## Metal Concentrations in Bivalves Living in and Around Copper Mine Tailings Released After a Tailings Dam Breach

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Environmentally safe disposal of mining waste products such as mill tailings is an ongoing concern for regulators and mine operators. In Canada, the discharge of tailings to the marine environment is not permitted. However, with ministerial consent, there is no limit on the concentration or quantity of effluent that can be deposited into a tailings impoundment (Metal Mining Liquid Effluent Regulations 1995). Therefore, the more common tailings disposal method is to store the tailings on-land under fresh-water in a pond or dammed enclosure. A layer of fresh water can prevent oxidation of the tailings thus reducing the release of potentially harmful metals (Brassard et al. 1996). The obvious downside to a tailings pond or dammed enclosure is the need to maintain the enclosures in perpetuity, or until some remedial action can be taken to stabilize the tailings so that they no longer pose an environmental risk. Unfortunately mining projects, by their very nature, have finite life spans with the subsequent abandonment of mining sites.

The failure of tailing pond dams and the accompanying release of large amounts of metal contaminated material is not uncommon (e.g. Grimalt et al. 1999). In our study a wooden-crib and rubble dam breached in 1991 and since then approximately 500,000 m³ of tailings from the abandoned copper mine have been transported into Little Bay Arm (Stirling and Roy 2000). To date the dam has not been repaired and tailings continue to flow into the arm. The area is a popular spot for the collection of mussels and clams for local consumption. As well, commercial mussel farms operate within Little Bay Arm.

The purpose of the study was to: 1. determine if the mussels and clams in the area closest to the dam breach were accumulating metals found in the tailings; and 2. compare the metal concentrations in the mussels and clams to the United States Food and Drug Administration's (USFDA) "levels of concern" for metal concentrations in shellfish (United States Food and Drug Administration 1993).

## MATERIALS AND METHODS

Samples of the common blue mussel, *Mytilus edulis*, the soft shell clam, *Mya arenaria*, and sediment were collected from Little Bay Arm in Notre Dame Bay, Newfoundland, Canada (49.60° N 55.93° W) in September 1999. Clams and mussels were depurated for 24 hours in clean sea water then frozen and transported to the laboratory. At the laboratory, clams and mussels were thawed and shucked using plastic implements. Owing to obvious contamination, clams had the sheath covering their siphon and their guts removed and discarded. The mussels were analyzed whole. Groups of five individual clams or mussels were selected haphazardly and placed in trace metal clean containers. The soft tissue was then dried at 100°C to a constant weight. Next, samples were dry ashed at 500°C and the ash was then digested in concentrated nitric acid. The resulting solution was diluted and analyzed for a suite of metals by ICP-MS. The accuracy of our results was confirmed by comparing the results from the National Institute of Standards and Testing (NIST) standard reference material (SRM) number 2976 (mussel tissue) to its certified values.

Results from the bivalve tissue analyses were compared by a two way analyses of variance with site and species as independent variables and metal concentrations as the dependent variable.

Sediment was digested in Teflon high-pressure closed vessels to ensure complete dissolution of refractory minerals. About 0.1 g of sample powder was dissolved in a HNO3-HF acid mixture for 2 days at 200C. Sensitivity factors were determined by external calibration to synthetic solutions and accuracy was evaluated by measurement of sediment reference materials PACS-1 and MESS-2. Detailed procedures are given by Diegor et al. (2001).

## RESULTS AND DISCUSSION

Blue mussels and soft shell clams have been shown to accumulate metals from their environment (Eisler 1977; Szefer et al. 1990; Walsh and O'Halloran 1998; Haynes and Toohey 1998). In this study the suspected source of metals was tailings from an abandoned copper mine. The tailings had been under a layer of fresh water from the time of disposal and remained undisturbed from the closing of the mine in 1969 until the tailings-dam breached in 1991. The tailings were then released into the marine environment where they formed a delta that now makes up part of the tidal zone in Little Bay Arm

The clams and mussels living near the dam breach are in constant contact with the released tailings. The soft shell clam lives burrowed 10-15 cm below the surface of the tailings near the outlet of the tailings pond. The blue mussel lives on the edge of the tailings delta attached to rocks. However, fine grained material surround the rocks and is re-suspended under windy conditions or when boats

pass by. Both species are filter feeders and it was assumed that they ingested tailings during feeding.

Concentrations of Cu, V, Mn, Co, and Fe were significantly (p<0.05) higher in the soft tissue of the mussels and the clams at the study site compared to samples from the control site (Fig. 1). There was also a significant species effect with mussels having the higher concentrations of all metals except Cu and Ni.

The guts of the mussels were not removed prior to the analyses as were the guts of the clams. Therefore, it was felt that the species effect may have been caused by tailings remaining in the guts of the mussels. However, there was no significant (p>0.5) species effect for Cu or Co (Fig. 1). The concentration of Cu and Co in the sediment at the study site is much higher than in the sediment from the control site (Table 1). Any contamination from sediment in the gut of the mussels would be expected to appear as an increase in the concentration of the more abundant metals, especially Co which is not an essential element. This was not the case here. It was concluded, therefore, that the bivalves in the area were accumulating excess metals from the tailings.

Consumption surveys were not carried out on the local population. However, it is common knowledge that the people of Newfoundland are regular consumers of seafood, and consumption of wild foods such as clams and mussels is common place. Of the metals reported here the USFDA have provided guidance documents for Cd, Cr, Pb, and Ni in shellfish (United States Food and Drug Administration 1993). Copper, which was of particular concern in this study is not included in the USFDA guidance documents. This may be in part owing to the fact that copper is an essential element and only lethal to humans at high doses (Chuttani et al. 1965; Jantsch et al. 1984). Nevertheless, the copper concentrations in *Mytilus edulis* at Little Bay are some of the highest values ever reported for wild mussel populations. Our mean Cu concentration of  $45\mu g \cdot g^{-1}$  dry weight is double the World Mussel Watch  $85^{th}$  percentile value of  $21\mu g \cdot g^{-1}$  dry weight for *Mytilus edulis* (Cantillo 1998). A comparison was, therefore, made between Cu in the bivalves from Little Bay and the World Health Organization's acceptable range of oral intake (AROI) for Cu (WHO 1998).

The data in table 2 shows that the concentrations of metals in the mussels and clams from this study are in the range of concentrations found in the 1985-86 FDA survey of contaminants in shellfish (United States Food and Drug Administration 1993). When comparing the metal concentration in our bivalves to the levels of concern in table 2 it can be seen that the greatest concern would be from Pb exposure. A child would have to consume 120g of *M. edulis* tissue from the study site to reach the daily limit for Pb. However, the 90<sup>th</sup> percentile of the 14 day average intake of bivalves in the United States for children 2-5 years is only 8 grams (United States Food and Drug Administration 1993a). Even with Newfoundland's propensity for seafood consumption it is unlikely that any child would be consuming 120 grams of mussels a day. Therefore, it appears that there

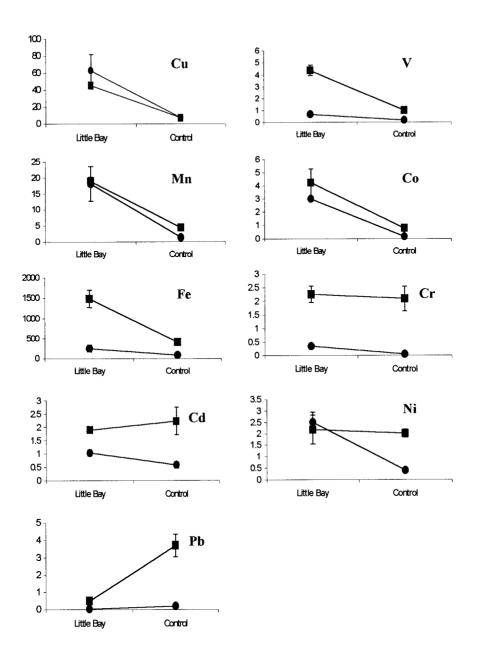


Figure 1. Mean metal concentrations ( $\mu g \cdot g^{-1}$  dry weight) in bivalves from Little Bay and a control site. Circles represent clams, squares represent mussels. Error bars are  $\pm 1$  standard deviation. Error bars smaller than the symbols are not shown.

Table 1. Concentration of total metals in the sediment from Little Bay and the control site

Metal	Little Bay (μg • g <sup>-1</sup> )	Control (μg • g <sup>-1</sup> )
Cu	532	12
V	208	143
Mn	1165	878
Co	181	12
Fe (%)	16.3	3.3
Cr	184	81
Cd	0.19	0.28
Ni	76	33
Zn	125	62
As	105	5
Sn	1	5
Pb	6	28

**Table 2.** Comparison of metal concentrations in study animals to USFDA survey values and USFDA/WHO levels of concern. All values are  $\mu g \cdot g^{-1}$  wet wt.

Metal	85-86 FDA survey <sup>†</sup>	Mean M. Edulis	Mean M. arenaria	Levels of concern µg/person/day
Cd	0.02-1.4	0.21	0.12	55
Cr	0.05-2.1	0.5	0.03	200
Pb	0.03-0.43	0.05	0.004	6-75 <sup>‡</sup>
Ni	0.0-2.2	0.24	0.29	1200
Cu	na	4 4	6.5	>3000*

<sup>†</sup>Range of mean values found in shellfish surveyed by the FDA in 1985-86. See appropriate guidance document for details (United States Food and Drug Administration 1993).

is very little health risk from metals studied here by consumption of the bivalves in the study area. However, guidelines were not available for Co, or Mn, which are elevated in the samples from the study site and are potentially toxic. As well, less is know about the toxic effects of mixtures of metals. Given a choice consumers should avoid any metal contaminated site when collecting wild foods for consumption.

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<sup>‡</sup>Range represents exposure levels for children to adults.

<sup>\*</sup>From WHO 1998.

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