

SEDIMENT QUALITY ASSESSMENT NEAR TWO ONTARIO MINE SITES: HOW RELEVANT ARE THE PROVINCIAL GUIDELINES?¹

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Abstract: Sediment quality guidelines have recently been issued in Ontario. These guidelines provide methodologies to assess the degree of impact, as well as outlining contaminant criteria for remedial action. Results from recent environmental studies carried out near two Noranda mine sites in Ontario were used to assess the relevance of these guidelines for river sediments near mining operations. Site-specific results (solid-phase total metal concentrations, porewater metal concentrations, sequentially extracted metal phases, benthic community assessment, and sediment toxicity testing) are presented and compared with the Ontario Ministry of the Environment and Energy (MOEE) Provincial Sediment Quality Guidelines (PSQG). Results from one particular site were used to predict lowest effect level (LEL) and severe effect level (SEL) values for sediment Cu, Pb, Cd, and Zn concentrations, using the MOEE PSQG development approach for metals. These site-specific LEL and SEL values are much greater than the PSQG values. Solid-phase sediment toxicity tests showed that increased mortality or reduced growth in test animals occurred at sediment metal concentrations well above PSQG SEL. This study suggests that the PSQG numerical criteria may be too conservative for some metals and should be used as a screening tool only, while site-specific data should be used to confirm the actual environmental effects on the benthic biota.

Introduction

As part of their environmental management program, many of the Noranda group operations have carried out studies to assess the degree and extent of impacts of their operations on the nearby environment. These studies have mainly focused on aquatic environment aspects such as water and sediment quality, along with effects on the resident biota (fish populations and benthic communities). The enrichment of aquatic sediment by various metals can be important in the vicinity of some mine sites. The resident benthic fauna could be directly affected by this contamination, depending on its degree and possibly on the forms of metal in the sediment.

Sediments quality guidelines have been recently issued by Ontario MOEE (Persaud et al. 1992) to protect the aquatic environment, and to provide guidance during the decision-making process in relation to sediment contamination, ranging from preventive to remedial action. The guidelines describe numerical values developed for the protection of aquatic biological resources (i.e., benthos), which can be directly impacted by contaminated sediments. Among the various approaches considered for developing sediment quality guidelines (Persaud et al. 1992, Chapman 1989, Procéan 1991, MacDonald et al. 1992), the Ontario MOEE PSQG have used the screening level concentration approach (developed by Neff et al. 1986) to derive their numerical criteria. Two levels of effects are described: the lowest effect level (LEL) and the severe effect level (SEL). The historical level of the contamination observed near some Noranda mine sites would be considered severe because sediment metal levels are much higher than the numerical guideline values (Prairie 1993).

Since these guidelines could potentially impact on Noranda mining activities in terms of regulatory response, it became important that the available information (on metal-contaminated sediments and the related effects on the

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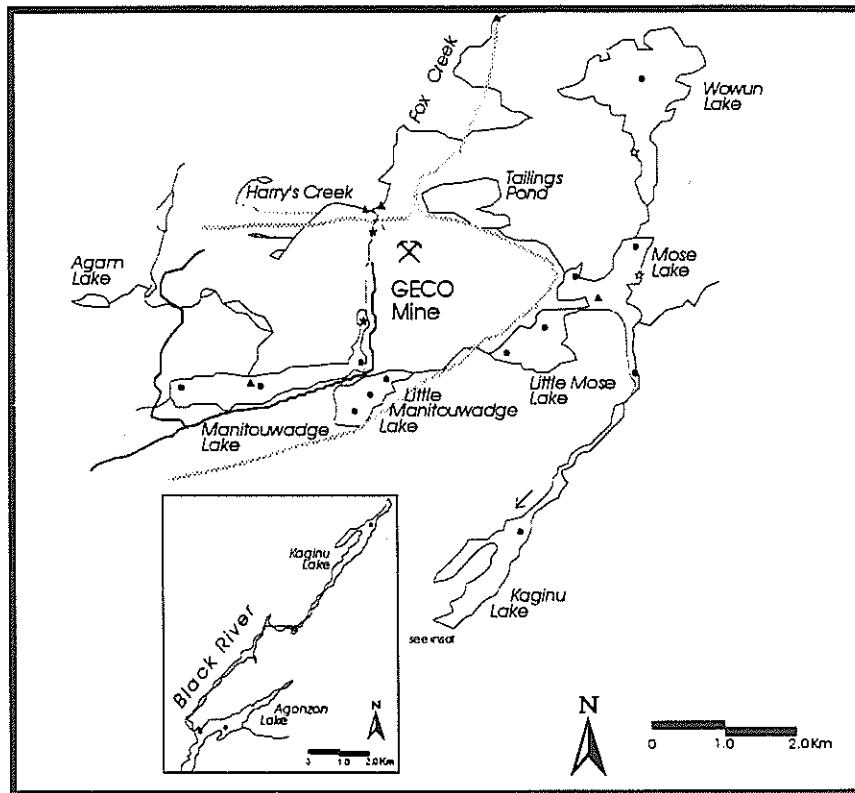
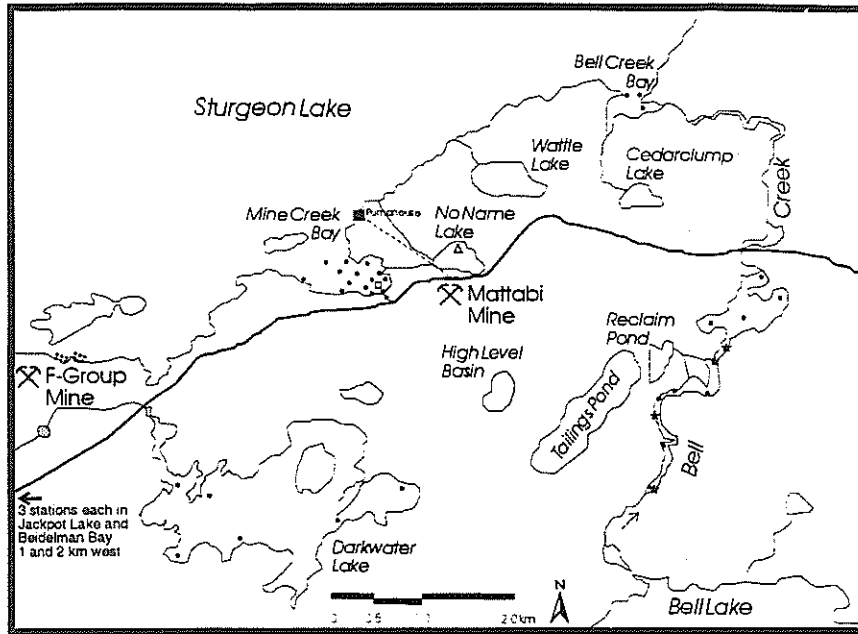
benthic biota) be reviewed and updated (via supplementary sampling and testing). Many of the Noranda group mine sites have recently carried out environmental studies to determine current environmental conditions as a baseline for the development of their closure plans. The objective of this paper is to describe some of the sediment chemical analyses and biological response results obtained from the testing of several river sediments collected downstream of discharges from two Noranda mine sites affected by acid mine drainage (AMD): Mattabi Mines Ltd (Mattabi) and Noranda Minerals Ltd, Geco Division (Geco), both located in northern Ontario.

Methods

Figure 1 illustrates the sampling site locations near Mattabi and Geco mine sites, between 1989 and 1992. Table 1 summarizes the number of samples and the type of analysis or tests carried out at Mattabi Mines and Geco along with the methods and protocols used for each of the parameters studied.

Table 1. Number of sites sampled or tested for the various topics near two Noranda mine sites, 1989-92.

Topics	Sampling methods	Mattabi	Geco	Laboratory analyses / methods
Solid-phase chemistry	KB Corer	66	21	Zn, Cu, Pb, Cd, Fe by graphite furnace or inductively coupled plasma (ICP)
Porewater chemistry	Peepers	6	4	Zn, Cu, Pb, Cd, Fe, by ICP
Sequential extraction analysis	Ekman grab	1	4	Zn, Cu, Pb, Cd, Fe, plus others; modification of Tessier et al. (1979) method, ICP
Simultaneously extracted metals / acid-volatile sulfide	Ekman grab	5	4	Simultaneously extracted Zn, Cu, Pb, Cd, and Ni by ICP; AVS, DiToro et al. (1992)
Benthic community structure	Ekman grab	66	21	Benthic identification at genus level
Sediment toxicity tests	Ekman grab			
<i>Hyalella azteca</i>		6	-	10-day mortality ; ASTM (1991a)
<i>Chironomus riparius</i>		4	-	8-day mortality and growth; ASTM (1992)
<i>Chironomus tentans</i>		2	7	10-day mortality and growth; Bedard et al. (1992)
<i>Hexagenia limbata</i>		-	7	10-day mortality and growth; Bedard et al. (1992)
<i>Pimephales promelas</i>		-	7	10-day mortality and growth; Bedard et al. (1992)



● Benthos, Sediment Chemistry	▲ Benthos, Sediment Chemistry, Sediment Toxicity, Porewater	✦ Benthos, Sediment Chemistry, Sediment Toxicity, Porewater, SEMAVS
▲ Benthos, Sediment Chemistry, Sediment Toxicity	■ Benthos, Sediment Chemistry, Sediment Toxicity, SEMAVS	○ Benthos, Sediment Chemistry, Sediment Toxicity, Porewater, SEMAVS, SEA
✦ SEA, SEMAVS, Porewater		

Figure 1. Location of sampling sites near Matabi and Geco mine sites, 1989-92.

Data described here were collected near the two Noranda mine sites between 1989 and 1992. The 1989 data for the Mattabi mine site were gathered by Noranda Technology Centre (NTC) during an extensive preclosure environmental study (Prairie et al. 1990, 1992). At both sites, Beak Consultants Ltd. (BEAK) carried out environmental studies during the 1991-92 period (Beak Consultants 1993a, 1993b) to assess current environmental conditions as a baseline to predict postclosure improvements.

Sediment Analysis

Sediment samples were collected for chemical analysis using a K-B corer; a total of 10 sub-samples were pooled for each desired depth. Cores were extruded within eight hours of collection and the outer smear zone removed. Samples were then placed in polyethylene bags and frozen within 48 hours. **Total metal concentrations** were determined on aqua regia extracts of the solid phase of the sediments at various depth increments, and are all reported on a dry weight basis. For the purpose of the present document, the surficial sediment (typically 0 to 5 cm) data will be used, as benthic communities are found generally in the top portion of the sediments.

Interstitial water (or **porewater**) concentrations of contaminants are good tools to predict toxic effects to the benthic biota (DiToro et al. 1991, Ankley et al. 1990). Peepers (technique described in Mudroch and MacKnight 1991), which collect in situ porewater by dialysis, were selected to sample the sediment interstitial water at both sites. Samples for dissolved metal determinations were removed in the field with a hypodermic syringe and preserved with HNO_3 . Metal determinations were done by ICP (BAS 1992).

Sequential extraction analysis (SEA) is an operationally defined procedure which provides a convenient means of determining major accumulation phases for metals in sediments. The SEA procedure identifies five fractions in the bulk sediment-exchangeable, carbonate bound, Fe-Mn oxide bound, organic complexes and residual metals. The Tessier sequential extraction procedure (Tessier et al. 1979) was used to evaluate metal (particularly zinc) chemical speciation in key sediment samples from both sites. In all cases, surficial sediments were collected by Ekman grab, transferred immediately to air-tight polyethylene bags and frozen. The Tessier et al (1979) extraction procedure was modified by keeping the sediment frozen until extraction and samples were thawed for analysis under N_2 to avoid oxidation and altered metal partitioning (Thomson et al. 1980; Rapin et al. 1986). Residual metals in the extraction series were extracted by aqua regia rather than hydrofluoric acid. The metals analyzed in the SEA included Zn, Cu, Pb, Cd, and Ni, and determinations were made by ICP (BAS, 1992).

Acid-volatile sulfide (AVS) is an operationally defined sediment parameter that consists of sediment sulfides that are cold acid soluble. Although acid-volatile sulfide has been studied for several years, it only recently has been recognized as a possible indicator of metal toxicity in sediments. Several recent studies (DiToro et al. 1990, 1992; Ankley et al. 1991) have identified a link between the toxic potential of trace metals such as Pb, Cd, Zn, Cu, and Ni to benthic invertebrates in sediment deposits and the amount of acid-volatile sulfur present in the sediments. They have found that no significant mortalities occurred relative to controls if the AVS concentration is greater, on a molar basis, than the simultaneously extracted metals (SEM). The above hypothesis was tested by BEAK at both sites by determining the AVS and SEM, and by carrying out sediment toxicity tests on a total of nine samples.

Biological Responses

The resident **benthic community** (insect larvae, clams, worms) which has been used extensively in past decades to assess impacts of effluents on the aquatic fauna has been also sampled during the various surveys at both sites. In these studies, benthic samples were sieved using a 500- μ m mesh and preserved in the field with 10% buffered formalin. All Mattabi samples were sorted using a microscope, identified and enumerated by L.Cloutier, University of Montréal. Geco samples were sorted by Ontario Ministry of Environment and Energy (MOEE) and were identified and enumerated in BEAK's biological laboratory; all stations were sampled and analyzed in triplicate. The identification of benthic organisms was carried out down to the genus level (whenever possible). To allow comparisons between stations, the enumeration and identification results were assessed according to the number of taxa, the total density (number of organisms per square meter), the relative density of organisms (%) in categories of pollution sensitivity, and the diversity index.

Although benthic community structure assessments are widely used, they have several limitations (e.g. different types of substrate, natural variations, ...). Therefore, the presence and absence of benthic invertebrates alone does not give much insight into the toxicity of sediments (Geisy and Hoke 1990). Specific benthic macroinvertebrate species have often been described as the optimal assessment tool in determinations of sediment toxicity. The close contact of tested organisms with bottom sediments and with interstitial and overlying waters, for extended periods, permits adverse effects to occur in the presence of contaminated sediments (Burton 1992). During our studies, different types of **sediment toxicity tests** were carried out (not systematically) at key locations near the two mine sites: *Hyallela azteca* (ASTM 1991a), *Chironomus riparius* (ASTM 1992), *Chironomus tentans* (Bedard et al. 1992), *Hexagenia limbata* (Bedard et al. 1992), and fathead minnows, *Pimephelas promelas* (Bedard et al. 1992). Sediment collection, handling and storage protocols were consistent with ASTM (1991b) standard guide.

Sediments from Mattabi were tested in BEAK's toxicity laboratory. Geco sediments were tested by the Ontario MOEE, although samples from two sites (identified as toxic by the MOEE in 1991) were resampled and tested by BEAK in 1992 to confirm the initial finding. All sediments sampled by BEAK were tested fresh (sediments collected and tests set up within 96 hours). Sediments were wet sieved without the addition of freshwater (overlying water present with the sediments used as wash water). Tests carried out by the MOEE were wet sieved as described in Bedard et al. (1992).

Results and Discussion

Although the concentrations of metals other than zinc in sediments (such as Pb, Cd, and Cu) have been determined during these studies and may very well be involved in the toxicity to the benthic biota, the following section uses zinc as a tracer for metal contamination in sediments. Of all the metals tested in these sediments, zinc shows the greatest degree of elevation in comparison with natural background. Also, the concentrations of the other metals were all significantly correlated with zinc (e.g., for Mattabi, $n=66$, $p<0.05$, $r>0.7$).

The 1991-92 resident benthic community results from the Mattabi mine site (Prairie et al. 1990, 1992; Beak Consultants Ltd 1993a) showed effects (reduced number of taxa and diversity along with increased proportion of tolerant organisms) as total metal levels in the sediments increased; the same observation was made using the 1989 data. Figure 2 illustrates the fluctuations of the number of taxa in relation to the total zinc concentrations (log scale) in the sediments, using all data pairs (Zn levels and number of benthic taxa) from 1989 and 1991-92 studies near

the Mattabi site. A majority of samples exhibited zinc concentrations above the PSQG Zn SEL values (820 $\mu\text{g/g}$); the total range of Zn concentrations in sediments samples (66) was 30 to 46,000 $\mu\text{g/g}$ (including reference sites). Also relatively high numbers of species are observed (up to 19 benthic taxa) at zinc levels above MOEE PSQG severe effect level. Although wide variations in the number of taxa can be observed, a linear inverse relationship exist between the log Zn concentration and the number of benthic taxa ($n=66$, $p<0.05$, $r=0.48$).

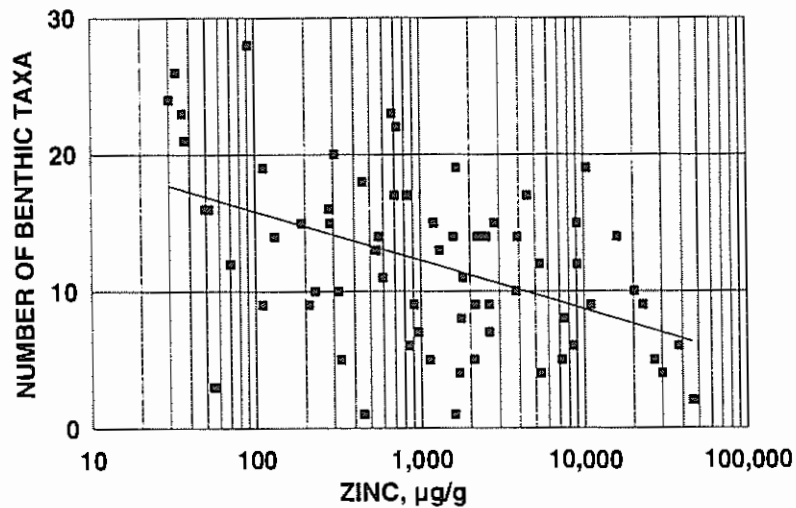


Figure 2. Zinc concentrations in sediments versus number of benthic taxa, Mattabi, 1989-92.

The toxicity tests results showed that no significant differences in mortality rates occurred (relative to controls) using *Hyaella azteca* ($p>0.05$);

significantly higher mortality rates occurred with *Chironomus* only when total zinc concentrations in the sediments reached 30,000 $\mu\text{g/g}$ ($p<0.05$). *Chironomus* growth rates were affected at zinc concentrations $>5,000$ $\mu\text{g/g}$ ($p<0.05$).

The benthic community data collected near the Geco mine site (Beak Consultants Ltd 1993b) showed similar trends where total zinc concentrations in the sediments samples (21) ranged between 54 and 9,600 $\mu\text{g/g}$ (including reference sites). A comparison of benthic responses (number of taxa and diversity index) to total zinc concentrations in the sediments was made using data from Mattabi and Geco. No significant differences between regression slopes for the two sites were observed ($p>0.05$). The toxicity tests carried out by Ontario MOEE in 1991 on seven key sediment samples collected near the Geco site (using *Chironomus tentans*, *Hexagenia limbata*, and *Pimephales promelas*) showed no significant differences in mortality rates (Tukey's multiple range test) relative to the control test, except for two sites where low surface water pH (3.9) and high un-ionized ammonia probably contributed to the observed mortalities (probably not related to metal levels in sediments). The range of total zinc concentration in the seven sediment toxicity tests was 30 to 6,000 $\mu\text{g/g}$.

The sequential extraction analysis (SEA) results from one Mattabi sample (3,400 $\mu\text{g/g}$ Zn), showed that most of the zinc (and also other metals such as Pb and Cd) was found in the Fe-Mn oxides phase. No toxicity (using *Hyaella* and *Chironomus*) was found for that sample, although the resident benthic community from that collection station appeared to be slightly impaired (lower number of taxa but relatively high diversity index values). The four Geco SEA results showed about the same conclusions, i.e. most of the metals, especially zinc, were found mainly in the Fe-Mn oxides phase (and 20 to 40% in the organic phase). At locations where samples were analyzed for both SEA and toxicity, none showed sediment toxicity values significantly different than the control test values, except for one sample where the fathead minnow test showed 100% mortalities and could probably be attributed to the high un-ionized ammonia levels. Therefore, the SEA results from the Mattabi and Geco are consistent with the nontoxic response observed since zinc was in a relatively non bio-available form (Fe-Mn oxide and organic phase).

proportion of total organic carbon; Mattabi sediments TOC values averaged 8%, while MOEE sediments' TOC values were closer to 2% (Hart et al. 1988). The differences in biological responses from the two sets of SLC values could be explained by the fact that a high organic carbon content in the sediments may bind metals and therefore inhibit toxic effects of metals to benthic organisms.

Table 2. Screening level concentration calculations (LEL and SEL) using MOEE (Great Lakes) and Noranda (Mattabi) databases.

Metal	Cu	Cu	Pb	Pb	Cd	Cd	Zn	Zn
Database	Mattabi	MOEE	Mattabi	MOEE	Mattabi	MOEE	Mattabi	MOEE
LEL, µg/g	388	16	213	31	5.2	0.6	1,600	120
SEL, µg/g	1,946	110	840	250	48.4	10	21,500	820

Conclusions

The current sediment quality guidelines encourage an assessment on a site-specific basis of the effects of elevated sediment metal concentrations on biota when concentrations exceed the specific numerical values. These studies suggest that, for some metals (particularly zinc), exceedance of numerical criteria should not mean automatic implementation of a specific remedial action or program. Based on the studies undertaken on sediment quality conditions at the two Noranda mine sites, it can be concluded that benthic studies, combined with confirmatory sediment toxicity tests, may be the most effective means of evaluating sediment quality impacts near mine sites. Reliance solely on MOEE PSQG values for assessment of bulk sediment chemistry data for Zn (and possibly Pb, Cu and Cd) near the mine sites considered would lead to exaggerated conclusions on impact. It is therefore concluded that the MOEE PSQG values for some metals should be used only as a screening tool for sediment quality evaluation near mine sites.

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