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Possible Effect of Sedimentary Phosphorus on the Accumulation of Lead in *Mytilus edulis*

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The use of biological indicators in trace metal monitoring programs has gained popularity during the last two decades. Although it has long been recognized that phosphorus (P) may alter the uptake and retention of lead (Pb) in mammals (Shields and Mitchell 1940), its effect on the availability of Pb toward aquatic invertebrates has largely been ignored. The interactions between these two metals may be particularly important in regions sustaining significant P loadings through anthropogenetic activity.

Phosphorus is not found free in nature and usually occurs in the fully oxidized state as phosphate. The most common sedimentary apatite deposits, better known as phosphorites, consist mainly of Fluorapatite ($Ca_{10}(PO_4)_6F_2$).The Belledune industrial complex, located on New Brunswick's north shore (Figure 1), has a daily consumption of about 1500 tons of Florida fluorapatite (P. Maloney, Brunswick Smelting and Fertilizer, pers. comm.). It is used in combination with sulfuric acid and ammonia to produce diammonium phosphate fertilizer. The main source of P loading in Belledune Harbor is from spillage during the unloading of the fluorapatite, and as wind blown particles as the rock is conveyed from the loading dock. The neighboring smelter, which supplies the sulfuric acid produced during the refinement of the Pb/Zn sulphide ores, represents the main source of trace metal pollution.

The sediments within this small ($\approx$ 1.0 km^2) harbor contain high levels of trace metals including Pb and have been the focus of numerous biological monitoring programs (summarized by Hildebrand 1985). None of these studies however, related the effects P may have on the uptake of trace metals by the indigenous invertebrate community. This study illustrates how varying levels of sedimentary P may affect the availability of Pb to the common blue mussel, *Mytilus edulis.*

MATERIALS AND METHODS

Sediment samples were collected from four stations within Belledune Harbor (Figure 1) by a diver using a clean acrylic boxcore. The superficial sediment layer (top 5 mm) was sampled and maintained frozen until

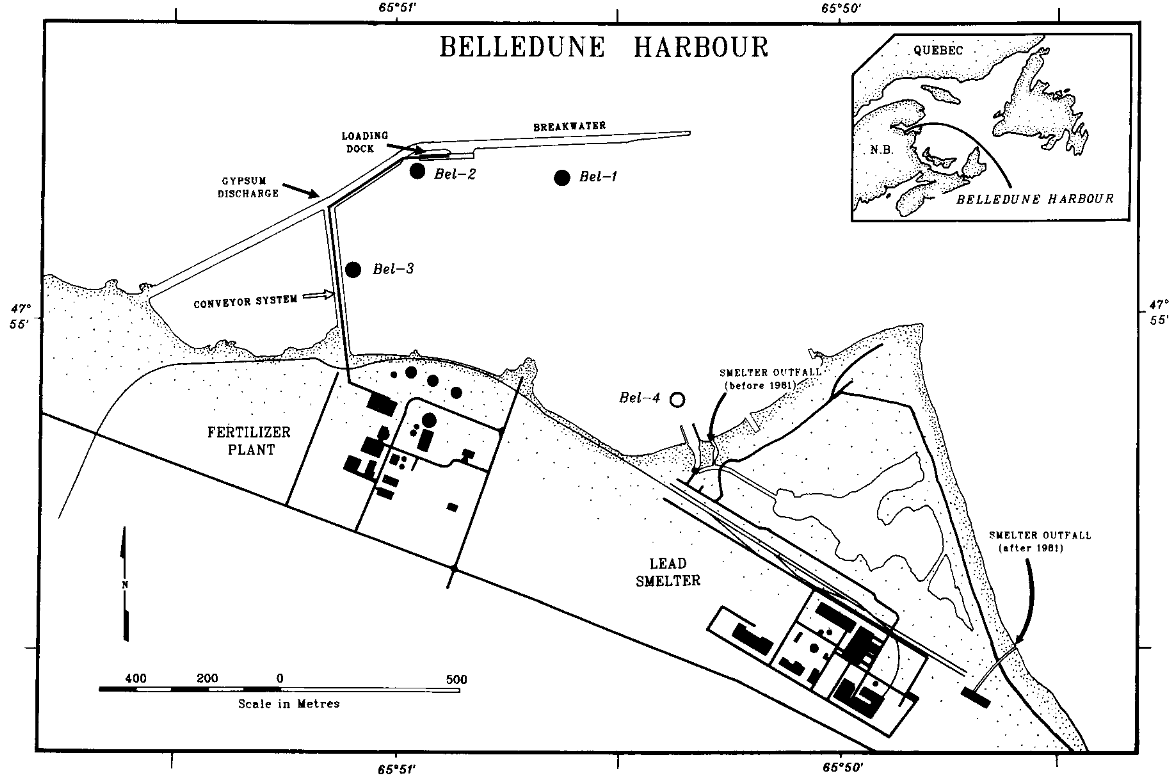

Figure 1 Location of sampling stations within Belledune Harbor: (●) bivalve and sediments samples, (O) sediments only. Smelter outfall was located within the harbor until 1981 when it was moved onto the coast. The effluent from the fertilizer plant is discaharged on the northern side of the breakwater.

further processing in the laboratory. Mussel samples were collected from three of the stations (i.e., Bel-4 excluded) after which they were allowed to depurate for 48 h in ambient seawater and then frozen pending analyses.

In the laboratory, thawed mussels were shucked, the tissues dried, and ground in an agate mortar. The calcite and nacreous shell layers were separated by a heat fracturing method (Bourgoin 1988). Nitric acid (BDH, Aristar) digestion techniques were employed for both the tissues and nacreous shell samples. Thawed sediments were wet sieved through 100 μm polyethylene mesh, the slurry centrifuged at 12000 g for 20 min, after which the supernatant was discarded. The sediment subsamples were dried, weighed, and submitted to a weak acid extraction 1N hydrochloric acid for 2 h (Luoma and Bryan 1978). The extract was separated from the sediments by filtration under pressure through pre-cleaned 0.45 μm Millipore filters.

The Pb concentrations in the extracts as well as in the tissue and shell digests were analysed with by flameless atomic absorption spectrometry (Perkin-Elmer 603, Downsview, Canada) equipped with a deuterium background corrector. A standard reference material, oyster tissue (NBS 1566), and an internal reference consisting of Pb spiked calcium carbonate (Aldrich, Gold Label), were analyzed with each group of tissue and shell samples (i.e., 10 samples / group), respectively. The P concentration in the sediment extracts was analysed by inductively coupled plasma - mass spectrometry (SCIEX ELAN model 250, Thornhill, Canada). The total P and Pb content in the sediments was determined on sediment subsamples by X-ray fluorescence spectrometry (Phillips model PW 1450, Scarborough, Canada). The accuracy of the analyses was checked by running two Canadian reference standards, BCSS-1 and MESS-1, and a South African standard, NIM-G. Nonparametric tests, Kruscal-Wallis, were used to determine the statistical differences in Pb concentrations among the three mussel samples.

RESULTS AND DISCUSSION

The Pb concentrations in the tissues and shells from mussels collected at Bel-1 and Bel-2 were significantly ($p < 0.05$) higher than the Pb measured in mussels sampled at Bel-3 (Figure 2). Conversely, the sediments at Bel- 3 contained twice the amount of Pb than the sediments at the other three stations (Table 1). Luoma and Bryan (1978) demonstrated that Pb levels in marine bivalves were best related not to the total Pb concentrations in the sediments, but rather to a relatively easily extracted fraction. Results from the weak acid extract experiment in this study indicated that all four sediment samples yielded similar amounts of Pb (Table 1).

The lower Pb levels in Bel-3 mussels may be explained by a higher amount of bioavailable P at this station as evidenced by the higher amounts of P extracted in the weak acid extract experiment (Table 1). Quaterman *et al.* (1978) observed in laboratory studies that the uptake of Pb by rats was

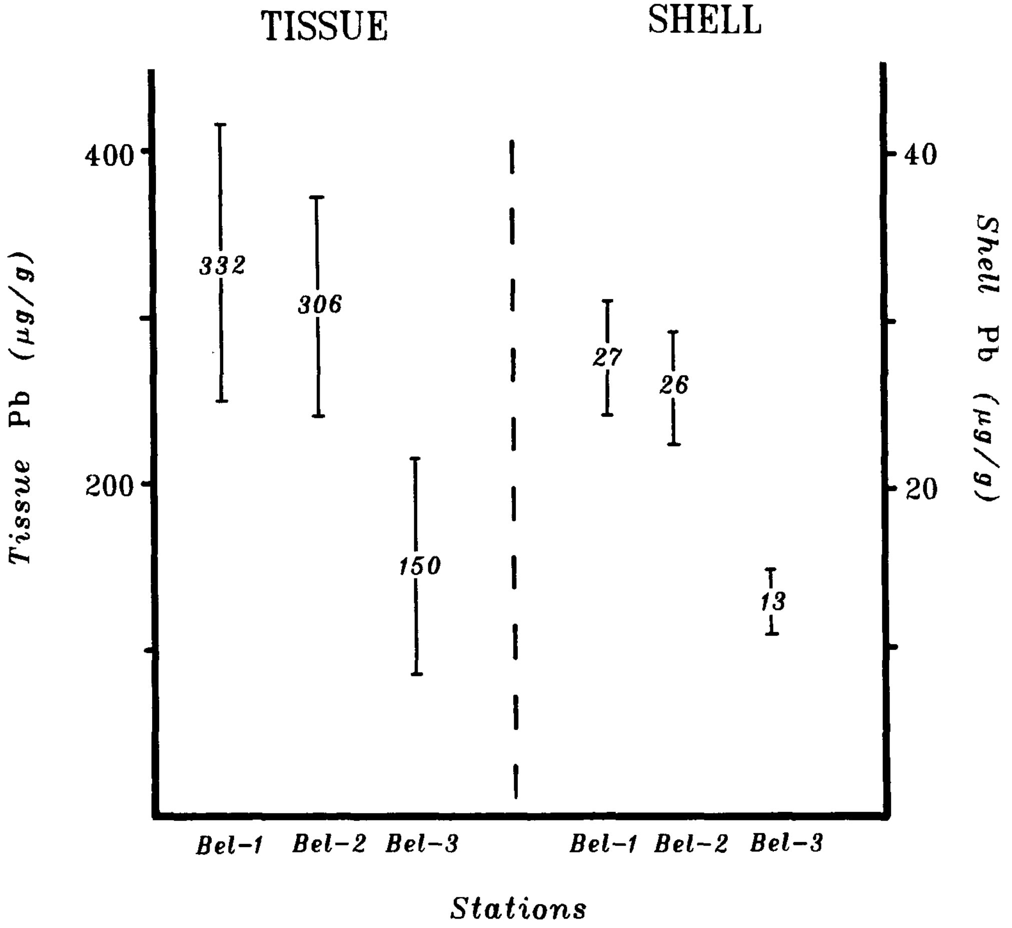

Figure 2 Lead concentration (µg/g, dry weight) in tissues and nacreous shell layers of *Mytilus edulis*. Averages of 10 analyses with 2σ confidence limits.

reduced by about half when dietary P (as phosphate) was doubled. Although the availability of particulate P in aquatic systems is still disputed (Bradford and Peters 1987), a widely accepted estimator of biologically available P is the algal assay (Butkus *et al.* 1988). Williams *et al.* (1980) reported that the P uptake by an algae species was related to the amount of inorganic P in the sediments. They further noted that the percentage of utilization of total P was generally highest when total P concentration in the sediments was itself high.

Earlier studies (Oakley *et al.* 1981; Luoma and Davis 1983) suggested that adsorption onto specific geochemical phases might control the trace metal concentrations in the ambient water at the sediment-water interface. The physico-chemical forms of trace metals in the sediments could affect the

Table 1 Phosphorus and lead concentrations (dry weight) in sediment samples collected within Belledune Harbor. TOTAL: total metal concentration determined by X-ray fluorescence spectrometry. EXTRACTED: amount of metal extracted with 1N HCl.

STATIONS	TOTAL		EXTRACTED	
	P (mg/g)	Pb (µg/g)	P (mg/g)	Pb (µg/g)
Bel-1	0.58	720	0.47	458
Bel-2	0.62	734	0.49	448
Bel-3	1.33	1520	1.21	421
Bel-4	0.67	790	0.51	432

bioavailability of particulate-bound trace metals. The fact that significant relationships have been established between various metal fractions in the sediments with metal levels in filter-feeding bivalves (Tessier *et al.*, 1984; Bourgoin 1987) supports this thesis. Others (Tessier and Campbell 1987) have proposed three mechanisms to explain the inverse relationships between metal concentrations in bivalves and the concentration of a potential sink in the sediments. While all three could be applied in this study, our results do not allow us to speculate which of these mechanisms would be most probable.

The biological significance of sediment-bound trace metals is complex and there is presently no satisfactory method for determining unambiguously the forms of association of particulate trace metals in natural sediments. The authors realize that the observations in this study are based on a limited data set, and that the relationships mentioned above may be circumstantial. The results, however, do warrant further investigations on the relationship between P and Pb as well as other trace metals and their uptake in aquatic organisms. Future work, either in the laboratory or field studies, should focus on the chemical form of the metals studied as this is usually the most important factor governing their bioavailability.

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