}_4$) was observed upon drying and storage of the mineral soil, from 0.4% of total Mn extracted to 2.9% over 30 weeks. However, as this Mn amounted to only a small fraction of the total Mn extracted, a concomitant decrease in less labile forms of Mn was not clear. No effect was observed for Mn in the organic-rich soil.

A growing body of literature is focused on the behaviour of elements in dredged sediments disposed of on land (Tack et al., 1998, 1999; Stephens et al., 2001a, b) and in sediments subject to alternating hydrological conditions (Van Den Berg et al., 1998; Astrom, 1998). Such studies as those mentioned

earlier have relevance in predicting the environmental impact of exposure to air of such sediments. Stephens et al. (2001b) studied the effects of drying a canal sediment core over time and found that most elements (e.g. Zn, Cu, Pb, Cr) showed a redistribution from the residual phase into more mobile phases as the sediment dried and oxidized. These changes were strongly correlated with the sulphide/sulphate ratio, with leachability increasing as the ratio decreased, indicating oxidation of sulphide. Interestingly, results for Cd (and As) were opposite in trend in that Cd, initially mostly associated with the available and reducible phases (using the European Commission's recommended protocol), became redistributed into the residual phase, in contrast to the findings of Saeki et al. (1993) and others.

Regardless of the aforementioned and other publications, perusal of both the analytical chemistry and applied geochemistry literature (e.g. Flores et al., 1997; Gutierrez, 2000; Rate et al., 2000; Howari and Banat, 2001; Turer et al., 2001; Siripinyanond et al., 2002; Turek et al., 2002) suggests that the practice of sample drying in air or an oven (up to 70°C!) prior to sequential extraction is the most common mode of preparation, probably to improve precision (but impair accuracy) by subsequent sieving and mixing of the sample. The work described in this paper focuses on the effect of air drying prior to application of a sequential extraction scheme to two lake-sediment cores. The effect of sample storage is not under study. The study was carried out in order to design a sample preparation protocol for sediments collected under the Metals in the Environment (MITE) Program of the GSC.

METHOD

Sample collection

Sediment core collection was carried out at 'Green' and 'Gravel Pit' lakes in the summer of 1998. 'Green' Lake is a kettle lake (0.24 km² in surface area) underlain by interlobate moraine deposits and situated in a remote area approximately 75 km southeast of the town of Rouyn-Noranda, Quebec. Extensive logging activities took place in the 1940s immediately to the west of the lake; pine is the dominant vegetation now, with spruce and birch. The lake is a relatively deep (19 m), groundwater-fed lake with a small drainage basin (1 km²) and a slightly acidic pH of 5.4. Its conductivity and dissolved organic carbon (DOC) values are 6 µ/cm and 8.9 ppm, respectively. 'Gravel Pit' Lake is a small (0.07 km²), shallow (4 m) lake located 10 km northeast of Rouyn-Noranda. Unlike 'Green' Lake, its drainage basin is large (1.04 km²) compared to its surface area. Sand and gravel excavations surround the lake. The pH, conductivity, and DOC parameters for this lake are 4.4, 31 µ/cm, and 8.2 ppm, respectively.

Sampling was carried out with a Kajak-Brinkman gravity corer fitted with a Lexan core tube with an internal diameter of 9 cm. The core was extruded on a Plexiglass platform and subsampled with a plastic spatula at 1 cm intervals directly into WhirlpakTM bags, which were squeezed to expel any entrained air. 'Green' Lake was sampled to a depth of 31 cm

and 'Gravel Pit' Lake, to 19 cm. Owing to the high water content of the near-surface samples in 'Green' Lake and hence the low final weight for analysis, 2 cm intervals were combined to produce five samples comprising the top 10 cm. Samples from the top 2 cm of 'Gravel Pit' Lake were combined. Samples were immediately put into iced coolers in the field and then kept in a refrigerator at 4°C for two weeks until analysis. Several cores were taken at each site for different purposes (e.g. determination of pollen, Pb²¹⁰).

Kliza and Telmer (2001) provide geochemical (based on aqua regia digestion) and descriptive data of these lake-sediment cores, amongst others sampled under the MITE program. The geochemical stratigraphy of the 'Gravel Pit' Lake sediment and, to a much smaller degree, that of 'Green' Lake show an impact by the Horne smelter in Rouyn-Noranda: the top 8 to 15 cm of the cores are significantly enriched in elements such as Zn, Cu, Cd, and As that are present in the emissions.

Reagents

Most reagents used in this project were from J.T. Baker (Phillipsburg, New Jersey); solids were 'analyzed-reagent' grade and acids were 'trace element' grade ('INSTRA-ANALYZED®'). Nitric acid used for dilutions was obtained from Seastar (Sidney, British Columbia) and was the 'BASELINE®' grade (double distilled). The standard stock solutions were purchased from High Purity Standards (Charleston, South Carolina) as the 'ICP-MS' grade. Sodium pyrophosphate, by Fluka Biochemika, was obtained from Sigma-Aldrich (www.sigmaaldrich.com) and was found to be superior to other brands in its low Sb content. Type I water (<18 MΩ, obtained from a Milli-Q system, was used throughout for making up reagents, dilutions, and rinsing all equipment. The leaches were performed in BD (Becton Dickinson) FalconTM conical polypropylene centrifuge tubes equipped with screw caps.

The 1.0 M CH₃CO₂Na leach solution was made up by adding 136.08 g of CH₃CO₂Na·3H₂O and 20 mL of glacial CH₃CO₂H to 1 L of Type I water. Before making up to the final mark, the pH was verified to be 5.0 ± 0.1; additional glacial CH₃CO₂H was added if necessary. Trace elements were removed by passing the reagent solution through a column of Chelex-100 resin.

The 0.1 M Na₄P₂O₇ leach solution was made up by dissolving 44.606 g of Na₄P₂O₇·10 H₂O in 1 L of H₂O. Before making up to the final mark, the pH was adjusted to 10 with 16M HNO₃ (approximately 60 mL).

The 0.25 M NH₂OH·HCl–0.1M HCl reagent was made up by dissolving 17.36 g of NH₂OH·HCl in 1 L of water containing 8.3 mL of 12 M HCl. The 1.0 M NH₂OH·HCl–25% CH₃CO₂H reagent was made up by dissolving 69.49 g of NH₂OH·HCl in 1 L of water containing 250 mL of glacial CH₃CO₂H.

Analysis

The inductively coupled plasma mass spectrometry (ICP-MS) analysis was carried out using a VG PlasmaQuad 2+ (Winsford, Cheshire, United Kingdom) instrument; the inductively coupled plasma emission spectrometry (ICP-ES) model used was the Perkin-Elmer Optima 3000DV in the axial mode. Elements reported by ICP-MS include B, Ba, Be, Bi, Cd, Ce, In, La, Li, Mo, Pb, Rb, Re, Sb, Th, Tl, U, Y, and Zn; those reported by ICP-ES include Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Ni, S, Sc, Si, Sr, Ti, and V. Isotopes and lines were selected to be optimum for this application; where interferences were present and unavoidable, appropriate corrections were made.

Arsenic was determined by hydride generation (HG) ICP-ES using the same hydride generation system described previously (Hall et al., 1997); 1% NaBH_4 solution was used as reductant. In this case the J-Y 38 sequential ICP emission spectrometer was employed, measuring at the As 193.759 nm line.

For all analytical techniques, calibration solutions were prepared by spiking, with known amounts of analytes, 'blank' solution of the particular extractants, and making the appropriate dilutions to matrix-match the sample solutions. A blank and a calibration standard solution were run after every eight samples to check and correct for any drift. Four of the 43 samples analyzed in each set (wet and dry) were repeated (i.e. separate weighings), and three blank reagent solutions and three subsamples of the certified reference material LKSD-4 (Lynch, 1990) were inserted regularly amongst each set.

Sequential leach

The individual sediment samples were removed from the refrigerator where they had been stored since collection and manually mixed in their bags prior to centrifuging. The excess water was removed by centrifuging (10 min at 2800 rev/min) and the residue split for a 'dry' and a 'wet' sample. A portion of the residue, equivalent to 1 g of dry material (predetermined from another separate core), was weighed (to 0.0001 g) immediately and then subjected to the first extraction of the sequential leach scheme. Another portion was taken for air drying to constant weight and subsequent application of the sequential extraction; this time interval was three weeks. It is realized that storage of the sample in an inert atmosphere (N_2) is desirable from the time of collection and superior to simply squeezing out entrained air in the field. However, the number of samples collected and sites visited made this impractical. In any case, changes in element distribution that had taken place between field collection and analysis are irrelevant for this study as both 'dry' and 'wet' samples would be equally affected (not split until leaching).

1M $\text{CH}_3\text{CO}_2\text{Na}$ leach ('AEC', adsorbed/exchangeable/carbonate)

The sample was weighed (equivalent to 1.0 g of dry material) into a 50 mL centrifuge tube and 20 mL of 1.0 M $\text{CH}_3\text{CO}_2\text{Na}$ (pH 5) were added to each sample. After capping, the sample

was suspended by vortexing (5–10 s). The samples were shaken horizontally for 2 h at 160 shakes/min. They were then centrifuged for 10 min at 2800 rev/min. The supernatant was decanted into a 50 mL centrifuge tube. Each residue was rinsed with 5 mL of Type I water and the tube was capped, vortexed, and centrifuged for 10 min at 2800 rev/min. The rinse was decanted into the original supernatant in the centrifuge tube. A second rinse was carried out (i.e. two 5 mL rinses in total were added to the approximately 20 mL supernatant).

Unlike many other samples carried through this procedure previously, these two cores proved difficult at this step. A second centrifuging was carried out on the supernatant to precipitate solid material visible in the solution. This residue was added to the test tube containing the sample for application of the next leach.

As for all leaches, the solution was divided into three portions for analysis by the three techniques (ICP-MS, ICP-ES, and HG-ICP-ES). Prior to analysis by ICP-MS and ICP-ES, the solution was diluted 40-fold with 1% HNO_3 and twofold with H_2O , respectively. For As, a 1 mL aliquot of solution was added to 4 mL of H_2O and 2.5 mL of HCl, making the solution 4M in HCl, optimum for subsequent reduction of As with 1% NaBH_4 solution. Any As^{V} was reduced to As^{III} by addition of 0.01 mL of a 10% solution of KI and ascorbic acid; the solution was allowed to sit for 3 h prior to analysis.

Sample residues were refrigerated immediately if not proceeding directly to the next leach (for all leaches). The laboratory work was scheduled so that a maximum of one night elapsed between leaches.

0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ leach ('ORG', labile organically bound)

To the residue from the previous leach were added 45 mL of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ solution. The sample was shaken by hand and then horizontally on a shaker for 1 h at 160 shakes/min. The solution was centrifuged for 10 min at 2800 rev/min and the supernatant decanted into a 50 mL centrifuge tube. Each residue was rinsed with 5 mL of water and the solution was vortexed and centrifuged. The rinse was added to the original supernatant and a second rinse was carried out in a similar manner.

Prior to analysis by ICP-MS, the solution was diluted 40-fold with water; a 2% HNO_3 rinse solution was used between samples. Analysis by ICP-ES did not require dilution unless concentrations (major elements) were too high for accurate measurement. For As, a 1 mL aliquot of solution was added to 4 mL of H_2O and 2.5 mL of HCl. An As^{V} stock solution was used for calibration as As is in the V valency state by after this leach.

The residue from this leach was subjected to a second 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ extraction to ensure that most of the labile organically bound fraction was dissolved before proceeding to digest the amorphous iron-oxide phase. This second leach was analyzed and the data were added to those of the first leach to represent the labile organic fraction.

0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.1M HCl leach ('amFeox', amorphous Fe/Al oxides)

To the residue from the previous step were added 20 mL of 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.1M HCl. The tube was capped, vortexed, and placed in a water bath at 60°C for 2 h with the cap loosened. Each sample was vortexed every 30 min (with the cap tightened). The solution was centrifuged for 10 min at 2800 rev/min and the supernatant decanted into a 50 mL centrifuge tube. Each residue was rinsed with 5 mL of water and the solution was vortexed and centrifuged. The rinse was added to the original supernatant (no second rinsing for this leach).

The solution was diluted 20-fold with 1% HNO_3 prior to analysis by ICP-MS; analysis was direct by ICP-ES. For As, a 2.5 mL aliquot of sample solution was added to 2.5 mL of H_2O and 2.5 mL of HCl prior to HG-ICP-ES analysis. Prereduction of As to As^{III} was unnecessary as As is present in this lower valency after application of this reducing leach.

1.0 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% $\text{CH}_3\text{CO}_2\text{H}$ ('cryFeox', crystalline Fe/Al oxides)

To the residue from the previous leach were added 30 mL of 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% $\text{CH}_3\text{CO}_2\text{H}$. The tube was capped, vortexed, and placed in a water bath at 90°C for 3 h with the cap on tightly. Every 30 min each sample was vented and vortexed (with the cap tightened). The solution was centrifuged for 10 min and the supernatant decanted into a 50 mL centrifuge tube. Each residue was rinsed with 5 mL of 25% $\text{CH}_3\text{CO}_2\text{H}$ and the solution was vortexed and centrifuged. The rinse was added to the original supernatant (no second rinsing for this leach).

The solution was diluted 20-fold with 1% HNO_3 prior to analysis by ICP-MS and 10-fold for ICP-ES analysis. For As measurement by HG-ICP-ES, a 1 mL aliquot of solution was added to 4 mL of H_2O and 2.5 mL of HCl; prereduction to As^{III} was unnecessary.

Aqua regia, 3 HCl:1 HNO_3 ('AR')

To the residue from the previous leach were added 6 mL of 12M HCl and 2 mL of 16M HNO_3 . The tube was capped and vortexed; the cap was then loosened and the sample allowed to sit in the fumehood overnight. The following morning, the solution was again vortexed, the cap loosened, and the tube placed in a water bath for 3 h at 90°C (temperature was gradually increased). The solution was vortexed every 20 min. Prior to the centrifuging step, the volume was made up to 30 mL with water. The supernatant was decanted into a 50 mL centrifuge tube; two 10 mL water rinses of the residue were carried out and added to the supernatant. Where necessary, the volume was adjusted to 50 mL prior to separation of aliquots for analysis.

The solution was diluted 50-fold with 1% HNO_3 prior to analysis by ICP-MS; ICP-ES analysis was direct. The preparation of samples for As analysis by HG-ICP-ES was similar to that for the $\text{Na}_4\text{P}_2\text{O}_7$ leach.

RESULTS

The results for the dry and wet splits of 25 samples from 'Green' Lake (D2) and 18 samples from 'Gravel Pit' Lake (D1) are attached as [Appendix A](#) and [Appendix B](#), respectively. All data are reported to the dry weight so that comparison is valid. Also provided with these results are detection limits for each element by leach and data for sample replicates (four), the LKSD-4 control (three insertions), and reagent blanks.

The repeatability of the extractions, as indicated by the four replicated samples (D1-15, D1-28, D2-11, and D2-16) is excellent across all elements and extractions, generally better than 10% relative standard deviation (RSD). The blank reagents taken through the procedures show that contamination was not a problem in any of the extractions. Table 1 lists the ranges in RSD obtained for LKSD-4 by element and leach in the 'dry' set of analyses; results for LKSD-4 were similar when analyzed amongst the 'wet' set of samples. Table 1 shows that the RSD for the majority of elements in all five leaches is better than 5%. Usually where the RSD is higher than this, the element concentration is within a decade of the particular detection limit. For example, the mean values for Sb (RSD 16%, Table 1) in LKSD-4 in the cryFeox phase and for Cr (RSD 22%, Table 1) in the AEC phase are 38 ppb (cf. detection limit of 16 ppb) and 0.7 ppm (cf. detection limit of 0.07 ppm), respectively (Appendix A). The data in Table 1 indicate that the precision associated with the five leaches is excellent and adequate to distinguish any significant differences in results obtained between wet and dry samples.

As the sequential leach was carried out immediately on the wet counterpart after sampling for wet and dry sub-samples, any changes in element patterns between the two sets of samples are assumed to be due to the effect of air drying. Results for several elements such as Re and B are not discussed as they were below detection limit for two or more leaches.

Peptization in the 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ leach: effect on Si

With the exception of Si, results for the total concentration of element extracted across all five leaches (the two pyrophosphate leaches are treated as one) applied to both cores agree well between the wet and dry samples. This is also true of the comparison of summed results with those based on aqua regia digestion of the replicate core reported by Kliza and Telmer (2001). However, the total amount of Si extracted from the wet sample was significantly more than in the dry counterpart for most of the samples, as shown in Table 2 for D2, 'Gravel Pit' Lake. Note that the data for the wet sample are also 'noisy' down the core, unlike those for the dry sample. Results for Al, S, Ni, and Cu are provided in Table 2 to demonstrate the excellent agreement between wet and dry data for all other elements determined. The poor agreement in Si was worse for D2 than for D1 and is thought to be due to peptization, the dispersion or suspension of colloidal material, in the 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ leach and to a lesser degree in the $\text{CH}_3\text{CO}_2\text{Na}$ leach, of the wet sample. This suspended material

Table 1. Relative standard deviation for three subsamples of CRM LKSD-4 taken through the sequential leach of the dry samples.

Phase	RSD ¹ (%)					
	0–5	6–10	11–15	16–20	21–25	>26
AEC	Y, Mo, Cd, Th, U, Al, Ba, Ca, Cu, Fe, Mg, Mn, Ni, P, S, Sc, Sr, Ti, V	Be, Zn, Rb, Sb, Cs, Ba, La, Ce, Ti, Pb, Bi, Si	Li, In, As	B, Co	Cr	
ORG	V, Mo, Cd, Sb, Ba, La, Ce, Ti, Pb, U, Al, Ca, Cu, Fe, Mg, Mn, S, Sc, Si, Sr, Ti, V	Li, Be, Zn, Rb, Bi, Th, As	Ag, Cs	Co	Cr, Ni	
AmFeox	Li, Be, B, Zn, Rb, Y, Cd, Cs, Ba, La, Ce, Ti, Pb, Bi, U, Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, S, Si, Sr, Ti, V, As	Ag, Sb	In			Mo, Th
CryFeox	Li, Zn, Rb, Mo, Cs, Ba, La, Ce, Pb, Bi, U, Al, Cu, Fe	Y, Cd, Ti, Mg, S, Si, Ti, V, As	Be, Ag, Mn	Sb, Sr	Co, Cr, Ni	Th, Ca
AR	Li, Be, Zn, Rb, Y, Sb, Cs, Ba, La, Ce, Ti, Pb, Bi, U, Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, S, Sc, Sr, Ti, V, As	Mo, Th, Co, Si				
Sum	Li, Be, Zn, Rb, Y, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Ti, Pb, Bi, Th, U, Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, S, Sc, Si, Sr, Ti, V, As	B, Co				

¹ RSD = relative standard deviation

Table 2. Comparison of total (summed across all five leaches) element concentrations extracted from wet and dry subsamples of 'Gravel Pit' Lake core.

Sample	Si (%)		Al (%)		S (ppm)		Ni (ppm)		Cu (ppm)	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
D2-01-02	1.08	0.89	2.62	2.52	3863	3558	37.6	38.8	773	778
D2-03	1.57	0.99	2.68	2.59	5204	5131	37.0	38.8	676	687
D2-04	1.57	0.94	2.91	2.72	4948	4850	36.4	38.4	485	477
D2-05	1.34	1.02	3.02	2.87	3023	3017	36.1	39.9	187	183
D2-06	0.96	1.16	3.01	3.01	1924	1970	39.4	40.2	126	125
D2-07	1.14	1.07	3.20	3.02	1422	1464	43.0	42.8	99.6	99.9
D2-08	1.42	1.02	3.34	3.01	1022	1059	42.5	43.6	51.6	47.1
D2-09	1.30	1.18	3.31	3.20	916	959	43.0	45.5	35.9	36.3
D2-10	1.04	1.12	3.35	3.21	979	952	44.1	44.0	37.4	36.2
D2-11	1.45	1.20	3.19	3.19	961	992	41.8	43.9	32.2	36.7
D2-12	1.58	1.13	3.47	3.12	1149	1066	44.4	41.6	43.1	37.6
D2-13	1.59	1.05	3.42	3.13	1175	1088	43.8	42.7	32.5	30.4
D2-14	0.97	1.08	3.39	3.03	1167	1124	42.8	41.1	33.4	29.8
D2-15	1.23	1.05	3.06	3.14	1023	1078	38.7	42.8	29.9	30.8
D2-16	1.33	1.11	3.54	3.18	1225	1169	44.8	43.7	36.8	32.8
D2-17	1.81	1.14	3.54	3.17	1346	1244	41.6	40.3	36.7	34.1
D2-18	1.26	1.24	3.37	3.21	1173	1120	41.5	40.5	34.8	32.3
D2-19	1.82	1.21	3.53	3.32	1061	1020	43.9	44.3	35.0	32.8

would therefore increase the result of the ICP-ES (or ICP-MS) analysis. This is demonstrated in Figure 1, where Si content in D2 is plotted by leach and total Si extracted against depth. The sediment of 'Gravel Pit' Lake was observed to have a much higher clay content than that of 'Green' Lake and was extremely hard to break up (using a pestle and mortar) when dry, as the particles had coalesced. Jeanroy and Guillet (1981) found that the $\text{Na}_4\text{P}_2\text{O}_7$ leach led to the dispersion in solution of finely divided (approximately 15 nm) ferruginous particles present in soils. In the present study, the silica-rich particles rather than the iron-rich particles appear to be dispersed in leaching the wet sample. Such fine-grained particles would have coalesced on drying and hence not report to the $\text{Na}_4\text{P}_2\text{O}_7$ leach.

Elements other than Si in D2 show the effect of peptization in the $\text{Na}_4\text{P}_2\text{O}_7$ leach, but their total extractable concentrations agree well. These elements include Al, Mg, Mn, Fe, and Ti. The profiles for Mn in Figure 2 are typical and suggest that the fraction of elements peptized during this leach of the wet sample would have reported to the two following oxide phases.

Sufficient sample of D2 remained in the refrigerator to apply the sequential leach again to the wet fraction, but this time incorporating ultracentrifugation (20 min at 16 000 rev/min) for the two 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ leaches to bring down suspended material. The results are presented in Table 3, together with the original dry set. Total Si extracted from the

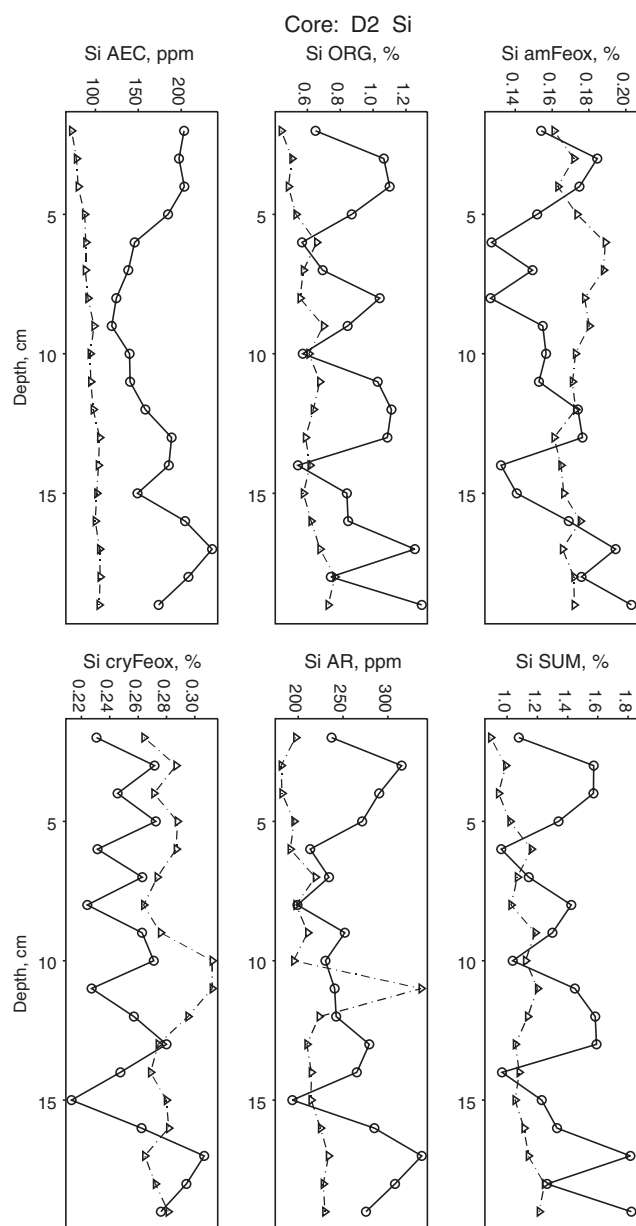


Figure 1. Geochemical profiles of Si in D2, 'Gravel Pit' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

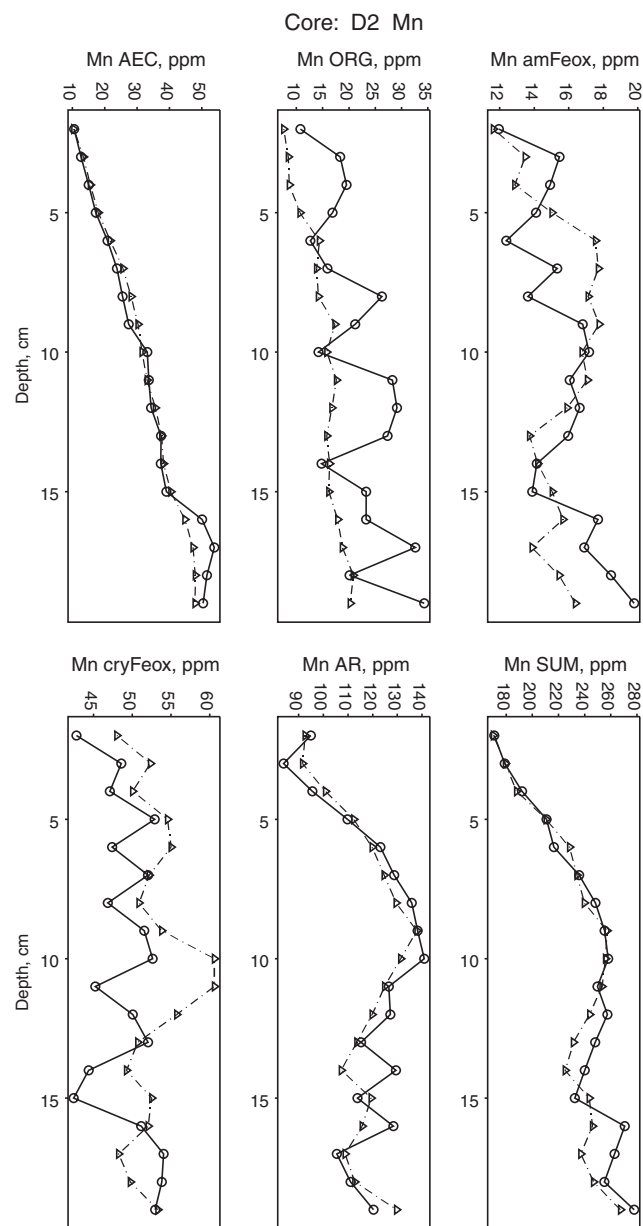


Figure 2. Geochemical profiles of Mn in D2, 'Gravel Pit' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Table 3. Comparison of Si results for the sequential leach applied to 'Gravel Pit' Lake core; results for the wet sample were obtained by ultracentrifuging (20 min at 16 000 rev/min).

Sample	AEC (ppm)		ORG (%)		AmFeox (%)		CryFeox (%)		AR (ppm)		Sum (%)	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
D2-01-02	505	72	0.47	0.44	0.14	0.16	0.23	0.26	305	197	0.93	0.89
D2-03	333	78	0.33	0.50	0.17	0.17	0.30	0.29	378	181	0.87	0.99
D2-04	550	80	0.56	0.48	0.19	0.16	0.33	0.27	417	182	1.18	0.94
D2-05	436	87	0.37	0.53	0.18	0.17	0.30	0.29	355	195	0.93	1.02
D2-06	517	89	0.39	0.65	0.16	0.19	0.27	0.29	314	191	0.91	1.16
D2-08	514	91	0.48	0.55	0.17	0.18	0.27	0.26	325	198	1.00	1.02
D2-09	766	98	0.39	0.70	0.15	0.18	0.25	0.28	305	211	0.90	1.18
D2-10	582	94	0.46	0.61	0.15	0.17	0.25	0.31	282	195	0.94	1.12
D2-11	747	94	0.47	0.67	0.16	0.17	0.28	0.31	330	337	1.02	1.20
D2-12	832	97	0.40	0.63	0.16	0.17	0.28	0.30	359	223	0.96	1.13
D2-13	494	105	0.40	0.59	0.15	0.16	0.26	0.27	299	210	0.90	1.05
D2-14	554	103	0.43	0.61	0.15	0.16	0.25	0.27	310	215	0.92	1.08
D2-15	473	102	0.43	0.57	0.15	0.17	0.27	0.28	297	214	0.93	1.05
D2-16	416	100	0.44	0.62	0.18	0.18	0.31	0.28	360	225	1.00	1.11
D2-17	489	105	0.49	0.67	0.16	0.17	0.28	0.26	319	234	1.01	1.14
D2-18	522	105	0.47	0.77	0.15	0.17	0.27	0.27	285	228	0.98	1.24
D2-19	510	104	0.54	0.72	0.16	0.17	0.25	0.28	283	230	1.03	1.21

wet and dry samples agree well, but consistently higher results for the wet sample were obtained in the AEC phase, with the reverse being true for the ORG phase. It should be kept in mind that the total Si extracted by the sum of these leaches was much less than the total Si in the sample as the strongest leach was aqua regia, in the absence of HF. As several weeks had elapsed since the initial sampling for the wet and dry sets, changes in phase distribution may have taken place (especially on exposure to the air) so that comparison of the dry data with the later wet ultracentrifuged data is not justified. The second set of results for the wet sample, however, indicates that ultracentrifuging should be used for the $\text{Na}_4\text{P}_2\text{O}_7$ leach in the application of such sequential leaching to clay-rich samples.

Results for Si in D1 are shown graphically in Figure 3; the wet samples from this core were not ultracentrifuged. Drying apparently reduces the amount of element reporting to the AEC and ORG phases, although the total Si leached from the wet and dry samples is in poor agreement for the top 14 cm of sediment. Thus the probable peptization of colloidal Si in this upper section of core invalidates a conclusion that drying has an effect on Si distribution amongst phases, other than to indicate coalescence of fine particles. The results from the lower section, however, suggest that coalescence is the only change occurring (Fig. 3). Titanium showed a behaviour pattern similar to that of silicon, although any changes between wet and dry samples were minimal and the total extracted Ti agreed well.

The following discussion focuses on the results for 'Green' Lake sediments and is organized according to the differences in patterns observed in the sequential leach results for wet and dry samples. Finally, results for 'Gravel Pit' Lake sediments are discussed where they differ substantially from those of 'Green' Lake sediments. Both lake-sediment cores showed overall enrichment in the top 8 to 15 cm in Zn, Cu, Pb, Cd, Tl, Ag, As, Sb, Bi, In, and S, elements emitted from the smelter.

'Green' Lake, D1

Sulphur (beryllium, scandium, titanium, thallium, and zinc)

No significant difference was found in the geochemical stratigraphy of S in the wet and dry cores of D1, as demonstrated by the six plots (for all phases, including the sum of leach data) in Figure 4. The agreement between these data sets is excellent, indicating both good precision in the application of these leaches and reasonable homogeneity in these samples. One sample in the dry set, at 28 cm depth, appears to be slightly enriched in Si (*see* 'SUM', Fig. 4), but this particular sample is anomalous in many other elements (e.g. Mg, Ca, Fe). As the samples above and below this sample show good agreement between wet and dry data, this anomaly is thought to be insignificant.

The top 12 to 14 cm of D1 show a dramatic enrichment of S in the labile AEC phase where soluble sulphates would report; the next two labile phases (ORG and amFeox) show a lesser increase in S concentration. The enrichment is probably caused by emissions from the Horne smelter, which began operation in 1926. The pattern of total S extracted is interesting: there is no steady decrease in concentration down the core to a constant minimum, rather there appears to be a decrease in S from about 9 to 22 cm after which there is an increase to about 0.5% S at a depth of 31 cm. Two distinct zones depleted in total S extracted occur, one at about 14 cm and another at 21 to 22 cm; such zones are observed for many elements. They are probably the result of an influx of (insoluble) sandy material that then dilutes the concentrations of the elements under study. Such enrichment in sand particles is clearly visible in the core. The 14 cm level coincides with a large increase in the *Ambrosia* pollen count, thought to indicate the establishment of the town of Rouyn-Noranda and the smelter (Grenier and Kliza, 2005). The reason for the influx of sand at the deeper level (22 cm) is unknown at this time.

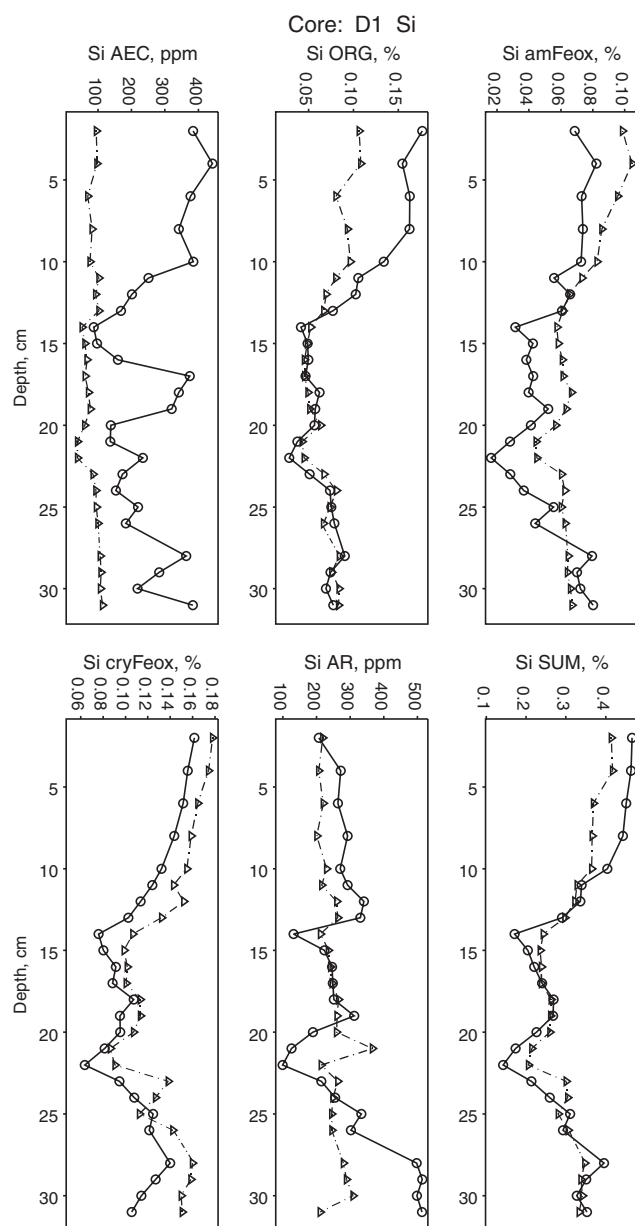


Figure 3. Geochemical profiles of Si in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

The agreement between wet and dry results for S in the lower part of the core is particularly interesting in that it may have been predicted that S, occurring as sulphide in this region, would have been oxidized to sulphate to some degree on air drying. The profiles for S in the aqua regia leach, thought to represent mostly sulphide-bound S, are in excellent agreement. This suggests that trace and minor elements present as sulphides will not show any change on drying. Beryllium, scandium, titanium, thallium, and zinc also show no redistribution of element associations on drying.

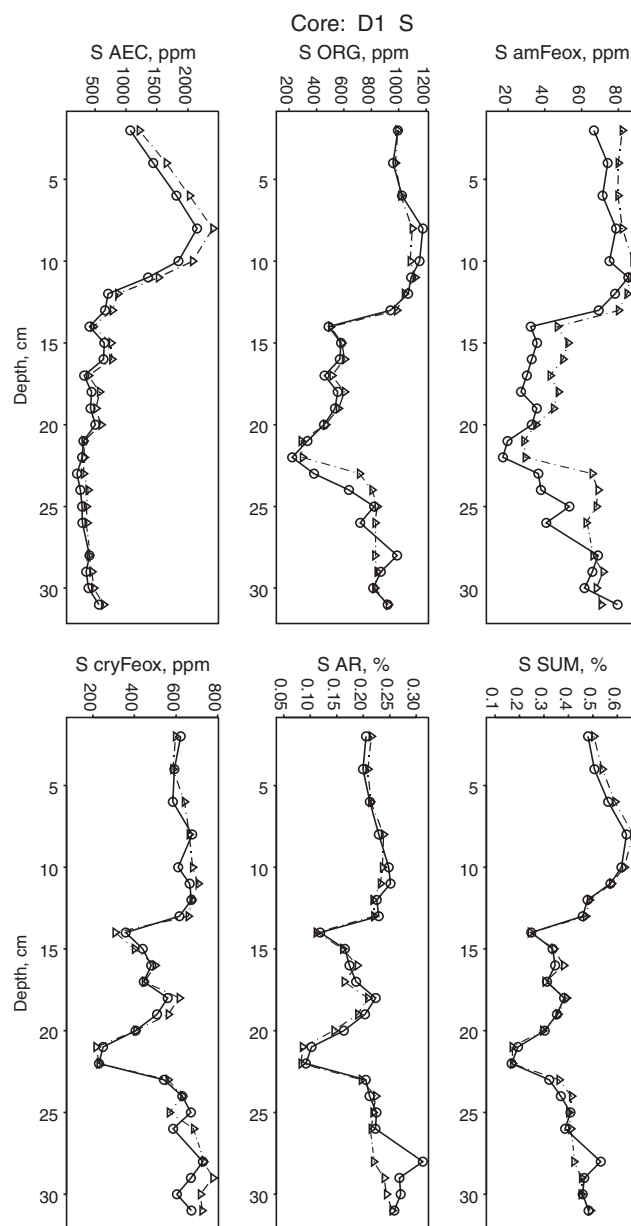


Figure 4. Geochemical profiles of S in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Calcium (strontium)

Not surprisingly, AEC is the dominant phase for Ca (Fig. 5). The only differences between wet and dry sample profiles are those for amFeox and cryFeox wherein the latter phase has a lower component throughout for the dry sample, as a greater amount was dissolved in the earlier amFeox leach. Furthermore, the profiles are different in shape but the absolute differences tend to be small (tens of parts per million) compared to the total Ca. The behaviour of Sr mimics that of Ca.

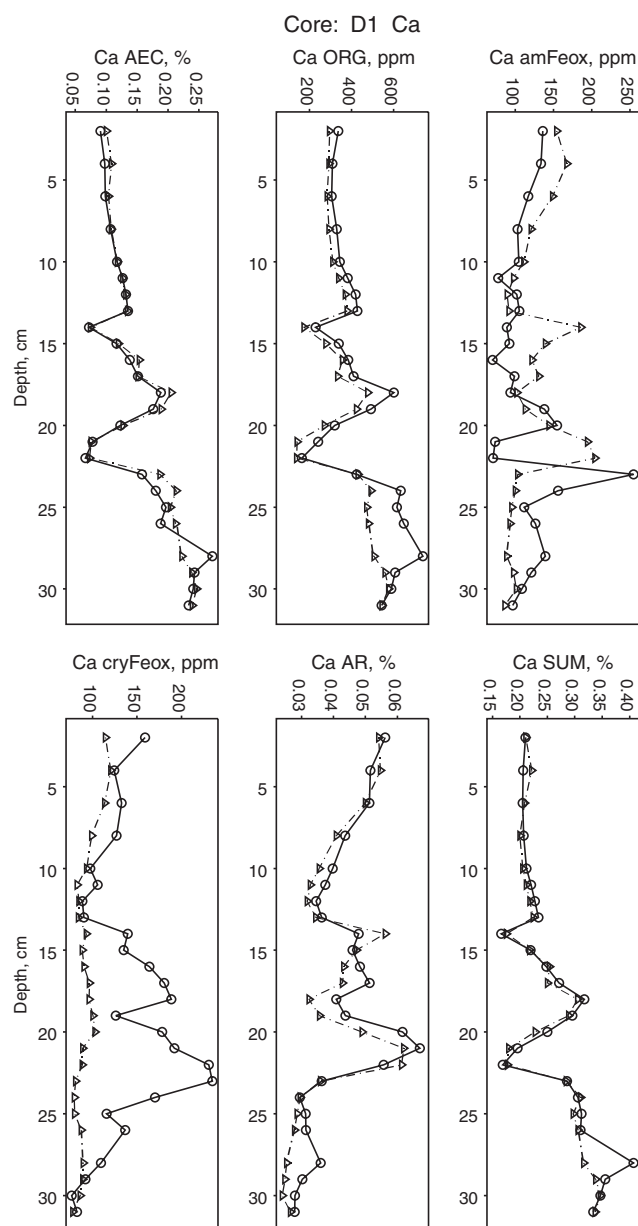


Figure 5. Geochemical profiles of Ca in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Magnesium (lithium)

Magnesium in the wet and dry samples shows differences in shape and intensity in the ORG and amFeox profiles, although these forms constitute only a fraction of the total Mg, most Mg being resistive to attack until the AR step (Fig. 6). A definite enrichment of ORG-Mg occurs in the upper 12 cm in the wet sample, but this is barely apparent in the dry sample. As this phase contains the least amount of Mg (approximately <3% of total extractable), this difference would not be a concern in studies where the overall distribution of Mg is under investigation; it would, however, where

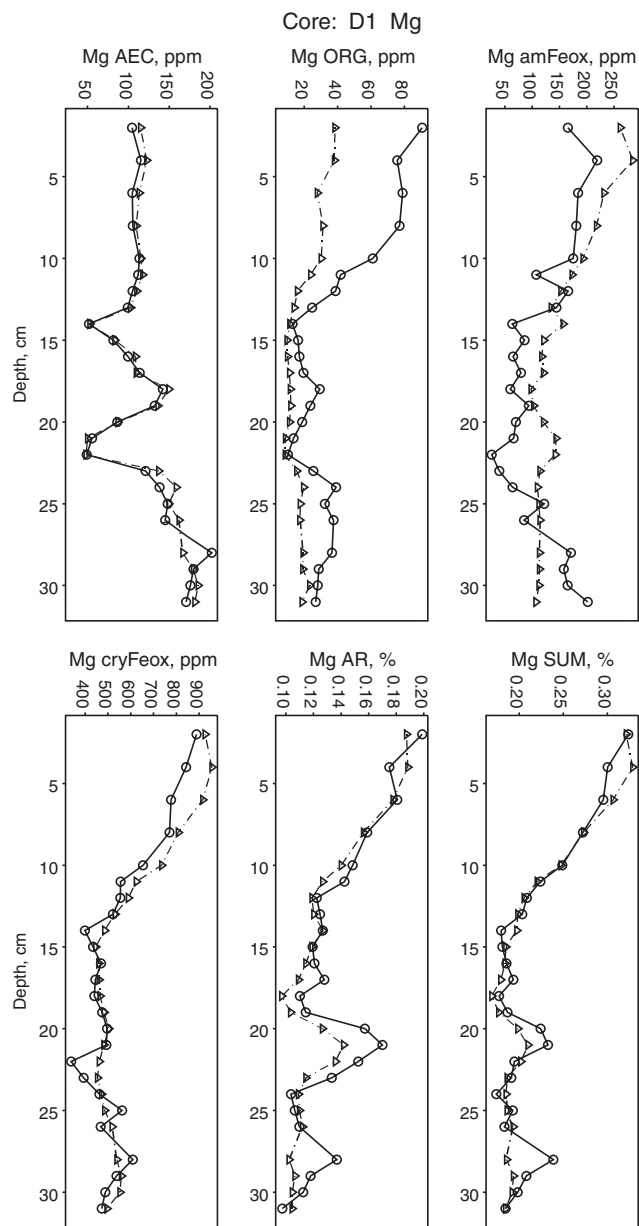


Figure 6. Geochemical profiles of Mg in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

this particular profile or phase association is the focus. Lithium, although approximately 250-fold lower in concentration, has profiles identical to magnesium profiles.

Iron (aluminium, copper, nickel, and cobalt)

The wet and dry profiles for Fe in the AEC and ORG phases are identical, although those in amFeox, cryFeox, and AR differ in absolute concentrations, but not in shape (Fig. 7). Iron appears to be more labile in the dry sample as higher concentrations of Fe are found in both oxide phases, leading to smaller amounts to be dissolved by aqua regia. Thus the effect of drying leads to an apparent enrichment in iron-oxide concentration in the upper 10 cm of the profile.

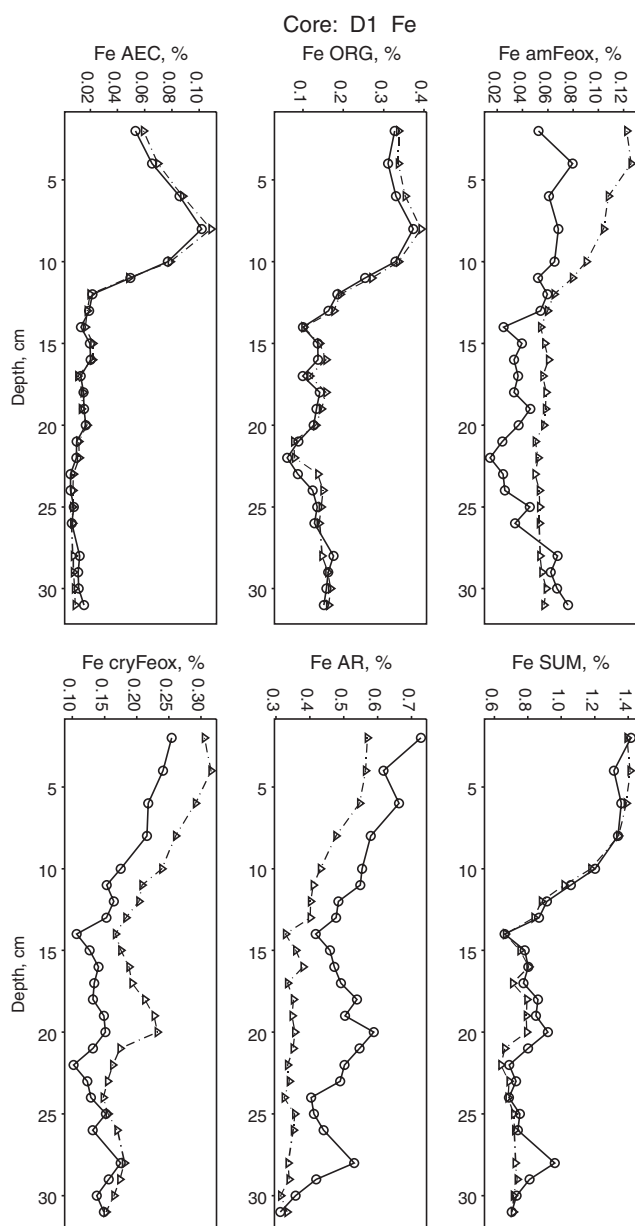


Figure 7. Geochemical profiles of Fe in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

The behaviour of Al is similar to that of Fe in all aspects including the distribution of Al amongst the phases, in the order Al in AR>ORG>cryFeox> (for Fe) or \approx (for Al) amFeox>AEC (Fig. 7). Copper, nickel, and cobalt behave like iron: drying promotes higher concentrations in the amFeox and cryFeox leaches, particularly apparent in the upper 12 cm. These differences in concentration, however, are small and in the order of a few parts per million for the trace elements as shown for Cu in Figure 8.

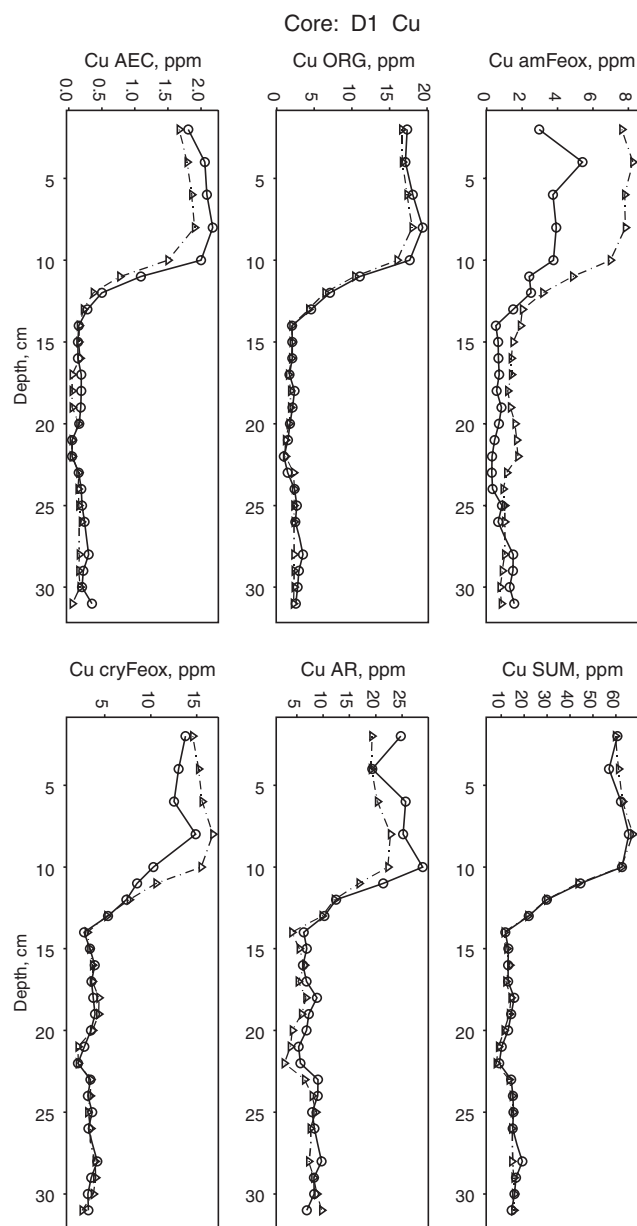


Figure 8. Geochemical profiles of Cu in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Manganese (arsenic and uranium)

Manganese appears to be more labile on drying in that significantly more is dissolved in the first leach (AEC) throughout the core (Fig. 9), apparently at the expense of dominantly AR-soluble Mn at the surface and amFeox- and cryFeox-associated Mn at depth. It is interesting that the greatest change in Mn, from the oxide phases to the most labile form, upon drying, occurs deeper in the core. This is the area of enrichment of the Mn-ORG association. The profiles themselves change in shape only in this region for these phases. Slightly higher levels of AEC-As occur in the dry sample, but the differences are below 10% of the total As (10–20 ppm) and do not lead to changes in the shapes of any profiles.

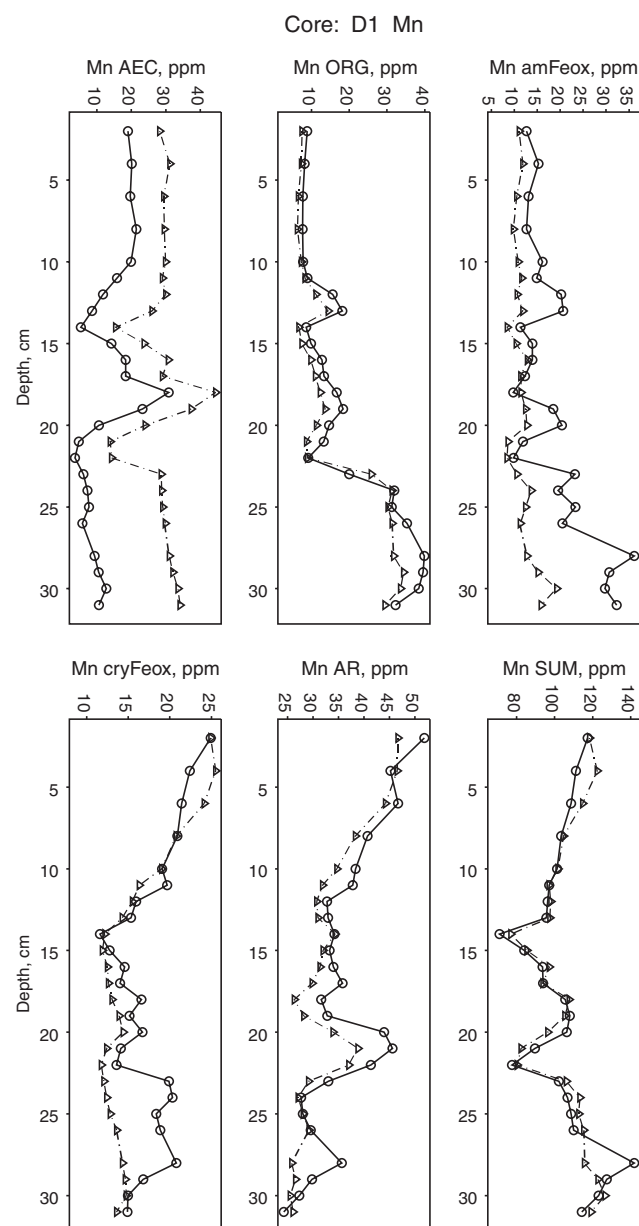


Figure 9. Geochemical profiles of Mn in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Uranium behaves in a manner similar to manganese in that a significant increase in the U-AEC component occurs on drying; however, the profile for the amFeox phase in the dry sample has a distinctly different shape (much flatter, and at lower concentrations; Fig. 10).

Lanthanum (all rare-earth elements, lead, indium, and silver)

Higher concentrations of labile REEs, In, Pb, and Y are found in the dry sample (AEC and amFeox), with concurrently lower values in the cryFeox and AR leaches (Fig. 11). However, the dominant phases for these elements, ORG and AEC, remain unchanged (Fig. 12, Pb). The profile shapes for Pb, In,

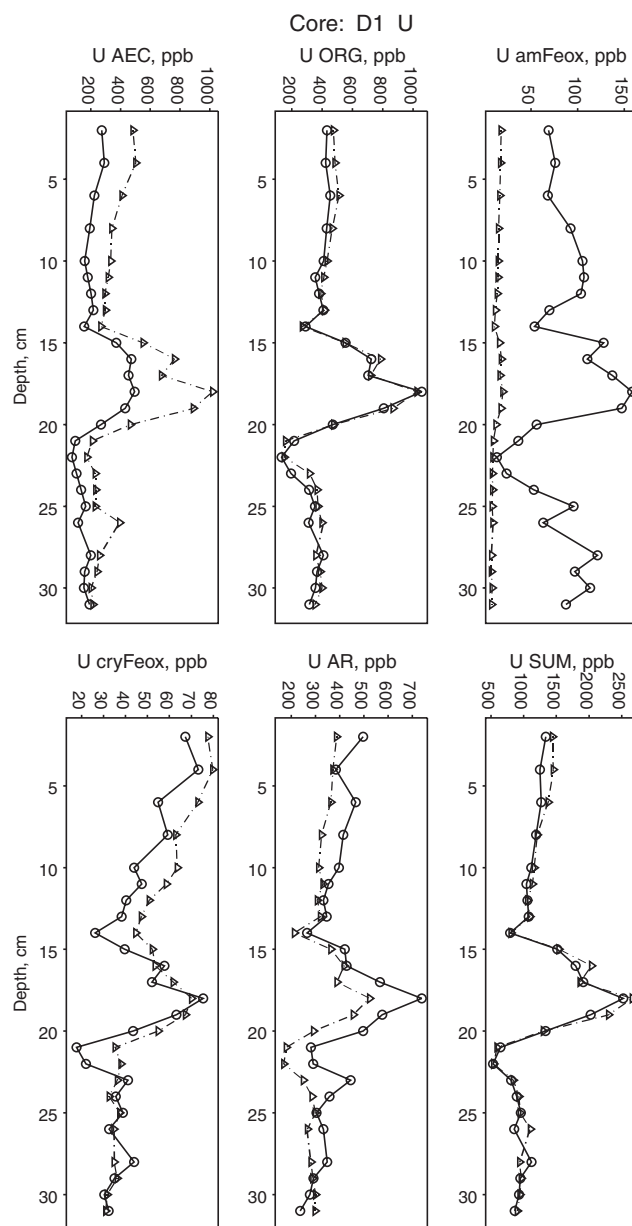


Figure 10. Geochemical profiles of U in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

and Ag differ from those of the REEs, showing a smooth enrichment in the upper 12 cm throughout. This level of enrichment is not changed greatly: for example, for Pb it increases from about 50 to 60 ppm to 70 to 80 ppm in the AEC phase (Fig. 12), compared to a background Pb concentration of approximately 2 ppm.

Rubidium (cesium and cadmium)

Concentrations of Rb, Cs, and Cd in AEC and amFeox phases are also higher in the dry sample, apparently at the expense of the ORG phase, and hence the enrichment in the upper 12 cm in the ORG form is diminished (Fig. 13, Rb).

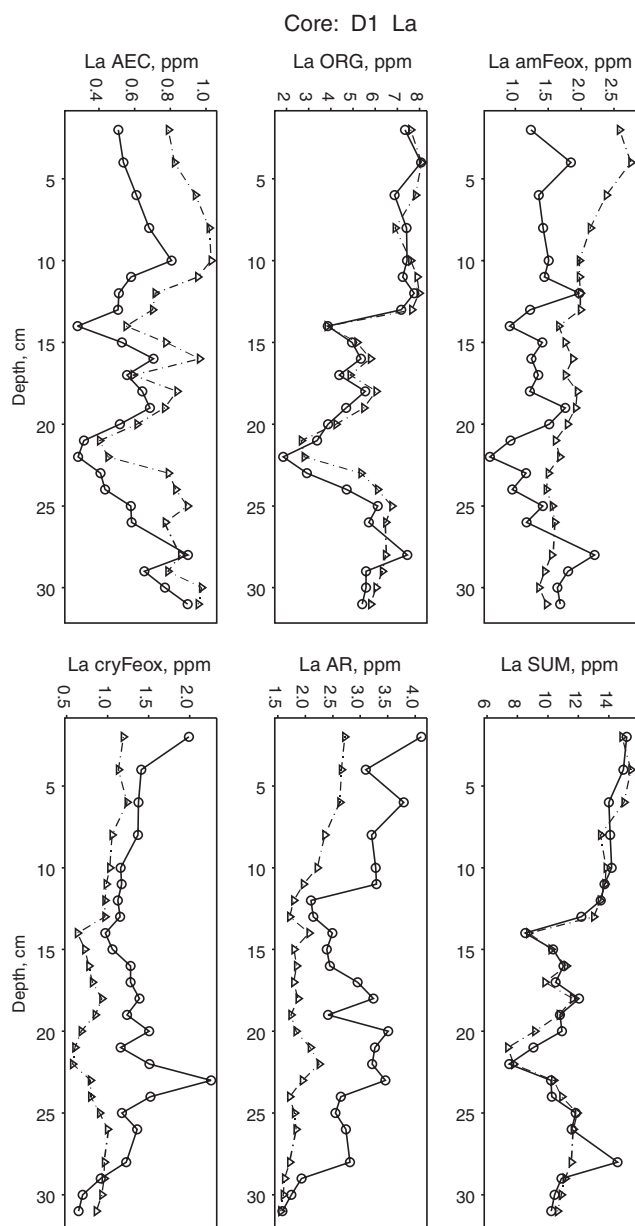


Figure 11. Geochemical profiles of La in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Vanadium (chromium, molybdenum, antimony, and barium)

Vanadium, chromium, molybdenum, antimony, and barium all show higher concentrations in the AEC and ORG phases on drying (Fig. 14, V). The amount of element dissolved by AR, and to a lesser degree that reporting to the amFeox phase, is consistently lower in the dry sample. The profile shapes for V, Cr, and Mo are similar, and very different to those for Sb where enrichment in the upper 12 cm is the main feature in all five phases. Both dry and wet sample patterns for Mo are similar to those for U (Fig. 10) with the sole exception that consistently about 20 to 25% more Mo-ORG is present in the

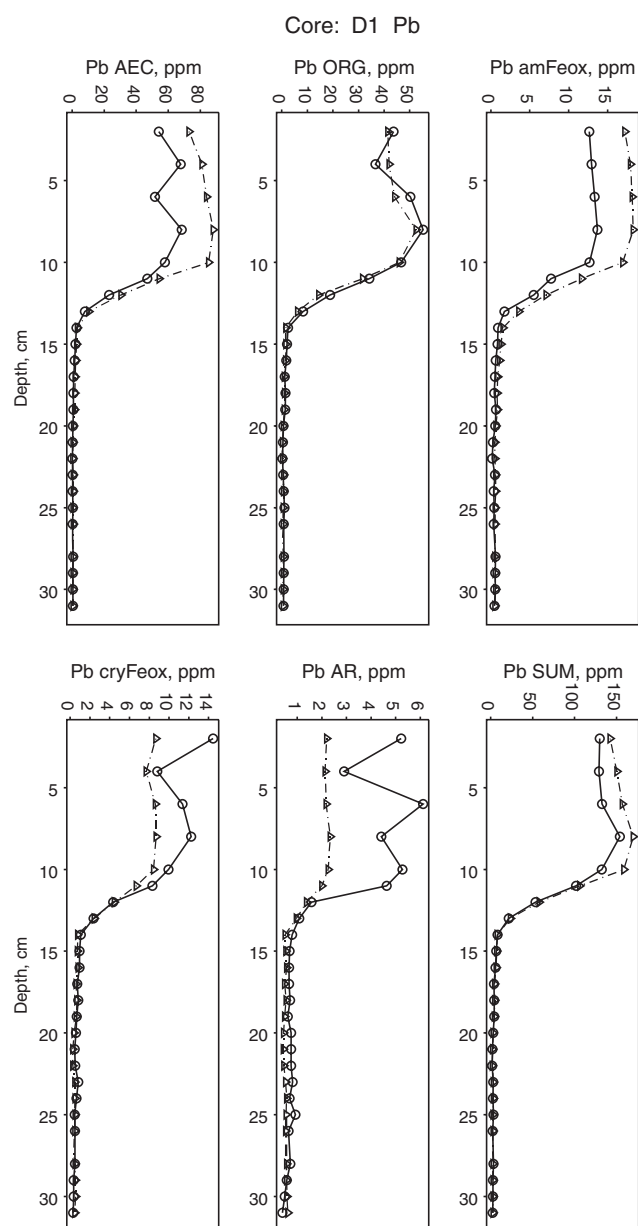


Figure 12. Geochemical profiles of Pb in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

dry sample. Although the profiles of Ba are similar in shape to those of Mg (Fig. 6), the changes occurring on drying mimic those shown by V.

Bismuth

The first four leaches dissolved more Bi in the upper 10 cm of the dry sample than in its wet counterpart, producing subsequently lower results in the AR dissolution (Fig. 15). The profiles are similar in shape to those for As, Sb, Pb, Cd, Cu, Tl, and Zn.

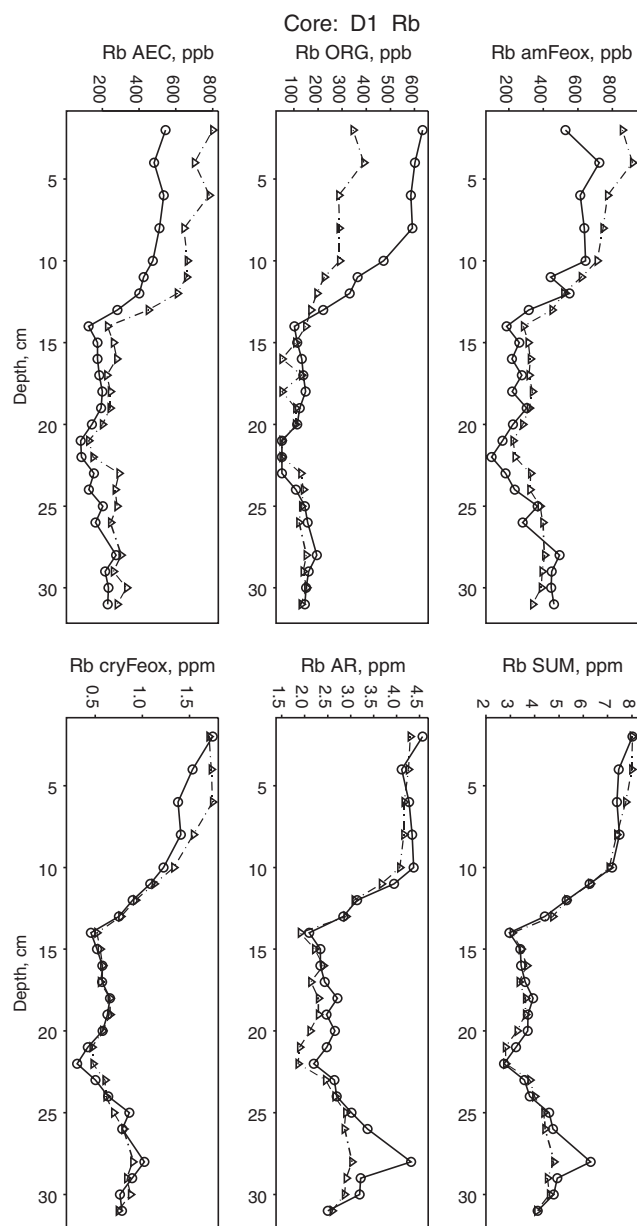


Figure 13. Geochemical profiles of Rb in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

'Gravel Pit' Lake, D2

Elements such as Cu, Zn, Pb, Ag, and As predominating in the smelter emissions show a very strong enrichment in the top 8 cm of the D2 core, consistent with the much higher *Ambrosia* pollen count encountered with the replicate core (Grenier and Kliza, 2005). Although the differences between wet and dry data for numerous elements (e.g. S, Rb, Cr, Cs, Tl, V, Zn) in D2 are similar to those in D1, there are elements whose changes in profile upon drying do not agree with those shown by D1. For example, no real change in profiles occurs for Fe (and Al) in the wet and dry samples, although the data are noisy (Fig. 16). However, Fe in D2 upon drying showed a significant shift to higher concentrations of the oxide phases,

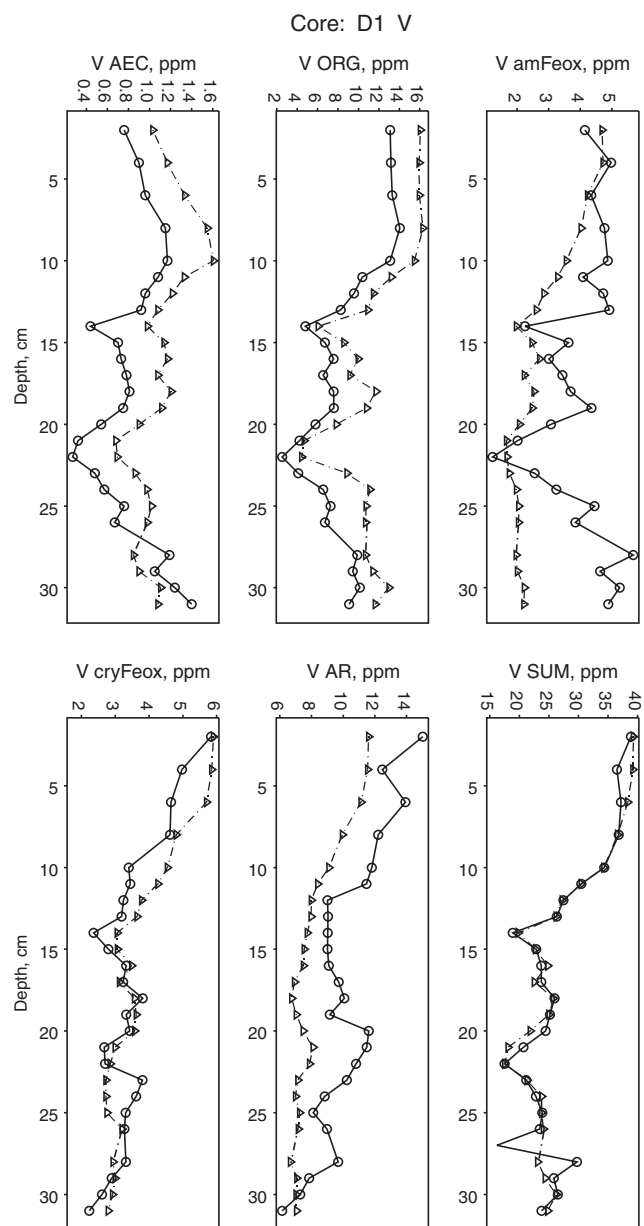


Figure 14. Geochemical profiles of V in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

from approximately 0.06% to 0.12% in the top 5 cm, with a commensurate decrease in aqua regia extractable Fe (Fig. 7). Thus, elements associated with the iron (and aluminium) oxide phases would also show a different behaviour in D2 compared to D1. For example, results for Cu and Co in wet and dry samples of D2 agree well (Fig. 17, Cu in D2). Also unlike the behaviour of D1, elements enriched in the top 8 cm of D2, such as Ag, As, Bi, Sb, and Pb, do not show any change in profile (concentration or shape) on drying and are similar to Cu. Figure 18 compares the profiles of Sb extracted in the first three leaches for D1 and D2: the shift to much greater amounts reporting to the AEC and ORG phases of D1 on drying is not reflected in the D2 profile.

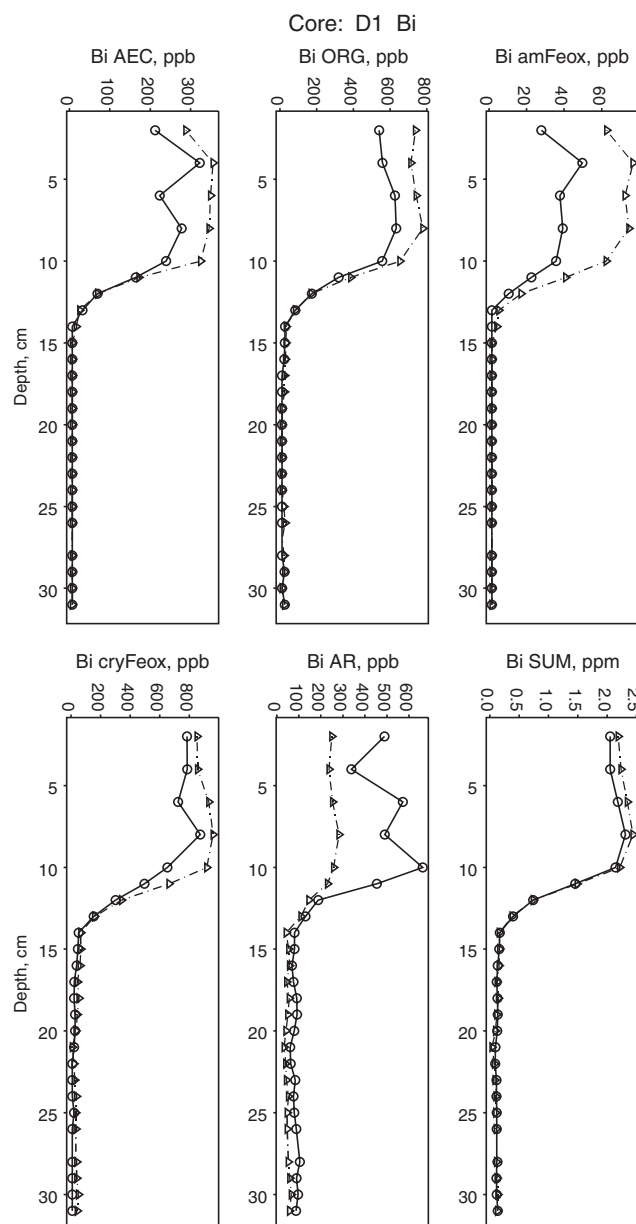


Figure 15. Geochemical profiles of Bi in D1, 'Green' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

The different behaviour of D1 and D2 sediment samples on drying indicates that the change in element distribution amongst phases is not only element-dependent, but also matrix-dependent, thus making a prediction difficult.

CONCLUSIONS

The behaviour of elements determined in the 'Green' Lake sediment core, upon sample drying, can be classified into the following three groups: those that show no redistribution (e.g. S, Zn, Tl); those that shift to more labile forms, dissolving earlier in the sequential extraction scheme (e.g. Fe, Mn, Cu, Pb, REEs); and those that shift to less labile forms (Mg, Li).

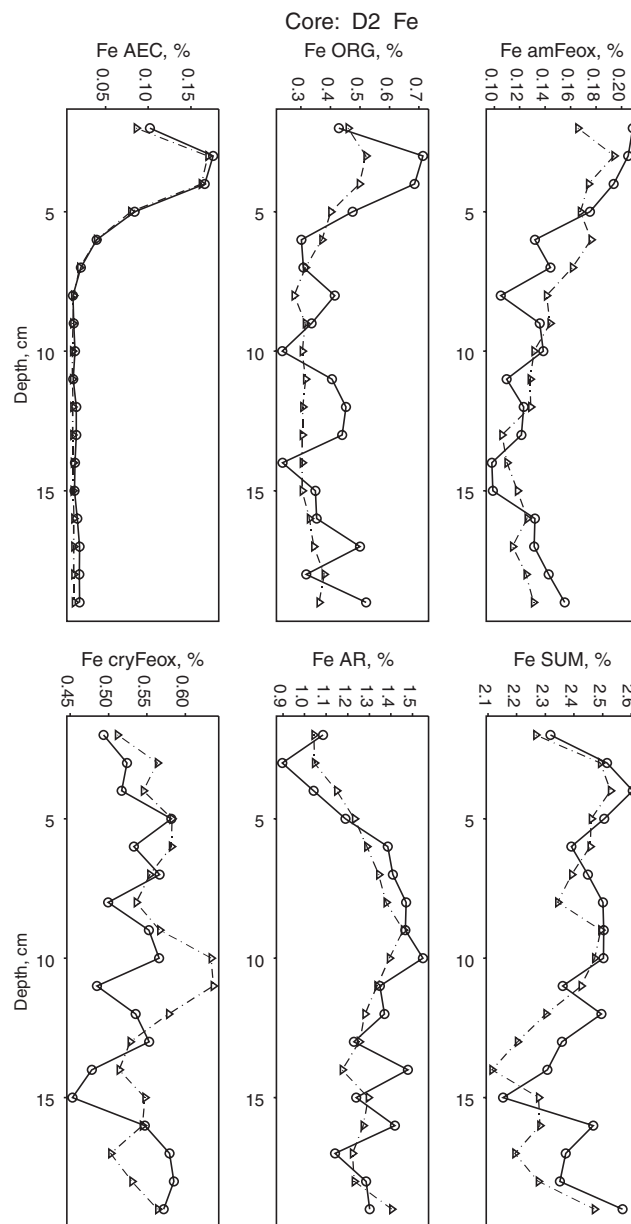


Figure 16. Geochemical profiles of Fe in D2, 'Gravel Pit' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

Most elements show redistribution to more labile forms, such as Fe where increases in the oxide phases were observed with a concomitant decrease in the amount of Fe reporting to the final aqua regia digestion. The nature of the shift to more labile forms differs in that increases may be encountered in the adsorbed/exchangeable/carbonate, 'soluble' organic and/or amorphous Fe/Al phases, with depletion in the crystal-line phases. These changes are generally small in magnitude (<10% of the total element extracted), but they can change the shape of the element profile down the core for an affected leach. This can have implications for studies focused on a single leach such as one designed to quantify the 'bioavailable'

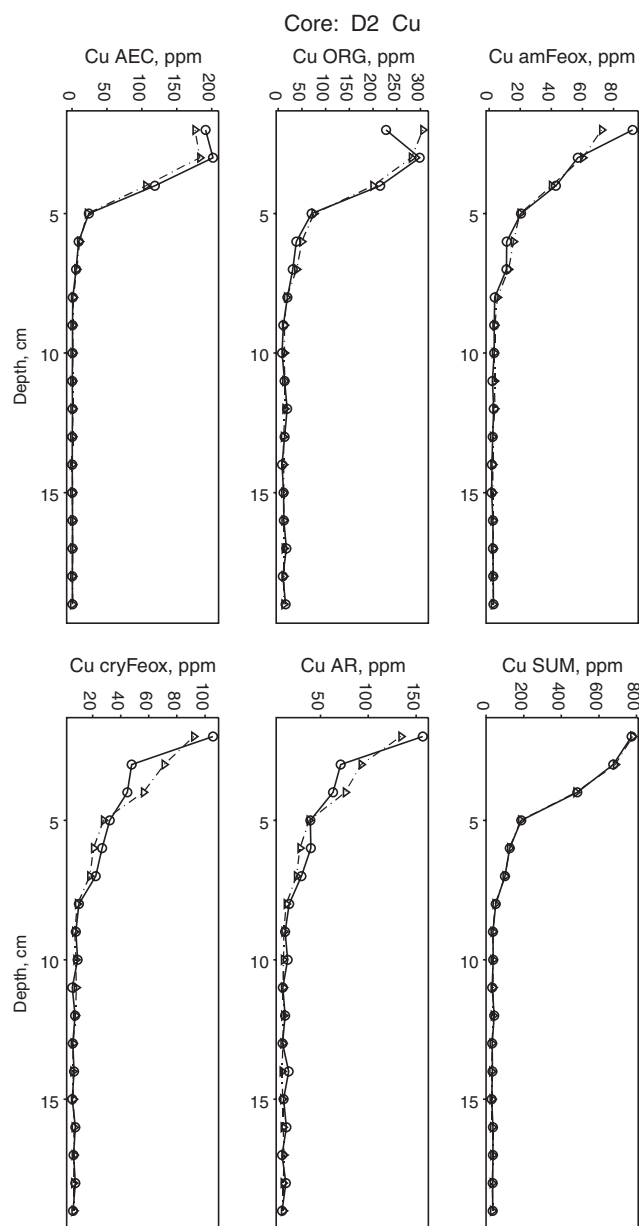


Figure 17. Geochemical profiles of Cu in D2, 'Gravel Pit' Lake sediment core; solid line, 'wet' sample; dashed line, 'dry' sample.

or easily labile form of an element where the amount indicated by a dried sample may be substantially greater than it should be.

The relatively small degree of element redistribution on drying found in this study and the stability of the S forms suggest that oxidation can be a long process and more serious problems would be encountered on storage of the dried sample. The fact that the 'Gravel Pit' Lake core showed different behaviour from the 'Green' Lake core for some elements such as Fe (no redistribution) indicates that these changes in element phase distribution are both element- and matrix-dependent, and hence difficult to predict.

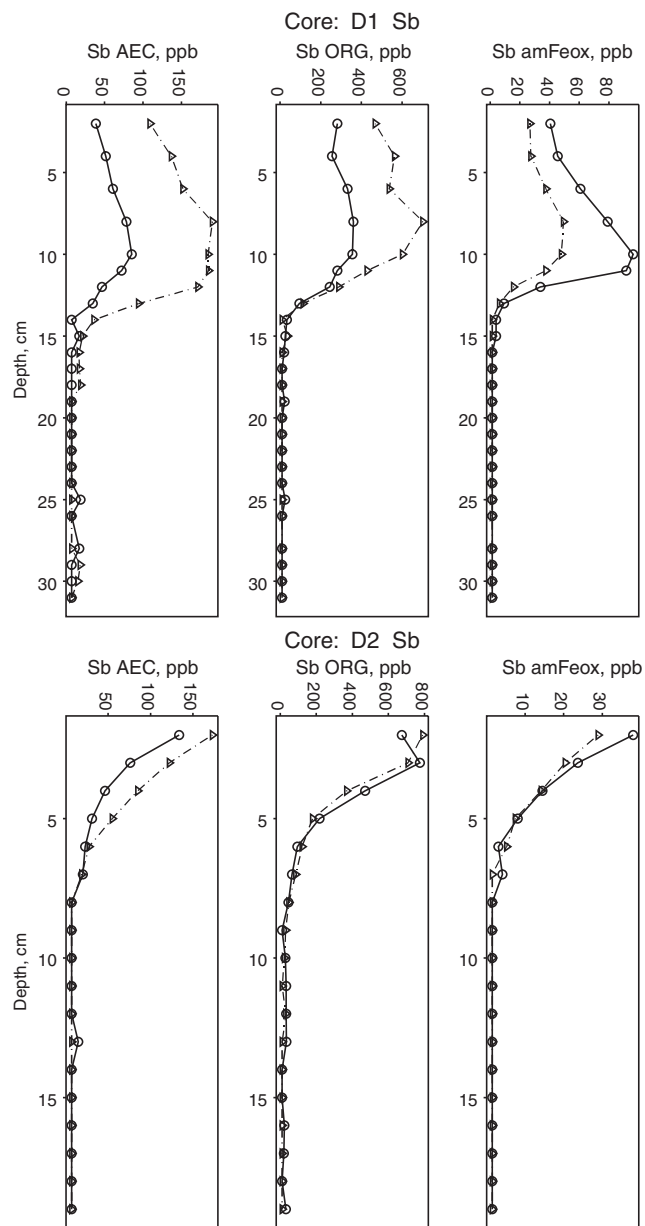


Figure 18. Geochemical profiles of Sb in first three phases of D1 and D2; solid line, 'wet' sample; dashed line, 'dry' sample.

In the application of sequential extraction analysis to lake sediments, it is recommended that samples be kept moist, cool (4°C), and in an inert atmosphere (N_2) upon collection and analyzed as soon as they are received in the laboratory. They should not be dried but rather centrifuged and the first leach begun. If the sediment is rich in clay particles, ultra-centrifuging should be employed for pyrophosphate, and perhaps acetate, extractions to minimize peptization and hence erroneous results.

REFERENCES

- Astrom, M.**
1998: Mobility of Al, Co, Cr, Cu, Fe, Mn, Ni and V in sulphide-bearing fine-grained sediments exposed to atmospheric O₂: an experimental study; *Environmental Geology*, v. 36, p. 219–226.
- Bartlett, R. and James, B.**
1980: Studying dried, stored soil samples — some pitfalls; *Journal of the American Soil Science Society*, v. 44, p. 721–724.
- Bunzl, K., Schimmack, W., Schramel, P., and Suomela, M.**
1999: Effect of sample drying and storage time on the extraction of fallout ²³⁹⁺²⁴⁰Pu, ¹³⁷Cs and natural ²¹⁰Pb as well as of stable Cs, Pb and Mn from soils; *Analyst*, v. 124, p. 1383–1387.
- Chao, T.T.**
1984: Use of partial dissolution techniques in geochemical exploration; *Journal of Geochemical Exploration*, v. 20, p. 101–135.
- Fiedler, H.D., Lopez-Sanchez, J.F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A.M., and Muntau, H.**
1994: Study of the stability of extractable trace metal contents in a river sediment using sequential extraction; *Analyst*, v. 119, p. 1109–1114.
- Filipek, L.H. and Theobald, P.K.**
1981: Sequential extraction techniques applied to a porphyry copper deposit in the basin and range province; *Journal of Geochemical Exploration*, v. 14, p. 155–174.
- Flores, L., Blas, G., Hernandez, G., and Alcalá, R.**
1997: Distribution and sequential extraction of some heavy metals from soils irrigated with wastewater from Mexico City; *Water, Air, & Soil Pollution*, v. 98, p. 105–117.
- Gatehouse, S., Russell, D.W., and Van Moort, J.C.**
1977: Sequential soil analysis in exploration geochemistry; *Journal of Geochemical Exploration*, v. 8, p. 483–494.
- Gilliss, L., Al, T.A., Blowes, D.W., and Hall, G.E.M.**
2004: Geochemical dispersion in groundwater from a weathered Cu-Zn deposit in glaciated terrain; *Geochemistry: Exploration, Environment, Analysis*, v. 4, issue 4, p. 291–305.
- Grenier, A. and Kliza, D.A.**
2005: Pollen analysis of sediment cores from lakes in the Rouyn-Noranda region, Quebec; in *Metals in the Environment Around Smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and Conclusions of the GSC MITE Point Sources Project*, (ed.) G.F. Bonham-Carter; Geological Survey of Canada, Bulletin 584.
- Gutierrez, M.**
2000: Trace element concentration patterns in sediments of the Lower Rio Conchos, Mexico; *Water, Air, & Soil Pollution*, v. 121, 259–270.
- Hall, G.E.M. and Pelchat, P.**
1999: Comparability of results obtained by the use of different selective extraction schemes for the determination of element forms in soils; *Water, Air, & Soil Pollution*, v. 112, p. 41–53.
- Hall, G.E.M., Gauthier, G., Pelchat, J.C., Pelchat, P., and Vaive, J.E.**
1996: Application of a sequential extraction scheme to ten geological standard reference materials for the determination of 20 elements; *Journal of Analytical Atomic Spectrometry*, v. 11, p. 787–796.
- Hall, G.E.M., MacLaurin, A.I., Pelchat, J.C., and Gauthier, G.**
1997: Comparison of the techniques of atomic absorption spectrometry and inductively coupled plasma mass spectrometry in the determination of Bi, Se and Te by hydride generation; *Chemical Geology*, v. 137, p. 79–89.
- Hall, G.E.M., MacLaurin, A.I., and Vaive, J.E.**
1995: Readsorption of gold during the selective extraction of the 'soluble organic' phase of humus, soil and sediment samples; *Journal of Geochemical Exploration*, v. 54, p. 27–38.
- Henderson, P.J., McMartin, I., Hall, G.E.M., Walker, D., and Percival, J.B.**
1997: The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba, Canada; *Environmental Geology*, v. 34, no. 1, p. 39–58.
- Howari, F.M. and Banat, K.M.**
2001: Assessment of Fe, Zn, Cd, Hg, and Pb in the Jordan and Yarmouk river sediments in relation to their physicochemical properties and sequential extraction characterization; *Water, Air, & Soil Pollution*, v. 132, p. 43–59.
- Howe, S.E., Davidson, C.M., and McCartney, M.**
2002: Determination of uranium concentration and isotopic composition by means of ICP-MS in sequential extracts of sediment from the vicinity of a uranium enrichment plant; *Journal of Analytical Atomic Spectrometry*, v. 17, p. 497–501.
- Jeanroy, E. and Guillet, B.**
1981: The occurrence of suspended ferruginous particles in pyrophosphate extracts of some soil horizons; *Geoderma*, v. 26, p. 95–105.
- Kelley, D.L., Hall, G.E.M., Closs, G., Hamilton, I., and McEwen, R.M.**
2003: The use of partial extraction geochemistry for copper exploration in northern Chile; *Geochemistry: Exploration, Environment, Analysis*, v. 3, no. 1, p. 85–104.
- Kersten, M. and Forstner, U.**
1986: Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments; *Water Science Technology*, v. 18, p. 121–130.
- 1989: Speciation of trace elements in sediments; in *Trace Element Speciation: Analytical Methods and Problems*, (ed.) G. Batley; CRC Press, Boca Raton, Florida, p. 245–317.
- Kheboian, C. and Bauer, C.F.**
1987: Accuracy of selective extraction procedures for metal speciation in model aquatic sediments; *Analytical Chemistry*, v. 59, p. 1417–1423.
- Kliza, D.A. and Telmer, K.**
2001: GSC-MITE Phase 1: lake sediment studies in the vicinity of the Horne smelter in Rouyn-Noranda, Quebec; Geological Survey of Canada, Open File 2952 (CD-ROM).
- Lazareva, E.V., Shuvaeva, O.V., and Tsimbalist, V.G.**
2002: Characterization of arsenic species in microbial mats from an inactive gold mine; *Geochemistry: Exploration, Environment, Analysis*, v. 3, p. 263–268.
- Lynch, J.J.**
1990: Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; *Geostandards Newsletter*, v. 14, p. 153–167.
- Pichler, T., Hendry, M.J., and Hall, G.E.M.**
2001: The mineralogy of arsenic in uranium mine tailings at the Rabbit Lake in-pit facility, northern Saskatchewan, Canada; *Environmental Geology*, v. 40, p. 495–506.
- Quevauviller, P., Rauret, G., Muntau, H., Ure, A.M., Rubio, R., Lopez-Sanchez, J.F., Fiedler, H.D., and Griepink, B.**
1994: Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments; *Fresenius' Journal of Analytical Chemistry*, v. 349, p. 808–814.
- Rate, A.W., Robertson, A.E., and Borg, A.T.**
2000: Distribution of heavy metals in near-shore sediments of the Swan River Estuary, Western Australia; *Water, Air, & Soil Pollution*, v. 124, p. 155–168.
- Saeki, K., Okazaki, M., and Matsumoto, S.**
1993: The chemical phase changes in heavy metals with drying and oxidation of the lake sediments; *Water Resources*, v. 27, p. 1243–1251.
- Simonetti, A., Bell, K., and Hall, G.E.M.**
1996: Lead isotopic ratios and elemental abundances for selective leaches from near-surface till: implications for mineral exploration; *Applied Geochemistry*, v. 11, p. 721–734.
- Siripinyanond, A.B., Barnes, R.M., and Amarasiwardena, A.**
2002: Flow field-flow fractionation-inductively coupled plasma mass spectrometry for sediment bound trace metal characterization; *Journal of Analytical Atomic Spectrometry*, v. 17, p. 1055–1064.
- Stephens, S.R., Alloway, B.J., Parker, A., and Carter, J.E.**
2001a: Towards the characterisation of heavy metals in dredged canal sediments and an appreciation of 'availability': two examples from the UK; *Environmental Pollution*, v. 113, p. 395–401.
- Stephens, S.R., Alloway, B.J., Parker, A., Carter, J.E., and Hodson, M.E.**
2001b: Changes in the leachability of metals from dredged canal sediments during drying and oxidation; *Environmental Pollution*, v. 114, p. 407–413.
- Tack, F.M.G., Singh, S.P., and Verloo, M.G.**
1998: Heavy metal concentrations in consecutive saturation extracts of dredged sediments derived surface soils; *Environmental Pollution*, v. 103, p. 109–115.
- 1999: Leaching behaviour of Cd, Cu, Pb and Zn in surface soils derived from dredged sediments; *Environmental Pollution*, v. 106, p. 107–114.

Tessier, A., Campbell, P.G.C., and Bisson, M.

1979: Sequential extraction procedure for the speciation of particulate trace metals; *Analytical Chemistry*, v. 51, p. 844–850.

Thomson, E.A., Luoma, S.N., Cain, D.J., and Johansson, C.

1980: The effect of sample storage on the extraction of Cu, Zn, Fe, Mn and organic materials from oxidised estuarine sediments; *Water, Air, & Soil Pollution*, v. 14, p. 215–233.

Turek, M., Korolewicz, T., Ciba, J., and Cebula, J.

2002: Sequential extraction and determination of chemical forms of zinc in sulfate sludge; *Water, Air, & Soil Pollution*, v. 135, p. 311–323.

Turer, D., Maynard, J.B., and Sansalone, J.J.

2001: Heavy metal contamination in soils of urban highways: comparison between runoff and soil concentrations at Cincinnati, Ohio; *Water, Air, & Soil Pollution*, v. 132, p. 293–314.

Van Den Berg, G.A., Loch, J.P.G., and Winkels, H.J.

1998: Effect of fluctuating hydrological conditions on the mobility of heavy metals in soils of a freshwater estuary in the Netherlands; *Water, Air, & Soil Pollution*, v. 102, p. 377–388.

Wang, X.

1998: Leaching of mobile forms of metals in overburden: development and application; *Journal of Geochemical Exploration*, v. 61, p. 39–55.