

Early Diagenesis of Sediment from Kelly Lake, Sudbury, Ontario- a Lake Contaminated by Sewage Effluent and High Levels of Copper and Nickel from Mining and Smelting

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Abstract

Since the 1880's (early settlement in Sudbury) Kelly Lake has been the major sink for contaminants from a mining community due to its location at the foot of Sudbury's watershed. This is seen by the 120cm of metal rich, nutrient rich sediment that has accumulated in the eastern basin of the lake.

Sediment cores 120cm long have been sub-sampled at a resolution of 1cm for the first 15cm, every 5cm from 15 to 60cm, and every 10cm from 60 to 120cm. The sub-samples have been sequentially leached to determine the concentration of Ni and Cu that is associated with the fractions referred to as 1. easily exchangeable, 2. carbonate bound, 3. Fe/Mn bound, 4. organic bound, 5. residual recalcitrant, and 6. residual. The pore water has been centrifuged; filtered with a 0.2µm mesh size and analyzed to determine mineralization using saturation indexes.

The leach has shown that the residual fraction (largely quenched smokestack particles with a silicate rim) based on profile averages contains 0.5% of the 8.7mg/g of Ni and 0.4% of the 4.8mg/g of Cu. Fe/Mn oxides bind 56% of the Ni, closely followed by the organic fraction binding 32% and the carbonate and residual recalcitrant portions both binding 4.5%. The oxide fractions of Ni and Mn have a strong correlation through sediment profiles suggesting that they are co-precipitates. The organic bound fraction complexes 90% of the Cu, likely as an organo-sulphur complex and the residual recalcitrant fraction binds 7%. Fractions not discussed above bind less than 2% of the metals. SEM analysis has shown covellite and mackinawite or amorphous FeS growth rims on air-borne stack particles that have been deposited in the lake. Pore water analysis shows an increase in DOC and a decrease in dissolved Cu with depth suggesting that the interaction between DOC and Cu is not sufficiently strong to prevent the formation of Cu sulphides.

Introduction

Sedimentary diagenesis refers to processes that bring about changes in sediment subsequent to its deposition in water. These processes may be physical (compactive), biogeochemical (bacterial decomposition), or biological (Callender, 2000). Good comprehension of diagenesis is important in determining the potential availability of deleterious substances in sediment (Berner, 1980; Song and Muller, 1999).

One of the most important reactions is the mineralization of organic matter, which is often biologically catalyzed (Callender, 2000; Song

and Muller, 1999). Organic matter is oxidized by the oxidant yielding the greatest free energy change per mole of organic carbon oxidized. When this oxidant is depleted, oxidation will proceed utilizing the next most efficient oxidant (Froelich et al., 1979 and Berner 1980). The main pathways for the degradation of organic matter from most to least efficient are aerobic respiration, denitrification, manganese reduction, iron reduction, and sulphate reduction (Callender, 2000; Song and Muller, 1999). The degradation of sedimentary organic matter by heterotrophic microorganisms is responsible for the zonation of redox conditions (Froelich et al., 1979). These redox transformations result in phase transformations of the above oxidants and associated metals (Callender, 2000).

Study Area

Kelly Lake covers 339 hectares and is 4.5 km long and 1.1 km at its widest point, with its major axis orientated along the NE to SW direction. The lake is divided into a deep basin area at the east end and a shallow shelf at the west end (Figure 1). The deepest part of the lake is just over 18 metres during high water periods, but commonly around 17 metres during the summer. Almost 20 percent of the lake is deeper than 12 metres and over 50 percent of the lake is less than 2 metres deep. Kelly Lake has two major inlets on the northwest end: Junction Creek and Lilly Creek. The lake's primary source of water is Junction Creek. Historically this water has been contaminated with phosphates, suspended solids and dissolved metals. The second source of water for the lake is Lilly Creek, coming from Robinson Lake (figure 1). This creek delivers a significantly lower volume of water but it is relatively clean as much of it is derived from Ramsey Lake, one of Sudbury's drinking water sources. The outflow from Kelly Lake is at its southeast end and from there water travels through a small chain of residentially populated lakes to the Vermilion and Spanish Rivers and eventually Lake Huron.

Kelly Lake Sediment

The sediment in Kelly Lake contains not only the products of early diagenesis, but a historical record of the growth and development of the upper Junction Creek watershed. Part of this historical record can be seen in the sedimentation rates in the Junction Creek delta in Kelly Lake over the past hundred years. The progradation rates of the delta indicate a period of maximum terrestrial sediment supply between 1928 and 1956 (Pearson, et.al., in press). Most of this increased sedimentation was due to erosion in the watershed that primarily supplied inorganic layers during periods of high surface runoff. Settling organic material deposited during productive times resulted in apparent varves (annual silt and organic couplets) in the sediment. Figure 2 shows a segment of the layered sediment taken 50 cm from the surface in a sediment core (station 38, figure 1). The

greatest sedimentation at station 38 was during the late 1980's/early 1990's, probably because by then the delta top had encroached closer to station 38. During this period of peak sedimentation nearly 3 cm per year accumulated at the bottom of the eastern basin of the lake. This rate is near the 5-10 cm yr⁻¹ limit that may hinder early diagenesis due to the limits of microbiologically mediated reactions (Callender, 2000).

Other key factors to be considered when examining this sediment are Inco Ltd's construction of the 371 metre smelter stack in 1972 and the Copper Cliff Waste Water Treatment Plant (1976). Smelting processes in the Copper Cliff smelter release metal rich microspheres into the air. They are then deposited as atmospheric fallout on the land and water. In Kelly Lake these microspheres are richest in the inorganic silt layer in the sediment (figure 4). Taller stacks disperse the contaminants over a greater distance than shorter stacks, therefore reducing the quantity of particulate falling close to the source. Furthermore, various precipitation techniques and processing changes followed the building of the stack and reduced metallic particulate emissions by more than 50% (Bouillon, 1995). The water treatment plant removes the majority of the dissolved metals before the effluent is released into the environment. These technological advances have substantially altered the geochemical composition of the sediment in Kelly Lake.

When studying lacustrine sediment cores, the question of whether the geochemical data represents distinct depositional events or early sedimentary diagenesis is often asked. Both distinct events and diagenetic effects have been studied in order to determine the potential release of Ni and Cu from Kelly Lake sediment. This has been achieved through detailed stratigraphic analysis and age dating cores using ¹³⁷Cs; sequential leaches of the particulate fraction of the sediment from cores; and analysis of the dissolved fraction and calculation of saturation indexes (Song and Muller, 2000; Belzile and Morris, 1980). The ion activity coefficient for the saturation index calculations was assumed to be 1 therefore the saturation line

was calculated as $\log(k/k_{sp})$. Dates for the sediment depths have been determined by counting paired laminations (Richard, unpublished data) and checking the inferred dates with ^{137}Cs (figure 3). These dates are labeled on figures to indicate distinct event signatures in the sediment.

Methods

Porewater Analysis

Three 120cm cores were taken in August, 2000 at 300 metres east of station 38 (figure 1) using an in situ freezing technique similar to the frozen finger method described by Verschuren (2000). The technique consisted of lowering a plastic lined tube filled with dry ice and capped on the bottom (the wand), into the sediment. The top of the wand was attached to a series of copper pipes with watertight seals that extended above the surface of the water. Rice sized, dry ice was fed into the wand from the water surface through these pipes for 20 minutes then left to stand for 10 minutes. The wand was retrieved by quickly pulling up the pipes and disconnecting them where required. The wand, with approximately a 5 cm thick sediment layer around the bottom tapering to a 1 to 2 cm thick layer around the top, was wrapped in plastic and packed in dry ice until it could be brought to the laboratory for preservation (placed in freezer) or subsampling.

The cores were sub-sampled at a resolution of 1cm for the first 15cm, every 5cm from 15 to 60cm, and every 10cm from 60 to 120cm. Subsamples from the same depths, from the three cores were combined to obtain sample sizes large enough for analysis. The pore water was centrifuged, then filtered with a 0.45 μm glass fiber filter and analyzed by ICP-OES and ultrasonic nebulizer and DOC by carbon analyzer. Porewater from 1 to 4 cm and from 5 to 8 cm had to be combined to provide sufficient volume for DOC analysis. The particulate fraction of the sub-samples was air dried and analyzed for ^{137}Cs by gamma spectroscopy. An additional core was taken from this site to extend the age dating samples to 150cm (pre-industrial sediments).

Sequential Leaching

Three cores were taken (July, 1998) from station 38 with a gravity corer prior to the use of in situ freezing. Because of the difficulty of field slicing sediment with the texture of soup, these cores were frozen then sub-sampled at the same resolution as the Frozen Finger cores. Freezing cores distorts the laminations, primarily at the ends of the core tube, with the greatest effect on the inner part of the sediment. This can be identified by the bulge or doming evident at the ends of the core. The observed distortion was regarded as acceptable when considering its greatest influence was on the upper two or three subsamples and the coarse subsampling resolution of the deeper subsamples. The section of the core below 15 cm for the particulate fraction is of greatest interest for this study. The in situ freezing method would be best in the future.

The sub-samples were freeze dried and sequentially leached using Tessier et al., (1979) sequential extraction procedure with an additional leach (20mL of concentrated nitric acid boiled at 100 °C for 1 hour) before the residual fraction was digested. This operational procedure results in six fractions referred to as:

1. easily exchangeable
2. carbonate bound
3. Fe/Mn oxide bound
4. organic bound
5. residual recalcitrants
6. residual fraction.

The supernatant was analyzed by ICP-MS and averages with standard errors were calculated.

Results

Nickel and Manganese

The sequential extraction and porewater analysis provide evidence that the majority of Ni and Mn traveled through the sediment together as oxides. Ni and Mn sequential extraction results (figure 5) show that Fe/Mn oxides bind most of the Ni, closely followed by the organic bound fraction. The carbonate bound and residual recalcitrant bound fractions were the smallest pools. The populations of Mn in the sediment from largest to smallest were Fe/Mn oxide bound, organic bound, carbonate bound, easily exchangeable, and residual recalcitrant.

Ni and Mn had two major peaks in their sediment profiles: one is at 35 cm, the other is at approximately 13 cm.

The Fe/Mn oxide bound fractions of Ni and Mn had a strong correlation shown by a R^2 value of 0.879 (figure 6). Below 50 cm, the fraction defined as organic bound becomes more significant for Ni whereas for Mn the organic bound fraction remains obviously less important than the Fe/Mn oxide bound fraction.

The dissolved Ni and Mn porewater profiles in figure 7 have an inverse relationship. Above 25 cm there was more dissolved Ni compared to Mn and below 25 cm there was more dissolved Mn. The saturation index for Ni (figure 8) shows that the porewater was undersaturated with respect to the formation of sulphides such as millerite (NiS) in this environment.

Copper

Copper was primarily bound to the operationally defined organic fraction of the sediment (figure 9). The greatest peak occurred at 70 cm in the sediment and smaller peaks were at 40 cm and 15 cm. The third peak, at 15 cm, was an enrichment zone. This is supported by a sharp decrease in dissolved Cu at 13 cm (figure 10). A general increase of DOC and dissolved Cu occurred with depth (figure 10). DOC versus dissolved Cu is plotted in figure 11 and a negative correlation with a R^2 value of 0.52 indicates that sulphides may be out-competing DOC for Cu. The saturation index plots for Cu in figure 12 suggest that chalcopyrite will not form, however covellite may form. Strong evidence of Cu sulphide growth is seen by the chalcopyrite overgrowth in figure 4.

Discussion

Enrichment Zone

Studying sediment geochemistry enables us to understand how and where metals are stored and released. Near surface enrichment zones have been identified that indicate the sediment is a sink for metals. These enrichment zones are parts of the sediment column where authigenic mineral precipitation occurs and are identified by a decrease in the dissolved fraction of an element and an increase of the particulate fraction. Such changes are often found below a

threshold redox boundary that is governed by microbiological activity (Berner, 1980; Song and Muller, 1999). In the Kelly Lake sediment, near station 38, this boundary was at a level between 8 and 15 cm. Below this transition zone particulate Ni and Cu were enriched.

Event Record

At a depth corresponding to the 1972 construction of the 381m smelter stack at Inco Limited's Copper Cliff plant, a peak in Ni and Cu concentration was expected in the sediment. This record would be evident between 55 and 60 cm in the sediment but it is not present. Therefore other factors must be considered when examining the impact of changes in anthropogenic sources.

Palmer et. al. (1989) dated and analyzed sediment cores from some lakes in the Sudbury area and found that sometimes Ni and Cu peaked at the same depth and in other lakes the peaks did not coincide. They also showed that changes in smelting production and technologies appeared to be directly recorded in the sediment by sulphur concentration whereas Ni and Cu peaks were not as strong an event marker. Nriagu and Rao (1987) and Dillon and Smith (1984) determined that the metal record in Sudbury sediments was a function of either internal lake processes related to acidification or the metal residence time associated with soil and vegetation.

The huge Cu and smaller Ni peaks at 70 cm (1962) (figures 5 and 9) were likely due to erosion of the landscape. This was at the end of the maximum delta growth period observed by Pearson, et. al., (in press). In the early 1980's (40 cm) Ni concentration in the sediment was highest and Cu had a smaller peak. Pearson, et. al. (in press) discussed the metal retaining effects of the new vegetation after the initial phases of the Sudbury re-greening program that began in 1978 and the positive effects seen in water quality. Dillon and Smith (1984) have shown that the residence time of metals in Sudbury's terrestrial environment increased as the vegetation increased. More Cu was transported in the late 1950's/early 1960's and more Ni was transported throughout the 1970's. Cu primarily bound to the organic fraction and Ni dominantly bound to the Fe/Mn fraction

indicates that soil with the dominant portion of organic matter was eroded first and then soil with the dominant portion of inorganic material was eroded later. The recently vegetated land and stabilized erosion in the early 1980's provides the best explanation for the decrease in Ni and Cu after this period, as well as reduced particle emissions.

Nickel and Manganese

The positive correlation and strong R^2 value (figure 6) indicate that Mn oxide was the primary complexant of Ni in the sediment. Carignan and Nriagu (1985) noted similar correlations and suggest co-transport of Ni and Mn until reductive dissolution occurs after burial in the sediment. Below 50 cm in the sediment the significance of the organic bound fraction of Ni increases. This is likely a function of the reductive dissolution of Mn and Ni and a possible reductive precipitation of a Ni sulphide. The operationally defined organic bound fraction likely can include some sulphides. The saturation index suggests that Ni sulphides will not form and SEM analysis did not identify Ni sulphides. Only 15 samples were analyzed with the SEM to represent the entire lake vertically and horizontally, so it is still possible that microenvironments with nucleating sites may exist.

Copper

The extraction results for particulate Cu show that the large majority was bound to the organic fraction. However the extraction procedure did not distinguish between organic bound and sulphide bound populations in the sediment.

The oxidizing nature of the organic bound leach step mobilizes some and potentially all sulphides. Because of this it is difficult to use the results of the particulate fraction to understand geochemical processes affecting Cu in a sulphide rich sediment.

The dissolved Cu and DOC have an inverse relationship, with DOC increasing with depth. Song and Muller (1999) have shown that this

relationship is evidence of sulphides out-competing DOC for Cu. The saturation index calculation (figure 12) shows that Cu may form covellite and should not form chalcopyrite in this sediment, but SEM photos (figure 4) prove that Cu was under-going diagenesis and forming chalcopyrite on microspheres. As suggested for Ni, nucleating sites were present as smelter particles and microenvironments were likely responsible for the discrepancy in results of the SEM and sequential extractions compared to saturation indexes. Crystal growth requires a nucleating site (embryo) and the formation of a nucleus from solution needs an increase in free energy. Sediment particles can act as a nucleus or seed crystal and if the precipitate and seed consist of the same material, the nucleation energy is minimal (Berner, 1980). In Kelly Lake sediment, airborne smelter particles that have been deposited in the sediment act as nucleating sites for Cu to precipitate (figure 4) on because of the low free energy required.

Conclusions

Distinct events recorded in the sediment and diagenetic processes have been distinguished from each other through the use of a sequential extraction of the particulate sediment, pore water analysis, saturation index calculations, SEM analysis, and a literature review. Enrichment zones existed near the sediment surface. Distinct events recorded in the sediment for Ni and Cu were primarily controlled by soil stability and not smelter emissions. Ni was primarily transported to the sediment with Mn and below 50 cm a fraction may be reduced and formed a sulphide. Cu was bound to the operationally defined organic fraction and Cu sulphide precipitation was occurring at depth. The diagenetic activity in this sediment appeared to be increasing the stability of the metals discussed in this study.

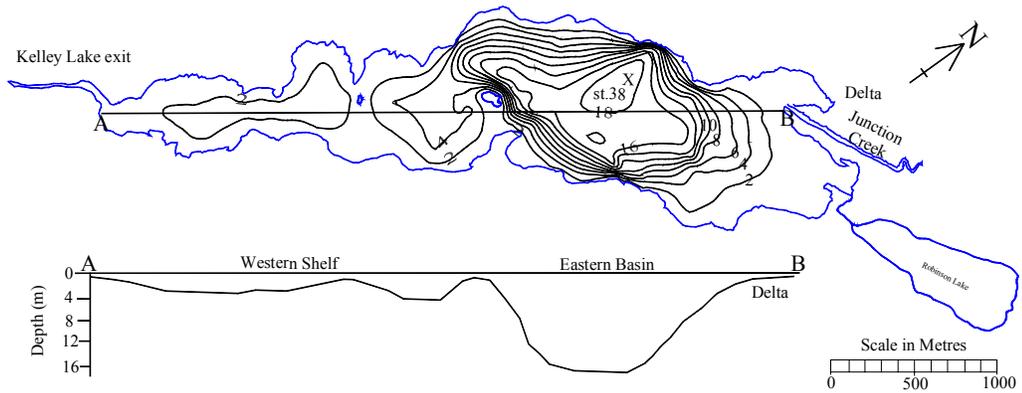


Figure 1. Bathymetric map and cross section of Kelly Lake showing the position of monitoring station 38.

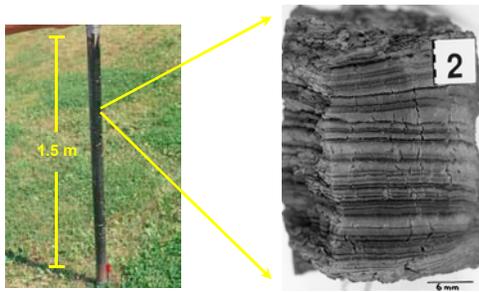


Figure 2. Sediment core from station 38 in the eastern basin (left) and section of core showing coupled organic dominated (dark) and inorganic dominated (light) layers.

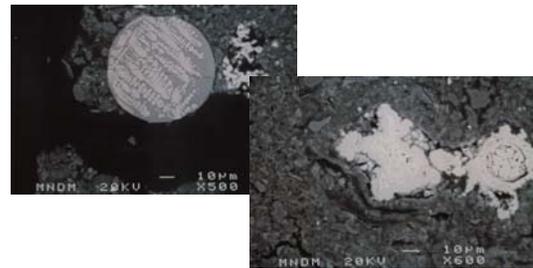


Figure 3. Nickel silicate smelter sphere (left) and covellite smelter particle with chalcopyrite overgrowth (right).

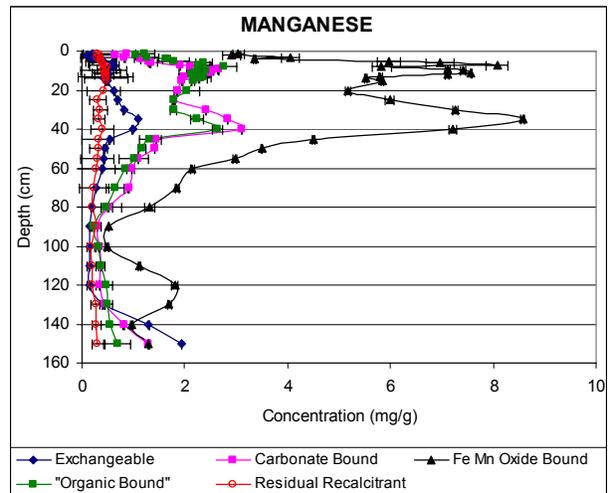
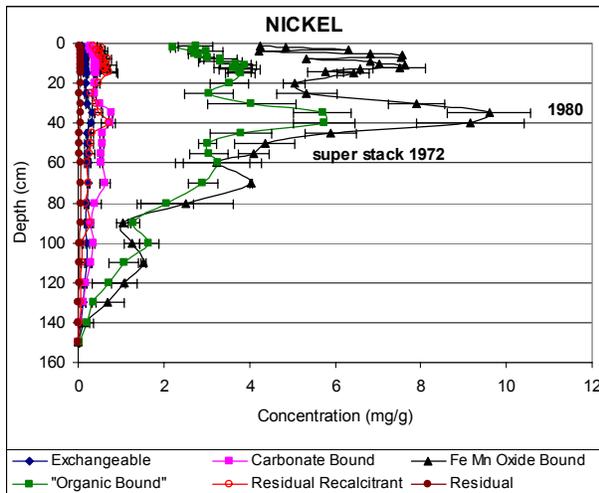


Figure 4. Sequential extraction of an average of three sediment profiles for Ni and Mn from station 38.

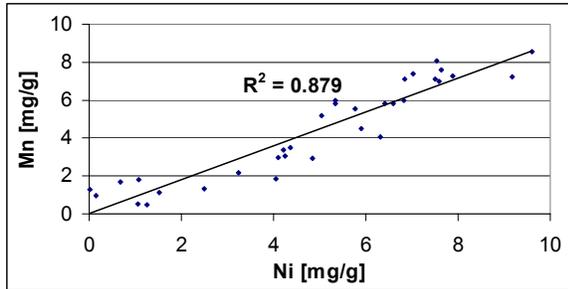


Figure 5. Correlation between the Fe/Mn oxide bound portions of Ni and Mn from the average of three sediment profiles from station 38.

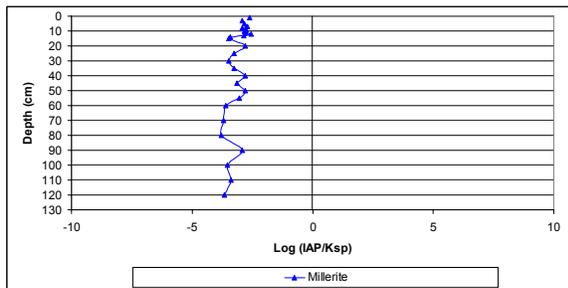


Figure 7. Profile of the saturation index of a Ni mineral in the sediment near station 38.

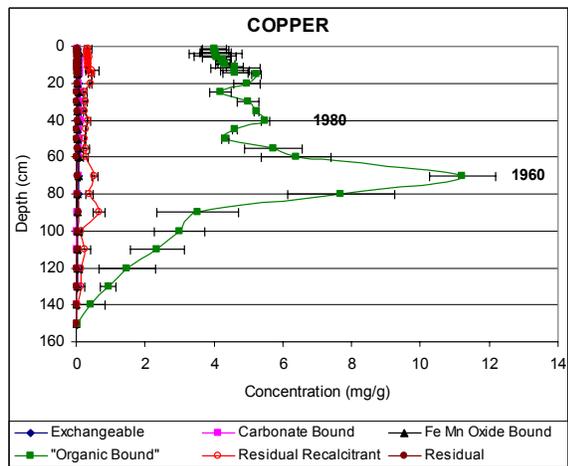


Figure 8. Sequential extraction of an average of three sediment profiles for Cu from station 38.

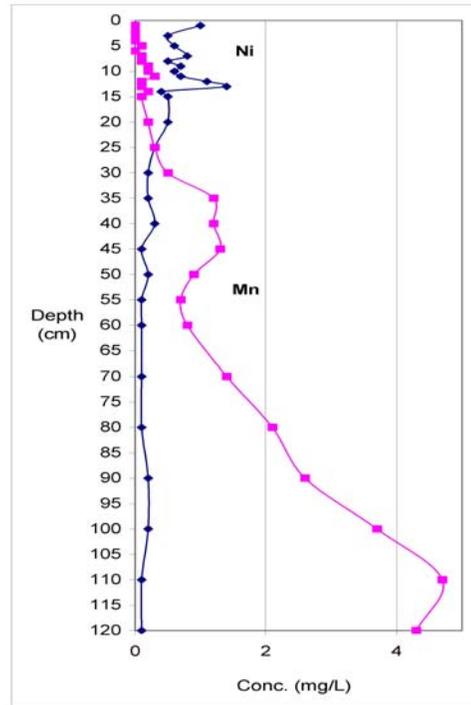


Figure 6. Dissolved Ni and Mn concentrations in porewater from a sediment profile near station 38.

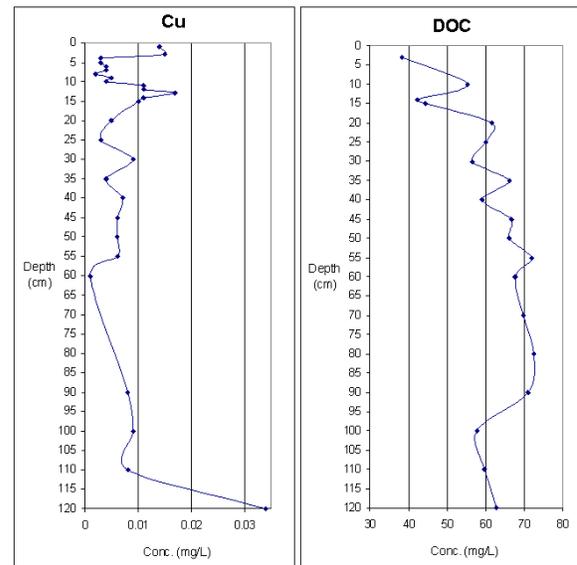


Figure 9. Dissolved Cu and DOC concentrations from a sediment profile near station 38.

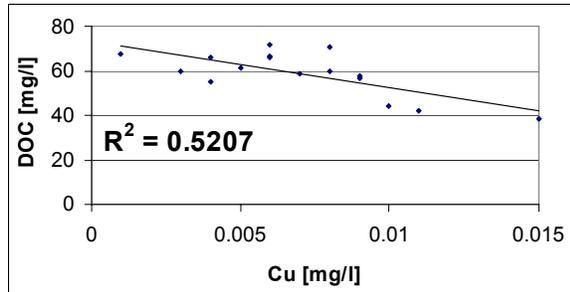


Figure 10. Correlation between DOC and Cu from a sediment profiles near station 38.

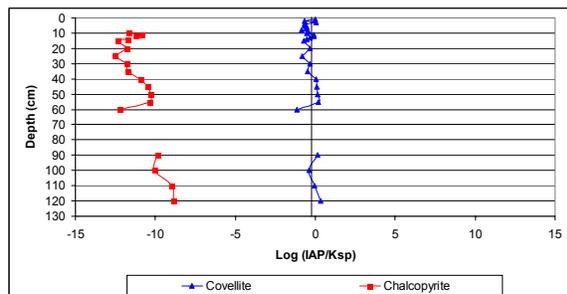


Figure 11. Profile of the saturation index of Cu minerals near station 38.

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