A Potential Remediation Strategy Using Wetland Vegetation and Aquatic Macrophytes in Kelley Lake, Sudbury, Ontario

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Abstract

Work has begun on developing a remediation plan for a 339 hectare, nutrient-rich lake contaminated by Ni, Cu, Fe and P in Sudbury, Ontario. Evidence shows that this system is acting as a sink for nutrients and heavy metals. The near neutral pH and low redox potential of the sediment facilitates storage of heavy metals as insoluble complexes with organics, oxides, and sulfides. These complexes render the metals immobilized, leaving very little amounts of Cu, Ni and Fe in the "exchangeable" or bioavailable fraction. Despite the lack of bioavailable metals, toxic amounts of metals have accumulated in three wetland species namely; *Myriophyllum spicatum, Scirpus acutus* and *Typha latifolia*. Combined estimates of standing crop, show values of 23.1 tonnes of Fe, 7.4 tonnes of Ni and 0.9 tonnes of Cu present in the plant population in the summer of 2000. Of the three plant species investigated *Myriophyllum spicatum* has shown to be more adept at sequestering metals. Using *M. spicatum* in a yearly harvest regime, would avoid a re-circulation of metals back into the system as plant material breaks down following senescence.

Introduction and Background

Nickel and copper have been mined in the Sudbury area for more than a century. Sulphur dioxide and metal particulate emissions from the mining process have been responsible for a severe degradation of the surrounding landscape, effects of which have been measured up to 150km away. Industrys' efforts to make technological changes to their operations, have greatly improved the quality of discharged wastewater and dramatically reduced the sulphur and metal content of stack emissions (Pearson *et al*.,1999). There are clear indications that the recent period of declining smelter emissions has resulted in both biological and chemical improvements in local lakes (Keller *et a*l.,1992).

Kelley Lake (46º27'N, 81º04'W) has recently become the focus of attention after complaints of large algal blooms in three residential lakes, five kilometres downstream. Kelley Lake has been the unfortunate recipient of a centuries worth of industrial metal pollution and municipal sewage effluent. This lake has been uniquely influenced in that it not only received its share of atmospheric fall-out from the smelter stacks just 3 km away, but was also the collecting basin for run-off from tailings, slag piles and wastewater from seven mines in the area (Pearson *et al*., 1999). It also receives run-off from the entire urban core of the city of Sudbury. Prior to 1972, virtually untreated sewage was discharged into the lake, resulting in eutrophication, internal phosphorus loading and the deposition of nutrient-rich sediment contaminated by metals, chiefly copper and nickel. Despite technological improvements made to wastewater treatment plants and the Sudbury sewage treatment plant, the contamination levels of the water leaving the lake still far exceeds Provincial water quality objectives

The Ontario Ministry of the Environment collected sediment from several areas in Kelley Lake in 1989. Concentrations of Ni exceeding 1%, was found throughout the lake, almost reaching 2% in one location. Similar concentration patterns were evident for Cu exceeding 0.4% and reaching 0.7% in some areas throughout the lake (Pearson,. *et al.,*1999). When dealing with such heavily contaminated sediment several processes of concern arise; (i) the release of metals to surface water from sediments, (ii) metal accumulation by benthic and wetland animals, (iii) runoff losses and (iv) leaching (Gambrell, 1994). One factor that should not be overlooked particularly in heavily contaminated systems is the possibility of transport of substantial amounts of metals from the sediment into macrophytes and a subsequent release into the water following senescence.

The ability of wetland plants and submergent macrophytes to accumulate metals is well documented (Jackson *et. al*,1993, Greger *et a*l.,1993, Taylor and Crowder, 1981, Gavrilenko and Zolutukhina, 1989, Welsh and Denny, 1980). In emergent plants metals and nutrients are mainly absorbed by the roots or rhizomes and translocated within the plant to the shoots and reproductive structures. In submergent species, the soil is usually the main pathway for metal and nutrient uptake, but depending on the species there can also be a direct absorption from the water in highly eutrophic lakes (Bole & Allan, 1977, DeMarte & Hartman,1974). Kelly Lake, being a eutrophic lake, harbors large populations of emergent and submergent plant species. One notable macrophyte species *Myriophyllum spicatum* covers a large proportion of the littoral zone in Kelley lake. Visual observations by local researches concluded that the colonization of *Myriophyllum spicatum* began in 1998. A study by Wang et al., 1996 explored the range of metal adsorptive capabilities of *Myriophyllum spicatum* to remove Cu, Ni, Cd, and Pb from solution for a period of 60 minutes, under different pH conditions. The maximum adsorptions were about 0.5% for Ni, 0.8% Cd, 1.3%Cu and 5.5%Pb at a pH between 5-7.8, indicating that water milfoil has a high metal adsorption capability in a relatively short contact time. This capacity for aquatic plants to take up metals and nutrients makes an investigation imperative to explore what role the biota plays in the metal and nutrient budget of the lake.

The primary objective of this project is to determine the distribution and abundance of vegetation species in the lake. A secondary objective is to quantify the metal and nutrient loading in the vegetation as well as the soil, in both the wetlands and littoral regions of the lake, which will aid in understanding the cycling of heavy metals and nutrients in the system. Lastly, to assess the use of the macrophyte *Myriophyllum spicatum* in a harvest regime, depending on its ability to capture and store toxic elements.

Methods

Lake Morphology

Kelly Lake is an elongate, eutrophic lake, which spans 339 hectares. It is divided into three different morphological components, a steep sided, 16m deep main basin, which is bordered by two shallow shelves on the east and westward sides, which have a depth of 1-4m. The eastern shelf and main basin function as a sediment trap, while the western shelf is susceptible to periods of sediment resuspension driven by wind mixing and to erosion during periods of high flow. Kelly Lake is dimictic and has an average epilimnetic temperature of 23ºC in the summer and ranges from 0 to 3.2ºC in the winter. The hypolimnion of the deep main basin is susceptible to periods of near anoxic-conditions with stable thermal stratification in mid-summer and mid-winter (Pearson *et al*., 1999).

Sampling

i)Vegetation

A vegetation survey was carried out in 2000, to see the diversity and distribution of vegetation in the lake. Several transects were set up (7 transects), to collect the submergent vegetation. The transects had a maximum depth of 1.5m. Plots were set up every 4m and measurements of % cover were taken within a 25x35cm quadrat and all vegetation within the quadrat was collected for biomass. The vegetation was collected using a rake, in most cases the plant shoots would break at the sediment surface, resulting in very few roots being collected. In the summer of 2000, four shoreline marshes were sampled, with transects running every 10m, and plots every 4m on the transects. Percent cover was measured within a $1m^2$ quadrat and below ground as well as above ground biomass was collected. All of the vegetation was brought back to the laboratory, washed with distilled water, sorted, dried at 80ºC, weighed and ground to a fine powder using a stainless steel mill. Three species of wetland plants were used for metal and nutrient

analysis; *Myriophyllum spicatum*, *Scirpus acutus* and *Typha* spp.. The vegetation was analyzed by x-ray fluorescence accompanied by EMMA (energy dispersive multi element miniprobe analyzer) attachment. Standard reference material was also analyzed and results closely agreed with known values (<10% variability).

ii)Water

Water samples were collected weekly (weather permitting) in 1999, from the inlet (Junction Creek), outlet and station 38 (centre of the lake), using a Van Doran water sampler. Surface samples were taken at the inlet and exit of the lake, whereas at station 38 samples were collected at every metre to a depth of 16m. The samples were preserved with HNO3 in the field and analyzed by ICPMS(Pearson, et al.,1999). The sampling program in 2000 was not as extensive, samples were collected once a month in April, September and October, to monitor any changes in nutrient and metal levels. Historically the concentrations of nutrients and metals changes very little from year to year.

iii)Soil/sediment

Soil was collected in the shoreline marshes using a soil auger, up to a depth of 20cm in 5cm increments (0-5cm, 5-10, 10-15, 15-20cm). Redox, pH, conductivity and a soil description were recorded at every 5cm increment. The top 2cm of soil was collected at the first, middle and last plot of the littoral transects using an Ekman grab. Sediment cores were taken with a Laurentian University R. Morris gravity corer when the water depth was greater than 3m. At a depth of less than three metres a standard vacuum corer was used. Both corers used a 5 cm diameter acrylic tube. Overlying water was siphoned off and the surface was consolidated by evaporation in cold (5ºC) storage for 72 hours, prior to extrusion. Sediment cores 120cm long 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. Each core section was air-dried and a sequential extraction was performed. The sequential extraction technique used was modified from Tessier *et al*., 1979, (Lock,.,& Pearson, 2001).

Water extractable analysis

Water was used in the extraction of bioavailable elements as opposed to ammonium acetate or DTPA, in the hopes of mimicking what would occur in the natural environment. Exactly 10 grams of wet soil and 50ml of distilled water were placed in labelled 125ml erlenmeyer flasks. In most cases 5 grams of dry soil is used in this kind of analyses but 10 grams was used to compensate for the added weight of the moisture. Parafilm was placed over the opening of each flask. The flasks were placed on a shaker (Model MK5). The shaker was set a t 300 R.P.M. for two hours. After the flasks were thoroughly mixed on the shaker, the liquid was filtered through 90mm diameter filter paper (qualitative #1). The filtrate was then filtered using 0.45 micron filter paper to remove the fine clay particles as well as humic acids. The filtrate was collected in 150 ml plastic containers and 2 to 3 drops of hydrochloric acid were added to each container as a preservative. The samples were analyzed for (K, Ca, Co, Cu, Fe, Mg, Mn, Na, Ni, Zn, DOC, total P, S) at the Elliot Lake Research Field Station using an ICP-AES (Inductive Couple Plasma Atomic Emission Spectrometer) and ultrasonic nebulizer.

Total metal content

To homogenize the soils, they were air dried and ground to a fine powder using a soil mill (pulverisette, type 08.303). Once milled, the soils were sieved using a No.45 sieve for approximately five minutes on a rotary sieveing unit (Ro-tap, model rx-29). The metal concentrations in the soil were determined using x-ray fluorescence accompanied by an Emma (Energy Dispersive Multi-element Miniprobe analyzer).

Results and Discussion

Abundance and Distribution of Vegetation

A vegetation survey was carried out in the summer of 2000. There is a total of (8) submergent species and (20) marsh species found. The perimeter of the lake harbors many shoreline marshes dominated by common cattail (*Typha latifolia*), hardstem bulrush (*Scirpus acutus*) and many carex species. While the littoral zones are dominated by three main species of submergent macrophyte; eurasian watermilfoil (*Myriophyllum*

spicatum), slender pondweed (*Potomageton pusillus*) and richardsons pondweed (*Potomageton richardsonii*). The largest plant population belongs to *M.spicatum*, it covered approximately 80% of the littoral zone in 2000. *M.spicatum* is an invasive species, not native to Ontario, it is an extremely aggressive plant, spreads quickly and chokes out all other species. The invasion of freshwater habitats by an invasive species such as *M.spicatum* is usually characterized by a very high rate of growth and spread, followed by a period of habitat stabilization and attainment of an equilibrium situation (Rorslett *et al* 1986). According to Mitsch and Gosselink (1993), an average measurement for macrophyte productivity in a coastal lake Erie wetland is 473 g/m^2. The biomass measurements collected from the macrophyte community in Kelley lake measured 203.9 g/m^2 in 1999 and 260.9 g/m^2 in 2000, indicating a below average productivity. An experiment conducted by Stanley (1974) concluded that the addition of a toxic element such as Cu inhibited root weight and shoot elongation by 50% at levels <20 ppm, far lower than expected values for Kelley lake sediment.
Scirpus acutus is the most abundant plant species in the shoreline marshes. The eastern shelf and western shelf had similar measurements of cover (approximately 30%) and the main basin was slightly lower(13%). These values are a direct reflection of the biomass measurements. The main basin has the lowest biomass measurement of 158 g/m^2 and the western and eastern shelves having similar measurements of 441 and 449 g/m^2. According to Mitsch and Gosselink (1993), the average biomass measurement of a North American freshwater marsh, that is dominated by large emergents such as cattails or bulrush, is upwards from 1000 g/m^2. Again showing a below average productivity. McNaughton *et al*.,1974 concluded that heavy metal contaminated soil causes a growth inhibition in large emergent plants such as bulrush and cattails. Taylor and Crowder (1982) found toxicity symptoms such as reduced leaf elongation and biomass production at Cu concentrations of 80 ppm in the leaf tissue. While Hutchinson (1975), cited a growth reduction at a copper concentration of 48 ppm.

Water analysis

The question arises is Kelley lake acting as a sink or source of toxic pollutants? In 1999, water samples were collected from the inlet and the exit of the lake, see Table 1. The concentration of all the elements either remain the same or decrease, as the water travels towards the outlet, indicating that the lake is acting as a sink. Nickel is the only exception, it's concentration increases from 546 ppm to 645ppm as it travels westward toward the exit. Despite the fact that the lake is storing a large portion of the toxic elements, the concentration of Cu, Ni, and Fe leaving Kelly Lake still far exceeds provincial water quality objectives

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Table 1. The concentration of metals and nutrients in water entering and leaving the lake, in 1999.

	Inlet	Lake Basin	Outlet	PWQO
pH		7.22		
	ppm	ppm	ppm	Ppm
PO4	237	130	128	no set limit
Total-P	59	6	12	10-30
Cu	85	30	33	5
Ni	546	639	645	25
Fe	1619	980	1027	300

Soil/sediment analysis

All soils collected in the shoreline marshes and the littoral zone had an organic matter content <10%, pH's ranging from 6-7 and were showing negative redox potentials (<-100 mv) indicating they were in a reducing state. Mineral soils having a near neutral pH and low redox potential favors metal immobilization, a higher proportion of the metals are firmly bound to the sediment and less is available to the plant. If Kelley lake is acting as a sink, metals such as Cu, Ni and Fe will be present in reduced form or combined with oxides, large molecular weight organics or sulfides and rendered insoluble (Gambrell, 1993). A sequential analysis was performed on one of the soil cores to see how strongly and in what fraction the metals were held. 90% of the copper is bound by organics, 33% of the nickel is bound by organics and 56% is combined with oxides, 39% of the Fe is bound with oxides and 38% is in the form of sulfides, 58% of the phosphorous is bound with sulfides and 23% is held by organics. If the soils maintain a reducing state and a near neutral pH the metals will remain immobilized, however if the pH becomes moderately to strongly acid, as can sometimes occur when reduced sediments become oxidized, these metals may be released to more mobile forms (Gambrell, 1993). Soil samples taken in the wetlands as well as the littoral zone generally show high concentrations of Ni (max=5023.6 ppm), Cu (max=2418.1 ppm) and Fe (max=47500 ppm). These values are comparable to those measured by Taylor and Crowder (1983), who collected soils from wetlands in the vicinity of the smelters, their values are higher for Ni (max=9372 ppm) and Cu (max=6912 ppm), while the concentration for Fe (max=45448) is relatively the same. It is important to know the extent of the metal contamination in the soils or sediment, however in this case what is bioavailable to the plants is most important. A water extractable technique was used to get a measurement of what is bioavailable to the plant. Considering the extent of the contamination in the sediments, there is very little available to the plants to be taken up (Table 2). Nickel appears to be the most bioavailable element, followed by Cu and Fe, there are negligible amounts of P available. There appears to be much less available at depths ranging from 10 to 20cm compared to the upper layers of sediment, interestingly the rhizomes of emergent plants would be found at that depth.

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Table 2. Average concentrations of bioavailable elements from sediments collected from wetlands and the littoral zone.

Depth (cm)	Ni (ppm)	Cu (ppm)	Fe (ppm)	Total-P (ppm)
0-5	239.7	62.6	49.2	0.4
5-10	181.6	72.2	164.6	0.7
10-15	90.3	26.8	133.1	0.5
15-20	84.2	22.1	20.8	0.4
Littoral (0-2)	166.8	80.5	11.6	0.5

Vegetation analysis

Three wetland species *Myriophyllum spicatum* (eurasian watermilfoil), *Scirpus acutus* (hardstem bulrush) and *Typha latifolia* (common cattail) were analysed for heavy metal uptake. Despite having very little Cu, Ni and Fe available to the plants to be taken up, a significant amount had accumulated in all three plant species, see Figure 1. The highest amount of metal accumulated by all three plant species was Fe, followed by Ni, and Cu had the least amount sequestered. *M.spicatum* had accumulated the most metals of all three plant species. In order to estimate the total amount these metals contained within a plant population, it was necessary to estimate the standing crop of plants.

From the average biomass measurements and the areas (ha) of plant populations measured from the vegetation surveys, it was possible to crudely estimate the standing crop of Cu, Ni and Fe for all three plant species (Figure 2). The three species had a combined standing crop of 23.1 tonnes of Fe, 7.4 tonnes of Ni and 0.9 tonnes of Cu. All three species had accumulated a large portion of Fe, however the two emergent species (*T.latifolia* and *S.acutus*) accumulated much lower amounts of Cu and Ni.

Plant-Soil interaction

Kelley lake sediments are in a reducing state with a near neutral pH, which should essentially immobilize the metals. A small proportion of the metals, which are complexed with organics, oxides and sulfides, are available for sequestration. Despite having low bioavailability of heavy metals all three species had sequestered toxic amounts of metals. One explanation could be that in most cases the higher plants (*S.acutus* and *T.latifolia*) oxygenate the surrounding media by transporting oxygen to the root surface through structures called aerenchyma, this will cause a lowering of the pH and oxidation of metals and the metals will be in taken up by the plants. This oxidized microenvironment at the root surface causes the formation of a plaque of an insoluble Fe+3 compound. This plaque may in turn bind metals such as Cu and Ni rendering them unavailable for uptake (Taylor and Crowder, 1982). This could explain why the two emergent species accumulated much lower amounts of Cu and Ni. It is a mystery how *M.spicatum* is able to sequester such large amounts of heavy metals when it lacks the aerenchyma structures to transport oxygen to the root surface. There are conflicting theories as to whether the roots are the main pathway for metal uptake or whether the metals are absorbed directly from the surrounding water. According to an experiment carried out by Bristow *et al*. (1971), 59% of phosphate absorption was derived from the roots as opposed to the surrounding water medium. It is the general concensus of several authors however (Denny, 1972, St-Cyr et al., 1997, Mayes et al., 1977), that both the sediment and surrounding water are of equal importance and that foliar metal contamination directly from the water column can be suspected to occur when there are high metal concentrations in the water column. An absorption of heavy metals from the water column could explain the accumulation in *M.spicatum*, it does however warrant further study.

Harvesting *Myriophyllum spicatum*

It is evident that *M. spicatum* is a proficient hyperaccumulator of heavy metals. A large amount of heavy metals is present in the plant population despite its below average productivity. If not harvested, this concentrated amount of metals will be recycled back into the system as the plant material breaks down following senescence. *M.spicatum* is an ideal candidate for a harvest regime. It is highly aggressive and adapted to its environment. It propagates from seed but in most cases will propagate from fragments as short as 1 inch long. This plant is considered a nuisance aquatic plant in many parts of Ontario, British Columbia and the United States. Researchers have tried several strategies to manage the populations, from mechanical harvesting, herbicides, bottom screens and biological controls such as phytophagus fish and insects, and have had no success. The plant communities in Kelley Lake seem to be stabilizing and reaching equilibrium.

Conclusion

Water samples collected at the exit of the lake show a decrease in concentration of heavy metals compared to the water entering the lake, indicating that the lake is acting as a sink for toxic elements. Metal concentrations in the sediments are high; Ni (max=5023.6 ppm), Cu (max=2418.1 ppm) and Fe (max=47500 ppm). Despite low concentrations of bioavailable elements, a large proportion of heavy metals have been sequestered by the three plant species namely *Myriophyllum spicatum, Scirpus acutus* and *Typha latifolia*. Combined estimates of standing crop, show values of 23.1 tonnes of Fe, 7.4 tonnes of Ni and 0.9 tonnes of Cu present in the plant population, in 2000. The metals contained in *Myriophyllum spicatum* could be recycled back into the system in the fall when plants begin to die-off. It is plausible that a harvest regime for *Myriophyllum spicatum* could drastically reduce the heavy metal content in the soil as well as the water column.

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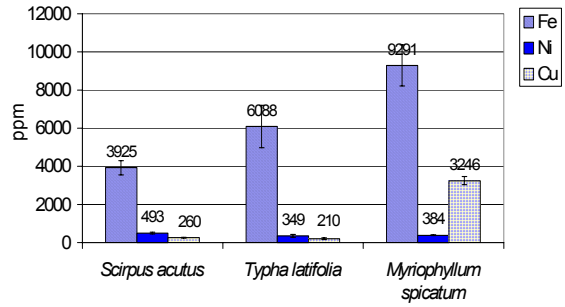

Figure 1. Average concentration (±s.e.) of heavy metal accumulation in three dominant species in Kelley Lake.

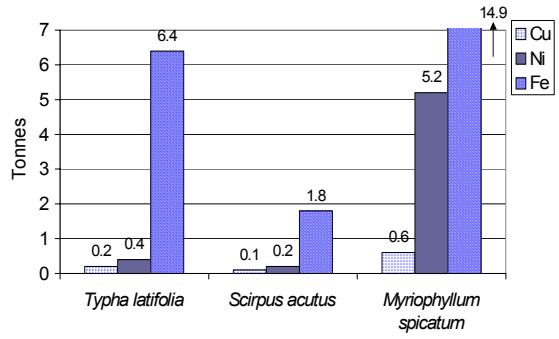

Figure 2. Estimates of standing crop for metals in three plant populations.