In-situ Sediment/Water Interface Reactions Experiment Examining the Aerobic and Anaerobic Mobility of Ni, Cu, and PO4 in Kelly Lake, Sudbury, Ontario

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Abstract
Kelly Lake, on the south west edge of the urban core of the Greater City of Sudbury is a 339 hectare, eutrophic lake that has received urban runoff, effluent from major smelting and refining complexes, and sewage effluent for over 100 hundred years. More than 120 cm of metal, nutrient, and organic rich sludge has accumulated in the 17 metre deep basin of the lake. Kelly Lake sediment has been identified as a source of phosphorus contamination to residentially populated lakes downstream. Aeration of the anoxic water is being considered as a possible remediation method to decrease the internal loading of phosphorus and help lower the nutrient load exiting the lake. Although aeration techniques have been successful in decreasing the internal loading of phosphorus in lakes, it may not be the ideal remediation plan for the metal rich sediment in Kelly Lake. Oxidation of organic mater and low to moderately stable sulphides may release associated metals into the overlying water column.

In-situ enclosure experiments indicate PO4 is more efficiently contained in the sediment if the overlying water column is oxygenated. Increased stability of PO4 in the sediment was observed to occur at dissolved oxygen concentrations of 1-2 ppm. The study suggested a fraction of Cu and Ni may be remobilized from the sediment if the overlying water is nearly saturated with dissolved oxygen, however low concentrations of dissolved oxygen did not appear to remobilize Cu and Ni.

Introduction
Kelly Lake, located at the southwest edge of the urban core of the city of Greater Sudbury, Ontario has received effluent from smelting and refining processes, air-borne metals, treated sewage effluent, and urban runoff for over 100 years. A large amount of these pollutants have been stored as nutrient and organic rich, ore grade, copper, nickel, and sulphur rich sediment (Pearson et al., 1999). Pearson et al. (1999) provided evidence of the lake being a seasonal source of phosphorus that likely added to downstream nutrient enrichment. The evidence primarily consisted of a progressive increase of dissolved phosphorus in the hypolimnic water, under near anoxic conditions. The identified times for seasonal releases were near the fall turnover and late winter periods of maximum anoxia.

Renewed interest in the Kelly Lake system was initiated by degraded water quality, indicated by algal blooms and dense macrophyte populations, in lakes downstream. Nutrient loads from Kelly Lake sediment were suspected as a significant source of pollution affecting lakes down stream. Organic rich sediments release dissolved phosphorus into an anoxic water column (Nurnberg, 1984), therefore aerating the water column should minimize internal loading of phosphorus. However, concern regarding the mobility of metals such as copper and nickel when changing from sediment covered by dominantly anoxic water that has apparently been a stable sink for metals to sediment covered by oxic water had to be addressed. Petersen and Willamowski (1997) showed that organically complexed metal that was resuspended into oxic water released some metals. Knowledge of this type of metal release, coupled with copper and nickel concentrations in the discharge water from Kelly Lake being above the Provincial Water Quality Objectives, reinforced the need to investigate the potential effects further. In situ enclosure experiments that permitted a portion of the sediment and water column to be partially isolated from the natural environment and still maintain some natural physical, chemical, and biological properties are used to address metal mobility.
concerns induced by various oxic and anoxic conditions.

Setting

The Lake covers 339 hectares and is 4.5 km long and 1.1 km at the widest point, with the 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 primary source of water is Junction Creek. Historically Junction Creek water has been contaminated with phosphates, suspended solids and dissolved metals. Lilly Creek delivers a significantly lower volume of clean water, originating from Ramsey Lake, one of Sudbury’s drinking water sources. The outflow from Kelly Lake is at the southeast end. Water travels from the outlet through a small chain of residentially populated lakes to the Vermilion and Spanish Rivers, and eventually Lake Huron.

Objectives

The purpose of this study is to help determine if oxygenating the hypolimnic portion of the water column, with the goal of minimizing the internal loading of phosphorus, has any effect on the mobility of copper and nickel in the sediment and hypolimnion. Results from this study are crucial in implementing a remediation strategy.

Enclosures

In situ enclosure experiments have typically been used to test the effects of stressors on biota. Schrader et al. (2000) is a good example of this where phytotoxic compounds were added to an enclosure and the phytoplanktonic community structure was evaluated. Most in situ enclosure applications are done in shallow water (< 5m) and the top of the enclosure extends above the water surface. Sanford (1997) stresses two factors that should be compensated for are turbulent mixing and time-averaged boundary layer flow. Effects from the later are typically seen over longer periods of time (> 16 days). Other more evident problems include limiting solar radiation, pumping action of soft walled enclosures, and drifting pH and dissolved oxygen concentration with time.

The Kelly Lake in situ enclosure experiments were conducted in an area with a water depth of approximately 12 metres. The top of the enclosure did not extend above the surface of the water. The top of the enclosures extended up into the thermocline that limited upward diffusion due to the bottom, cold water having a greater density than the warmer water above the thermocline (Chapra, 1997 and Schnoor, 1996). Naturally settling particulate matter from the epilimnion was included in the experiment because the enclosure did not extend up to the surface.

Methods

System Description and Setup

Three hard wall, plastic, cylindrical enclosures, 5 metres tall and a 1.5 metre diameter were constructed. Teflon lined sampling tubes were attached on the inside and outside from 1.5, 2, 3, and 4 metres above the bottom (figure 2). The neutrally buoyant enclosures were each weighted down with sand bags attached to the outside of the enclosures 2 metres above the bottom. The enclosures were sunk in approximately 12 metres of water. They were gently lowered to 1 metre above the sediment surface and then released allowing the bottom to settle approximately 1 metre below the sediment surface. This provided water sampling depths of 0.5, 1, 2, and 3 metres above the sediment surface for the tubes.

The top of the enclosures extending up, into the thermocline is crucial for the experiment to work because it acts as a barrier, limiting upward diffusion. If metals and nutrients are dissolved in the enclosure or released from the sediment, they accumulate in the enclosed water due to limited upward diffusion. Accumulation of dissolved metals and nutrients is shown by increased concentrations. By early July the thermocline encompassed the top of the
enclosures and by early September it encompassed most of the enclosures. This provided a 2 month window (July and August) to operate the experiment.

Aeration units (figure 3) suspended inside the enclosures approximately 2 metres above the sediment served two purposes, aerating the water column and mixing within the enclosures. Oxygen cylinders secured to a dock above the enclosures supplied the aeration units with oxygen. A rubber aquarium sparger was used to maximize the surface area of the oxygen bubbles released into the water. The top of the aeration unit was a half sphere made from plastic that caught the residual oxygen. An oxygen discharge tube attached 2 centimetres below the top of the half sphere extended to the surface and acted as a conduit for the residual oxygen discharge. Estimates of effective sparging rates were made by comparing the oxygen cylinder regulator setting and the amount of residual oxygen discharged.

The aeration units were suspended from the dock so that wave action would move the aeration units up and down within the enclosures. This served as the mixing mechanism to provide some turbulence in the enclosed water column.

**Monitoring, Sampling, and Analysis**

Aeration of enclosures 2 and 3 began in early June to maintain oxic conditions in the water columns in these enclosures. Enclosure 1 was not aerated, enclosure 2 was aerated to a moderate level (4-7 ppm), and enclosure 3 was aerated to a low level (1-2 ppm). The enclosures were monitored 2-3 times a week with a YSI 6920 sonde and a 650 MDS hand held meter that logged and displayed real time data. Profiles were recorded every metre from the top of the enclosures to 50 centimetres above the sediment. Measured parameters included dissolved oxygen, conductivity, pH, nitrate, ammonium, and chlorophyll.

Initially, dissolved oxygen concentrations were to be maintained within the desired range for a minimum period of two weeks before sampling to provide sufficient time for reactions to achieve an equilibrium state. Because of excessive mixing during periods of high winds, weather predictions were monitored to allow sampling before storm events.

Water was sampled from the inside of all three enclosures and outside of one enclosure on July 18, August 1, August 27, and September 2, 2002 using a vacuum pump to draw the water up the sampling lines. Total, 0.45 µm filtered, and some 5 µm filtered water samples were analyzed for orthophosphate, total organic carbon, sulphate, and dissolved metal content.

**Results**

Metal and nutrient concentrations in the hypolimnic water of Kelly Lake increased from the spring to late summer. These temporal trends are seen in the enclosure results and must not be mistaken for sediment release due to oxic or anoxic water conditions. Because of the temporal accumulation of metals and nutrients the results must be interpreted by comparing metal, nutrient, and dissolved oxygen concentrations for each enclosure, focusing on one sample period at a time.

On July 18 enclosure 1 had the lowest dissolved oxygen concentration, enclosure 2 had the highest and enclosure 3 was between 1 to 2 ppm dissolved oxygen (figure 4). Total phosphorus concentration was highest in enclosure 1 and similar in enclosures 2 and 3 (figure 4). Total copper was highest in enclosure 2 and lower in the moderately aerated and non-aerated enclosures (figure 5). Total nickel concentration was similar in enclosures 1 and 3, however enclosure 2 had a higher concentration (figure 6).

The sample period on August 1 was conducted during a period of high winds. This caused the water in the enclosures to be mixed with water from the thermocline. Dissolved oxygen concentration was low in all the enclosures this day. Despite the mixing indicated by low dissolved oxygen, total phosphorus, copper, and nickel trends were similar to that of the July 18 sample period. Enclosure 2 that was typically well oxygenated had the lowest phosphorus concentration, enclosure 3 that was moderately aerated had the second lowest concentration, and enclosure 3 that was not aerated had the highest concentration (figure 4). Total copper was
highest in enclosure 2 and lower in the moderately aerated and non-aerated enclosures (figure 5). Total nickel concentration was highest in enclosure 2 and lower in enclosures 1 and 3 (figure 6).

Shortly after August 1, the aeration unit in enclosure 3 malfunctioned. Due to this change, aeration of enclosure 1 commenced and enclosure 3 became the non-aerated control.

From August 27 to the end of the experiment, the epilimnion encompassed the top 3 metres of the enclosures, therefore the 0.5 and 1 metre depths above the sediment are the only sampling depths relevant to this investigation. All depths sampled have been included in the results to show the growth of the epilimnion.

Discussion

All sample periods for the enclosure experiment did show lower phosphorus concentrations in an oxygenated water column than an anoxic water column (figure 4). Iron oxides and oxyhydroxides may form complexes with phosphates in oxygenated water and can settle to the sediment surface (Chapra, 1997 and Schnoor, 1996). This is likely why lower phosphorus concentrations were seen in the oxygenated enclosures. Results from the July 28 and August 1 sample periods for enclosure 3 suggest that dissolved oxygen concentrations between 1-2 ppm is sufficient to promote iron oxide and oxyhydroxide complexations with phosphorus.

The July 28 and August 1 sample periods indicate that copper and nickel are less efficiently removed from an oxygenated water column or a fraction of copper and nickel is released from the sediment if the overlying water column is oxygenated. Petersen, et al. (1997) showed that metals may be remobilized from some sediments that are resuspended into oxygenated water. A similar type of remobilization may be occurring in the oxygenated enclosures.

Copper and nickel results from the August 27 and September 2 sample periods contrast the results of the earlier sample periods. Concentrations are lower in the aerated enclosures than the non-aerated enclosures. This may be a function of the growing epilimnion that encompassed most of the enclosures by late August. As the epilimnion grew deeper, an oxygenated water column replaced water that was previously anoxic. This could result in newly formed oxides and oxyhydroxides that would settle down the water column. It is possible that copper and nickel oxides and oxyhydroxides were rapidly settling into the enclosures and being remobilized in the anoxic enclosures and continue settling in the oxygenated enclosures.

Conclusions

Removal of phosphorus from the water column and containment of phosphorus in the sediment appears to be more effective when the water overlying the sediment is oxygenated and low concentrations of dissolved oxygen show similar results to near saturation concentrations. Copper and nickel removal and storage efficiency was not constant under oxic and anoxic conditions. Early summer results suggest copper and nickel are remobilized from the sediment if the overlying water is near saturation with respect to dissolved oxygen. Late summer results, when increased settling of Fe/Mn oxides and oxyhydroxides are expected, suggest efficient removal of copper and nickel from the water column occurs under oxygenated conditions.

References

Chapra, S., 1997. Surface water-quality


Figure 1. Bathymetric map and cross section of Kelly Lake.

Figure 2. Attachment of water sampling tubes inside and outside the enclosure.

Figure 3. Aeration Unit.
Figure 4. Dissolved oxygen (lines) and phosphorus (bars) concentrations inside enclosures measured at 0.5, 1.0, 2.0, and 3.0 metres above the sediment from July to September.

Figure 5. Dissolved oxygen (lines) and copper (bars) concentrations inside enclosures measured at 0.5, 1.0, 2.0, and 3.0 metres above the sediment from July to September.
Figure 6. Dissolved oxygen (lines) and nickel (bars) concentrations inside enclosures measured at 0.5, 1.0, 2.0, and 3.0 metres above the sediment from July to September.