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by Maria Helena Furtado Viveiros for  
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**FOSSIL AND MODERN FRESHWATER BIVALVES  
AS RECORDERS OF METAL POLLUTION  
IN THE GREAT LAKES BASIN**

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AS RECORDERS OF METAL POLLUTION  
IN THE GREAT LAKES BASIN**

by

**MARIA HELENA FURTADO VIVEIROS**

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**TITLE:** Fossil and Modern Freshwater Bivalves as Recorders  
of Metal Pollution in the Great Lakes Basin

**AUTHOR:** Maria Helena Furtado Viveiros

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## ABSTRACT

This study analyzed fossil and modern freshwater bivalve mollusc shells, from in and around lakes Ontario and Erie, for the following trace metals: Cu, Ni, Zn, As, Pb, and Mn. *Elliptio dilatata*, *Elliptio complanata*, and *Lampsilis radiata siliquoidea* shells were analyzed by ICP-MS for differences in shell metal levels between species and genera, through time and due to anthropogenic inputs.

Regardless of age, all three species showed high concentrations of Zn and Mn, and little or no changes in Cu, Ni, Zn, and Pb concentrations with time. *E. complanata* shells were generally poorer in Pb, but richer in As and Mn, than were the *E. dilatata* and *L. radiata siliquoidea* shells. Fossil *Elliptio* samples did not possess low background, or baseline, trace metal concentrations. These samples were richer in As, Pb, and Mn than were modern samples from post-industrial environments. Among the modern shells, the *E. complanata* showed no differences in metal concentrations between samples from high- and low-contamination sites, while the *L. radiata siliquoidea* showed changes in Ni, As, and Mn concentrations among the same sites. Modern *L. radiata siliquoidea* may be more likely to represent environmental metal changes than are modern *E. complanata*. Historical change in environmental metal concentrations of the Great Lakes region is not recorded as a *simple* change in shell metal concentrations of these freshwater bivalve molluscs.

**In appreciation of the efforts of  
Nellie Mooney McClung (1873-1951)**

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1. These fossil samples from Cleveland could not be included in this study because they were too fragmented for species identification.

2. Samples obtained from Mr. Grant were shell button blanks dated *post 1860*. These samples could not be included in this study because we cannot prove that they were local to the Great Lakes Basin. Some local button factories imported mollusc shells from around the world (Ferris, 1986).

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## INTRODUCTION

Pollution in the aquatic environment can be investigated by analyzing the biota living in that environment. The accumulation of contaminants in the food chain allows researchers to monitor their bio-availability by analyzing their concentrations in the biomass. This is an important step in determining the potential risk to the health of a water system and the life it supports. Bivalve molluscs are useful biomonitors of water pollution because they accumulate a variety of pollutants and toxic substances into their soft tissues and shells.

Although most investigations have focused on marine coastal waters, current research is directed towards determining the effectiveness of freshwater bivalves as biomonitors for river and lake environments (Forester, 1981). Evidence of post-industrial metal contamination, attributed to anthropogenic inputs from industrial, domestic, and agricultural activities, has been found in the coastal sediments of Lakes Ontario and Erie (Kemp and Dell, 1976). Unionacean clams and mussels, abundant in the Great Lakes Basin, have provided evidence of anthropogenic trace metal contamination in their shells (Dermott and Lum, 1986; Tevesz, Mansoff, Frank, and McCall, 1989).

It does not necessarily follow that trace metal levels in the shells of freshwater bivalves directly reflect the environmental levels (Dermott and Lum, 1986). In this investigation fossil shells from pre-industrial sites were compared with modern shells from post-industrial sites. The objective was to determine how trace metal concentrations in fossil and modern freshwater bivalve shells compared with pre-industrial and modern environmental concentrations.

## REVIEW OF LITERATURE

### BIVALVE MOLLUSCS AS BIOMONITORS OF POLLUTION

Unionacean clams and mussels are an ideal monitoring agent for pollutants in aquatic environments. Many species of these bivalve molluscs meet the following the following criteria (Forester, 1981):

- (1) tissue residues are formed from a variety of pollutants which may be concentrated above environmental levels;
- (2) position in the food chain is low (filter feeders) and they reflect environmental levels directly with little interaction with other trophic levels;
- (3) longevity and limited mobility enable them to integrate environmental levels over a period of time at one location;
- (4) growth lines on the shell enable correction for age bias in samples and facilitate comparison of data;
- (5) local abundance and wide distribution encourage use in regional sampling programmes;
- (6) hardiness enables them to be transported for use in field and laboratory conditions; and
- (7) size provides adequate material for chemical analysis.

Analysis of the bivalve shell offers some advantages over the analysis of its soft tissues (Bourgoin, 1987a; 1988). Shells are more easily collected, identified, preserved, and cleaned than are soft tissues. The problem of whether or not to allow the organisms to depurate the contents of their digestive tract is avoided. More precise statistical inferences are possible with shell analysis because it reveals lower variances in contaminant concentrations than do the soft tissues. Most important, the shells of certain species allow for the identification of long-term trends within the lifespan of the organism (Bourgoin, 1987a; Dermot and Lum, 1986), and shells preserved in the fossil record have the potential to reveal historical change in trace metal concentrations within their environments (Bertine and Goldberg, 1972; Bourgoin and Risk, 1987; Tevesz, Mansoff, Frank, and McCall, 1989).

## FRESHWATER BIVALVES

Freshwater bivalve molluscs, which share many biological similarities with their marine counterparts, may be useful as biomonitors of contaminants in lakes and rivers (Forester, 1981). Investigations have shown that several species of freshwater unionacean calms and mussels concentrate metals, radionuclides, and organic substances above environmental levels.

### Soft Tissues

The soft tissues of some species of freshwater bivalves have been reported to concentrate various pollutants. Analysis of the soft tissues of *Elliptio complanata* has revealed that this bivalve takes up and accumulates organic contaminants such as hexachlorobenzene and octachlorostyrene (Ronald, Frank, and Gobas, 1989), and polychlorinated dibenzo-dioxins (Hayton, Hollinger, Tashiro, and Reiner, 1990) above environmental levels. Investigations of trace metal concentrations in the soft tissues of *Elliptio complanata* have revealed that the highest such concentrations are found in the gills and mantle (Tessier, Campbell, Auclair, and Bisson, 1984). Some researchers suggest that an analysis of the gill tissues alone might be a better bioindicator of available metals than the whole body tissues (Servos, Malley, Mackie, and LaZerte, 1987). But analysis of the gill tissues of *Elliptio complanata* revealed that tissue concentrations did not directly reflect metal levels in the water (Hinch and Stephenson, 1987). An in-situ monitoring experiment, analyzing whole body tissues of *Lampsilis ventricosa*, revealed lead and cadmium tissue concentrations correlated with main sources of lead and cadmium discharge (Czarnecki, 1987).

## Shell Material

The shells of some species of freshwater bivalves have been reported to concentrate various pollutants. Metal concentrations in shells of fingernail clams (Family Pisidiidae) were examined in bivalves prior to, and after, three months of exposure to effluent from a gold mine (Duncan, Tevesz, and Towns, 1987). The exposed shells revealed higher iron, lead, and zinc levels, but lower copper levels.

Some investigators have looked for interspecific differences in shell metal levels between different species of freshwater bivalves (Tevesz, Manoff, Frank, and McCall, 1989). They found no correlations between shell morphology, age, or sex of bivalves and the manganese concentrations in the shells. Their investigation did reveal a pattern of manganese levels between genera as follows: *Fusconaia* > *Anodonta* > *Lampsilis*. Modern samples of *Lampsilis radiata luteola* were collected from three separate localities, and no differences in metal concentrations were detected between them. However, fossil *Lampsilis* shells contained significantly higher metal levels than their modern counterparts. This is a warning that one cannot always assume that pre-industrial samples will necessarily be lower in all, or any, trace metal levels than modern bivalve samples.

Analysis of modern *Elliptio complanata* bivalves revealed that zinc had a stronger affinity for the soft tissues, and lead for the shell (Dermot and Lum, 1986). Not only were most metal levels higher in the soft tissues of bivalves, but metals also tended to be higher in the outer periostracum of the shell than in the inner prismatic shell layer (Dermot and Lum, 1986; Bourgoin, 1987a). These are warnings that shell trace metal levels may not directly correspond to environmental levels.

## HISTORICAL CHANGE IN METAL LEVELS

Most studies of historical change in shell trace metal levels have focused on marine bivalves. One study, investigating what effect one hundred years of anthropogenic contamination of marine inshore environments had on the shell composition of various species of clams and mussels, found no correlation between metal concentrations in the shells and in the aquatic environment (Bertin and Goldberg, 1972). Studies using *Mya truncata* showed that modern shells contained significantly higher lead concentrations than fossil shells (Bourgoin and Risk, 1987). The modern lead levels were attributed to anthropogenic contamination. Another study using the same species revealed higher zinc levels, but lower copper levels, in modern shells (Bourgoin, 1988).

Few investigations of historical change in metal levels have been conducted using freshwater bivalves. One study found that fossil *Lampsilis* shells contained significantly higher manganese levels than their modern counterparts (Tevesz, Manoff, Frank, and McCall, 1989).

In this investigation the shells of freshwater bivalve molluscs were analyzed for a wide suite of trace metals. Fossil and modern shells were analyzed for copper, nickel, zinc, arsenic, lead, and manganese. The objective was to assess what effect the input of these metals into Lakes Ontario and Erie had on the shell composition of their bivalve mollusc population.



## RATIONALE

Previous investigations suggest that a record of past levels of trace metal pollution in the aquatic environment may be found within the shells of bivalve molluscs (Bourgoin, 1987a, Bourgoin and Risk, 1987). Bivalves absorb, accumulate, and concentrate a variety of pollutants, including trace metals. While most studies have focused on the marine coastal environment, there is mounting evidence that freshwater molluscs may be useful as bio-indicators of contaminants in lakes and rivers (Forester, 1981).

This investigation attempted to find evidence of historical change in levels of metal pollution in the Great Lakes Basin. Fossil and modern freshwater bivalves, collected from Lake Ontario and Lake Erie, were analyzed to determine the feasibility of their use as recorders of metal availability through time in this region. No samples were taken from areas known to be point sources of metal pollution. The objective was to determine if metal concentration signatures corresponded to dates of intense urbanization and industrialization of this region.

A second objective of this investigation was to compare the metal signatures in bivalve mollusc shells of distinct genera (ie *Elliptio* and *Lampsilis*), and of distinct species (ie *Elliptio complanata* and *Elliptio dilatata*). Insignificant variation between species and/or genera would allow for the compilation of a more complete record of past lake metal levels.

## MATERIALS AND METHODS

### STUDY AREA

The Great Lakes basin, which contains roughly 18% of the world's supply of fresh water (Botts and Krushelnicki, 1988), has been accumulating pollutants since agricultural and industrial development of this region began. The basin supports  $\frac{1}{4}$  of Canada's population and  $\frac{1}{10}$  that of the U.S.A.'s (Botts and Krushelnicki, 1988). The lakes provide water for consumption, transportation, recreation, agriculture, power, industry, and waste disposal. At the turn of the century agriculture and industry in the basin area intensified, subsequently increasing the amount of organic chemical and trace metal pollution in the lake waters.

Pollutants entering the lakes are retained and concentrated with time. Nonpoint sources allow diffuse amounts of pollution to enter the lakes via tributaries, land runoff, groundwater movement, and atmospheric deposition. Point sources allow concentrated amounts of pollution to enter the lakes via direct shore discharge. The shoreline of the lower Great Lakes region is under continual stress since little of it remains undeveloped (Botts and Krushelnicki, 1988).

The major industries in the Great Lakes region produce steel, paper, chemicals, automobiles, and other manufactured goods. Steel industries are concentrated here because iron ore, coal, and limestone can be transported on the lake waters from mines and quarries to the steel mills.

This study focused on sites in the southwestern section of the basin, in and around Lake Ontario and Lake Erie. Archaeological and modern sites were investigated. None of the sites sampled are direct point source areas of pollution.

### Pre-1700 Sites

Fossil *E. complanata* and *E. dilatata* shells were obtained from archaeological sites around the western tips of Lakes Ontario and Erie (FIGURE 1). Dates derived for these shells range from 900 to 1651. At this time there was no anthropogenic input of metal pollution into the nearby river and lake waters because there was no large scale agriculture or industry. Metal concentrations in shells from these sites may be indicative of pre-industrial or natural background levels.

### 1964 Sites

Modern *Elliptio dilatata* and *Lampsilis radiata siliquoidea* shells, dated at 1964, were obtained from the Bay of Quinte which feeds into Lake Ontario (FIGURE 2). In 1949 Thermal Sets Ltd., a division of Union Carbide, established itself in Belleville and began releasing chemical waste products into the Bay. The IJC (International Joint Commission) recognises the Bay of Quinte for its high levels of heavy metal output (Botts and Krushelnicki, 1988).

### 1991 Sites

Modern shells dated at 1991 include *Elliptio complanata* from Barry's Bay which feeds into the Madawaska river, and *Lampsilis radiata siliquoidea* from the beaches of Port Colborne and Cleveland, Ohio which feed into Lake Erie (FIGURE 2). Barry's Bay waters remain relatively clear today (W.C. Noble, pers. comm., 1991). Port Colborne has a nickel refinery, and Cleveland has steel mills which process iron ore. Both Port Colborne and Cleveland are recognized for producing high heavy metal outputs (Botts and Krushelnicki, 1988).

**FIGURE 1.** Location map of the pre-industrial sites where fossil bivalve molluscs were located.

- \* *Elliptio dilatata*: Van Besian, 900-940 CE  
Cleveland, 1520-1540 CE  
Mannen, 1580-1600 CE
- + *Elliptio complanata*: Gunby, 1320 CE  
Hamilton, 1630-1651 CE

10 mi.  
10 Km



Lake Ontario

+ Gunby

+ Hamilton

\* Mannen

\* Cleveland

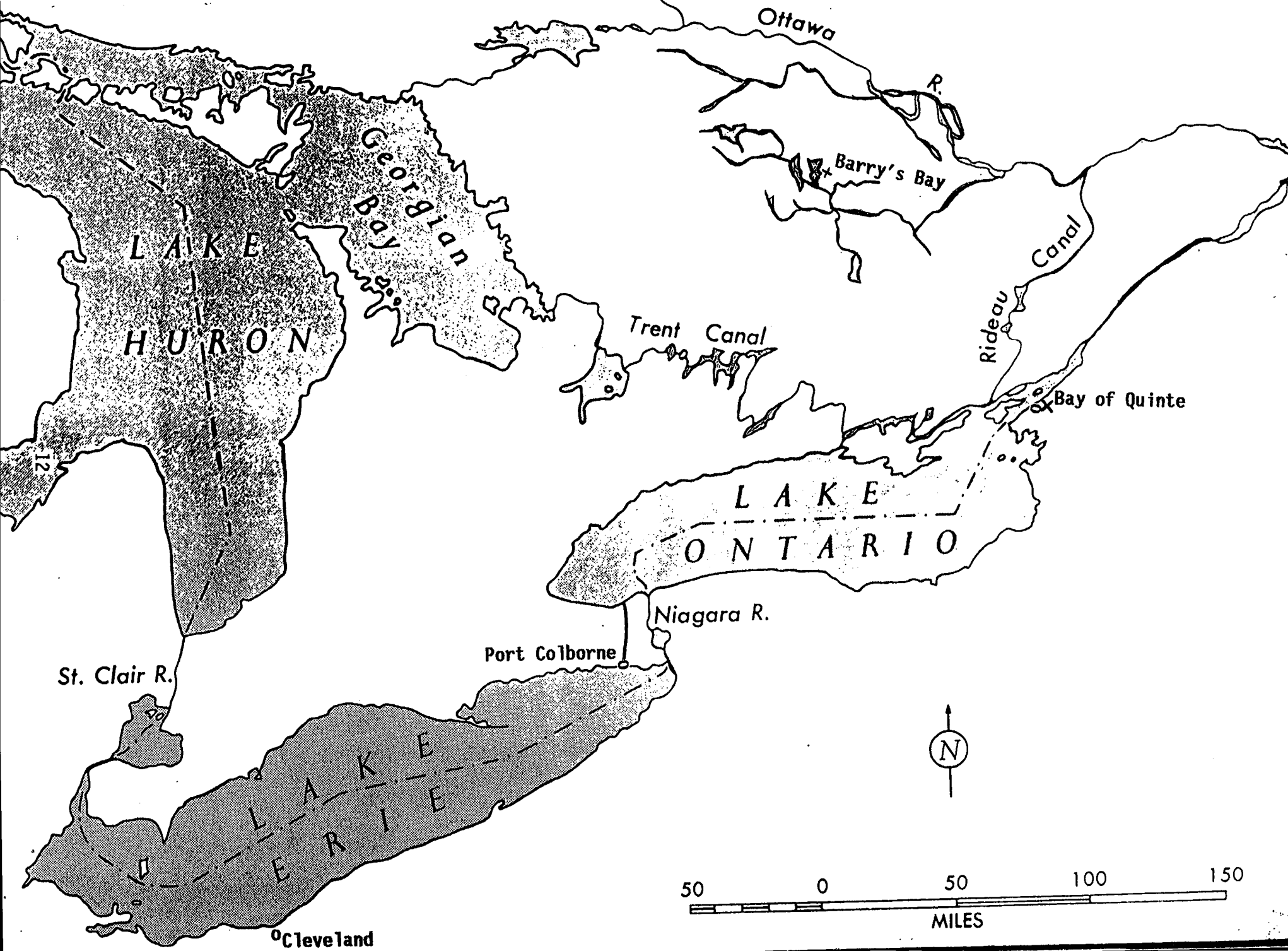
Grand River

\* Van Besian

Lake Erie

**FIGURE 2.** Location map of the post-industrial sites where modern bivalve molluscs were located.

- + *Elliptio complanata*: Bay of Quinte, 1964  
Barry's Bay, 1991
  
- o *Lampsilis radiata siliquoidea*: Bay of Quinte, 1964  
Port Colborne, 1991  
Cleveland, Ohio, 1991



## BIVALVE SHELL SAMPLES

### Shell Collection

A total of 43 valves of freshwater bivalve molluscs were used in this study. Radiocarbon dated fossil samples were obtained from museum and private archaeological collections. Modern samples, dated at 1964, were obtained from private collections. Modern samples, dated at 1991, were personally collected off beaches of Lake Erie.

### Shell Identification

All sample species were identified by the author (using the guide in Clarke, 1981), with the exception of the Bay of Quinte samples which came identified from the donor. The bivalve molluscs used in this study are *Elliptio complanata*, *Elliptio dilatata*, and *Lampsilis radiata siliquidea*.

Species identification of fossil samples was difficult because these valves had fractured edges and/or abraded dentitions, and lacked most of their periostracum.

### Shell Cleaning and Storage

Empty shells were lightly scrubbed with a nylon brush under running distilled water to remove surface dirt, and then dried at 40°C. The periostracum and top 1 mm (approximately) of the outer shell surface were removed with a diamond file under running distilled water. This portion of the carbonate shell is likely to have been exposed to particulate and dissolved trace metals (Bourgoin 1988, 1987a). Again samples were dried at 40°C until required for further processing. Valve length was measured and recorded.



Shell samples were ashed in a 400°C muffle furnace for 4 hours to destroy the organic matrix, remove any remaining periostracum, and help facilitate powdering (Bourgoin 1988, 1987a). Unglazed ceramic crucibles were used to hold samples in the muffle furnace. At the end of the 4 hours, samples were removed and allowed to cool to room temperature. As a further precaution against surface contamination, sample valves were soaked in 50% HNO<sub>3</sub> for 15 seconds and rinsed with milli-Q water (procedure modified from Shen and Boyle, 1988). Samples were again dried at 40°C.

Since both *Elliptio* and *Lampsilis* bivalve shells are wholly aragonitic (Kennedy, Taylor, and Hall, 1969) individual valves were ground to a fine homogeneous powder with an agate pestle and mortar. All powdered samples were stored in polystyrene tubes until required for further processing.

## **ANALYSES**

Polyethylene gloves were worn, and Parafilm coated forceps and spatulas were used when handling all samples and reagents. A complete set of nalgene beakers and polystyrene tubes were washed in 10% nitric acid and rinsed in milli-Q water before being used for sample processing (Jim McAndrew, pers. comm., 1992).

### **Shell Processing for Metal Analyses**

Powdered shell material was prepared for trace metal analyses using a method whereby the calcium carbonate solution is purified by calcium oxalate precipitation (Jim McAndrew, pers. comm., 1992). A 1.0 g subsample of shell material (weighed on a Mettler balance) was transferred to a 15 ml polystyrene tube. This sample was dissolved by the addition of

3 ml of 50% HNO<sub>3</sub> (BDH, Aristar), added in 0.5 ml intervals, and shaken to complete the dissolution. This aliquot of sample was then adjusted to pH 5.0 using minimal amounts of HNO<sub>3</sub> (25% and 10%) and NH<sub>4</sub>OH (50%, 25%, and 10%). The calcium was precipitated by the addition of 6 ml of oxalic acid solution, saturated at 20°C. With each group of 5 shell samples a blank was prepared using reagents only.

Samples and blanks were allowed to stand for 12 hours, and were then centrifuged for 20 minutes. The supernatant was decanted, and diluted to 300% with the addition of milli-Q water.

### **Metal Analyses**

All processed shell samples and blanks were analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Perkin-Elmer/Sciex Model: Elan 250). Plasmachem ICP-MS standard solutions were used as starting materials for preparation of standards by dilution to a 10 ppm stock of all analytes (from 1000 ppm elemental standards). Individual standards were made by weighed dilutions, from the 10 ppm stock, to give a range of 0-500 ppb for all analytes (Jim McAndrew, pers., comm., 1992).

### **Statistical Analyses**

All metal concentration levels measured in the bivalve shells were compared between genera (ie *Elliptio* and *Lampsilis*) and between species (ie *E. dilatata* and *E. complanata*) for the main time periods (ie pre-1700, 1964, and 1991) by Student's independent t-test procedures using Sigmaplot 4.0. All pre-1700 *E. dilatata* samples were combined in one group, as were all pre-1700 *E. complanata* samples, to make up two sufficiently large fossil sample sets for statistical analyses.

## RESULTS

### SHELL METAL LEVELS

#### Copper

Table 1 summarizes the mean ( $\pm$  STE) concentrations (ppm) of copper measured in the bivalve shells. Figure 3 represents the concentrations measured for each time period. Statistical analysis revealed no significant differences in mean copper levels, neither between genera nor between species, for each of the three time periods.

#### Nickel

Table 2 summarizes the mean ( $\pm$  STE) concentrations (ppm) of nickel measured in the bivalve shells. Figure 4 represents the concentrations measured for each time period. Statistical analysis revealed no significant differences in nickel levels between genera for each of the three times periods. Between the species *Lampsilis radiata siliquoidea*, the mean nickel concentration of the LQ samples is significantly ( $p < 0.04$ ) higher than that of the LC samples by  $3.0 \pm 1.4$  ppm.

#### Zinc

Table 3 summarizes the mean ( $\pm$  STE) concentrations (ppm) of zinc measured in the bivalve shells. Figure 5 represents the concentrations measured for each time period. Statistical analysis revealed no significant differences in zinc levels, neither between genera nor between species, for each of the three times periods. Samples showed a higher affinity for zinc, by one order of magnitude, than for other metals.

**FIGURE 3.** Copper concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte  
(P) Port Colborne  
(C) Cleveland, Ohio

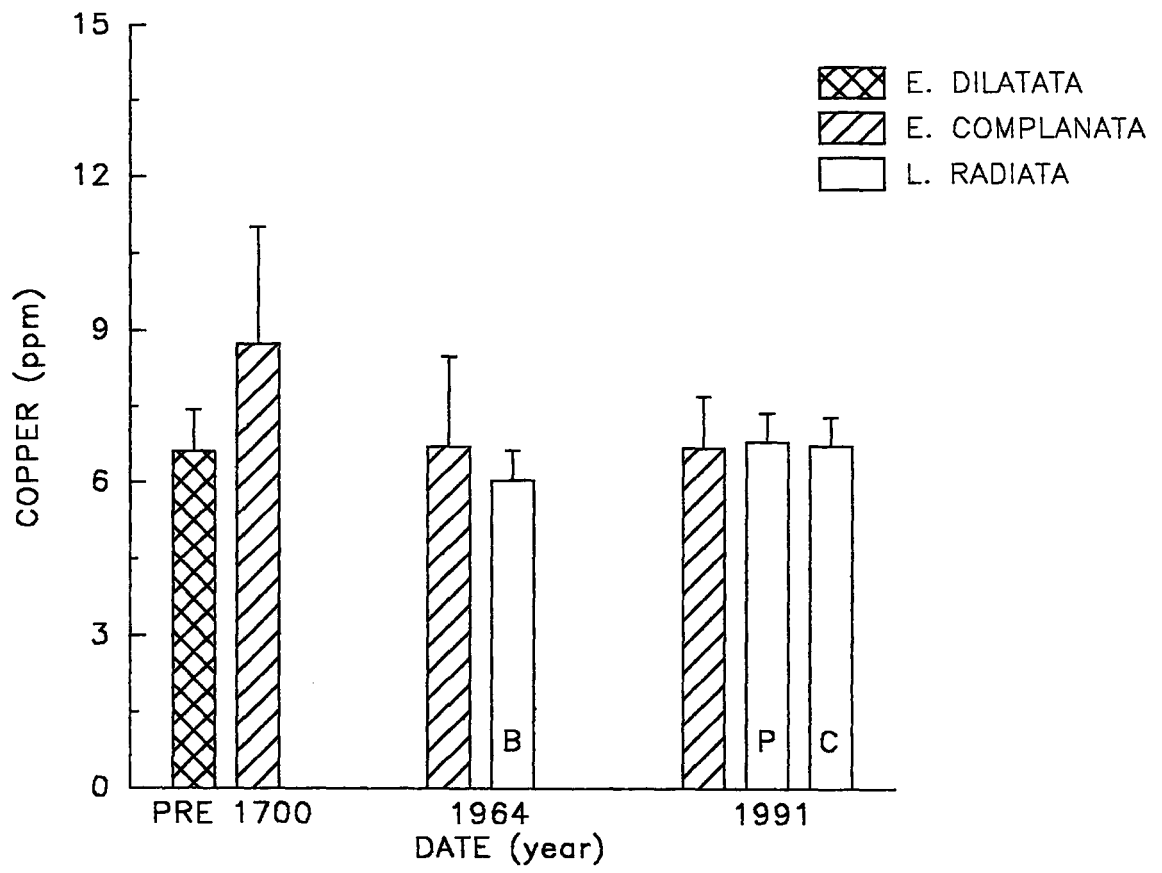


TABLE 1: Mean copper concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

[Cu]:	...PRE-1700....		.....1964.....		.....1991.....		
	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	6.6	8.7	6.7	6.1	6.7	6.8	6.8
STE	0.8	2.3	1.8	0.6	1.0	0.6	0.6
n	6	5	7	7	5	7	6

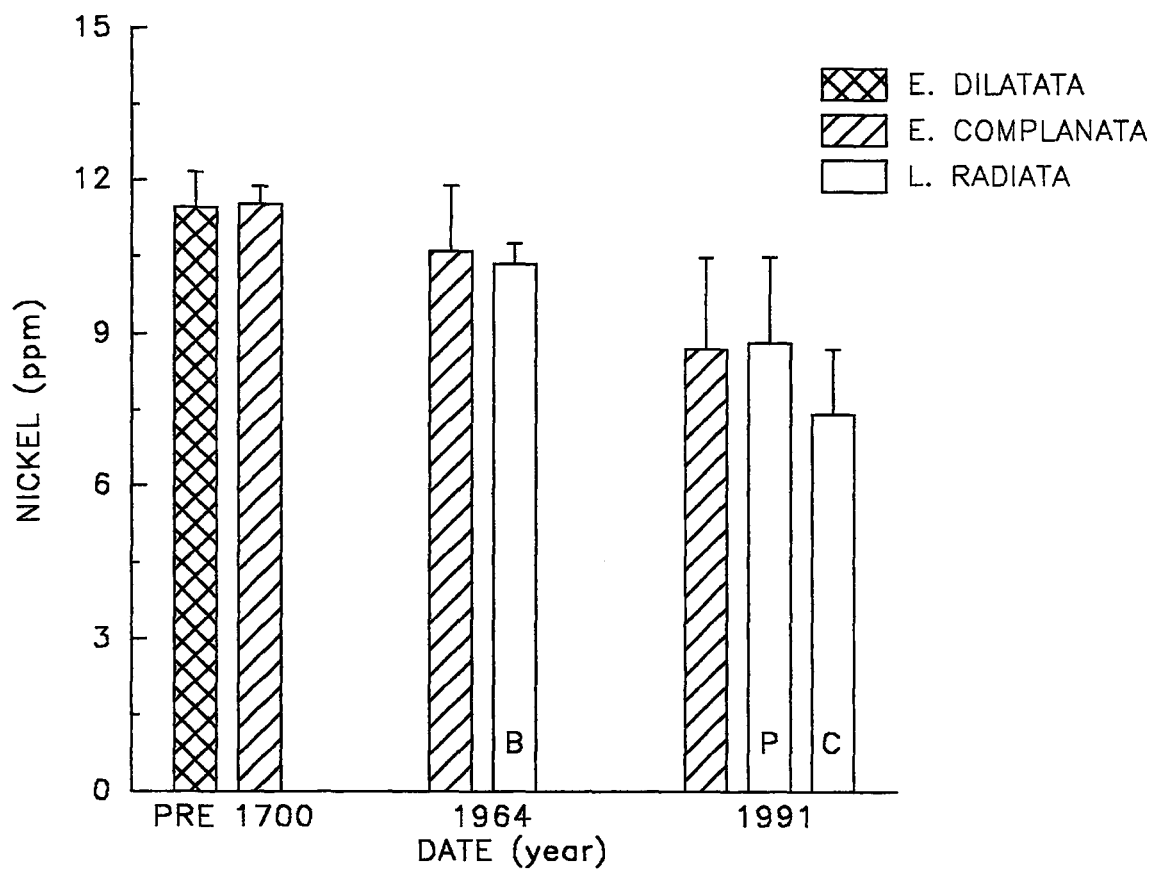
PRE-1700: ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

1964: ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

1991: ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio

**FIGURE 4.** Nickel concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte  
(P) Port Colborne  
(C) Cleveland, Ohio





**TABLE 2:** Mean nickel concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

	...PRE-1700....		.....1964.....		.....1991.....		
[Ni]:	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	11.5	11.5	10.6	10.4	8.7	8.8	7.4
STE	0.7	0.4	1.3	0.4	1.8	1.6	1.3
n	6	5	7	7	5	7	6

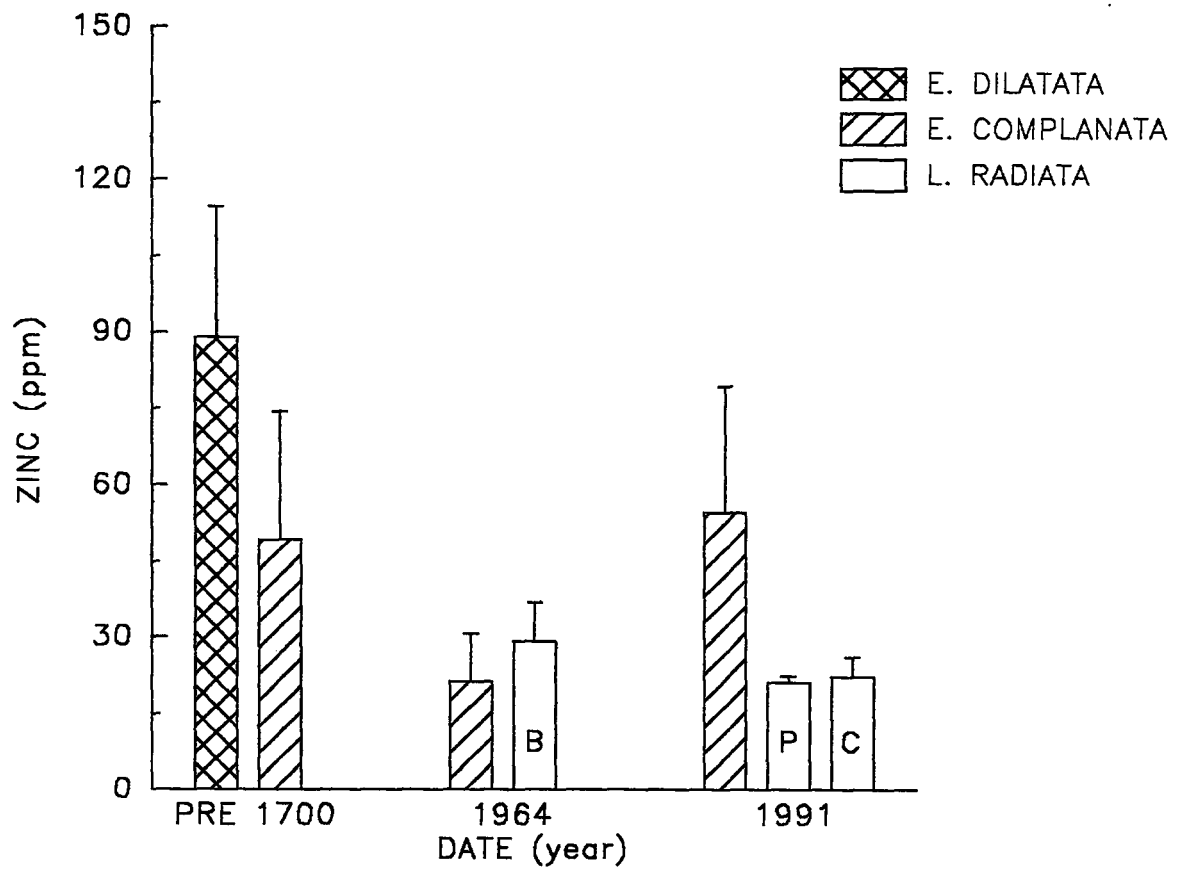
**PRE-1700:** ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

**1964:** ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

**1991:** ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio

**FIGURE 5.** Zinc concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte  
(P) Port Colborne  
(C) Cleveland, Ohio



**TABLE 3:** Mean zinc concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

[Zn]:	...PRE-1700...		...1964...		...1991...		
	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	88.9	49.3	21.3	29.1	54.7	21.2	22.3
STE	25.7	25.0	9.4	7.7	24.7	1.3	3.8
n	6	5	7	7	5	7	6

PRE-1700: ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

1964: ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

1991: ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio

## Arsenic

Table 4 summarizes the mean ( $\pm$  STE) concentrations (ppm) of arsenic measured in the bivalve shells. Figure 6 represents the concentrations measured for each time period.

The fossil samples revealed a significant ( $p < 0.00001$ ) difference between species. The mean arsenic concentration measured in the ED group is lower than that of the EC group by  $4.7 \pm 0.5$  ppm. The Bay of Quinte samples revealed that the concentration of the ECQ group is significantly ( $p < 0.00008$ ) higher than that of the LQ group by  $3.7 \pm 0.5$  ppm. The 1991 samples revealed that the concentration of the ECK group is significantly ( $p < 0.03$ ) higher than that of the LC group by  $2.2 \pm 0.9$  ppm.

For the *Elliptio complanata*, the mean arsenic concentration measured in the EC group is significantly ( $p < 0.007$ ) higher than that of the ECQ group by  $2.5 \pm 0.7$  ppm, and significantly ( $p < 0.02$ ) higher than that of the ECK group by  $3.0 \pm 1.1$  ppm. There is no significant difference between the modern sample groups, ECQ and ECK.

For the *Lampsilis radiata siliquoidea*, the mean arsenic concentration measured in the LQ group is significantly ( $p < 0.0003$ ) lower than that of the LC group by  $1.0 \pm 0.1$  ppm. There is no significant difference between the 1991 sample groups, LP and LC.

## Lead

Table 5 summarizes the mean ( $\pm$  STE) concentrations (ppm) of lead measured in the bivalve shells. Figure 7 represents the concentrations measured for each time period.

The *Elliptio complanata* samples revealed a significant ( $p < 0.04$ ) difference in metal levels between the pre-1700 and 1964 groups. The mean

lead concentration measured in the EC group is higher than that of the ECQ group by  $0.4 \pm 0.2$  ppm.

Samples from the Bay of Quinte revealed a significant ( $p < 0.01$ ) difference in metal levels between genera. The mean lead concentration measured in the ECQ group is lower than that of the LQ group by  $0.8 \pm 0.3$  ppm.

### Manganese

Table 6 summarizes the mean ( $\pm$  STE) concentrations (ppm) of manganese measured in the bivalve shells. Figure 8 represents the concentrations measured for each time period. Samples showed a higher affinity for manganese than for the other metals: by two orders of magnitude greater than for zinc, and by three orders of magnitude greater than for to all other metals.

The fossil samples revealed a significant ( $p < 0.004$ ) difference between species. The mean manganese concentration measured in the ED group is lower than that of the EC group by  $973.9 \pm 374.8$  ppm.

For the *Elliptio complanata*, the mean manganese concentration measured in the EC group is significantly ( $p < 0.007$ ) higher than that of the ECQ group by  $1139.3 \pm 311.9$  ppm, and significantly ( $p < 0.002$ ) higher than that of the ECK group by  $1743.7 \pm 381.3$  ppm. There is no significant difference between the modern sample groups, ECQ and ECK.

The 1964 samples revealed differences between different genera. The mean manganese concentration measured in the ECQ group is significantly ( $p < 0.05$ ) higher than that of the LQ group by  $584.0 \pm 267.9$  ppm.

For the *Lampsilis radiata siliquoidea*, the mean manganese concentration measured in the LQ group is significantly ( $p < 0.000002$ )

higher than that of the LP group by  $1040.4 \pm 123.6$  ppm, and significantly ( $p < 0.0005$ ) higher than that of the LC group by  $944.3 \pm 140.2$  ppm. There is no significant difference between the 1991 sample groups, LP and LC.

The 1991 samples revealed differences between genera. The mean manganese concentration measured in the ECK group is significantly ( $p < 0.004$ ) higher than that of the LP group by  $1020.0 \pm 327.6$  ppm, and significantly ( $p < 0.01$ ) higher than that of the LC group by  $923.9 \pm 334.2$  ppm.

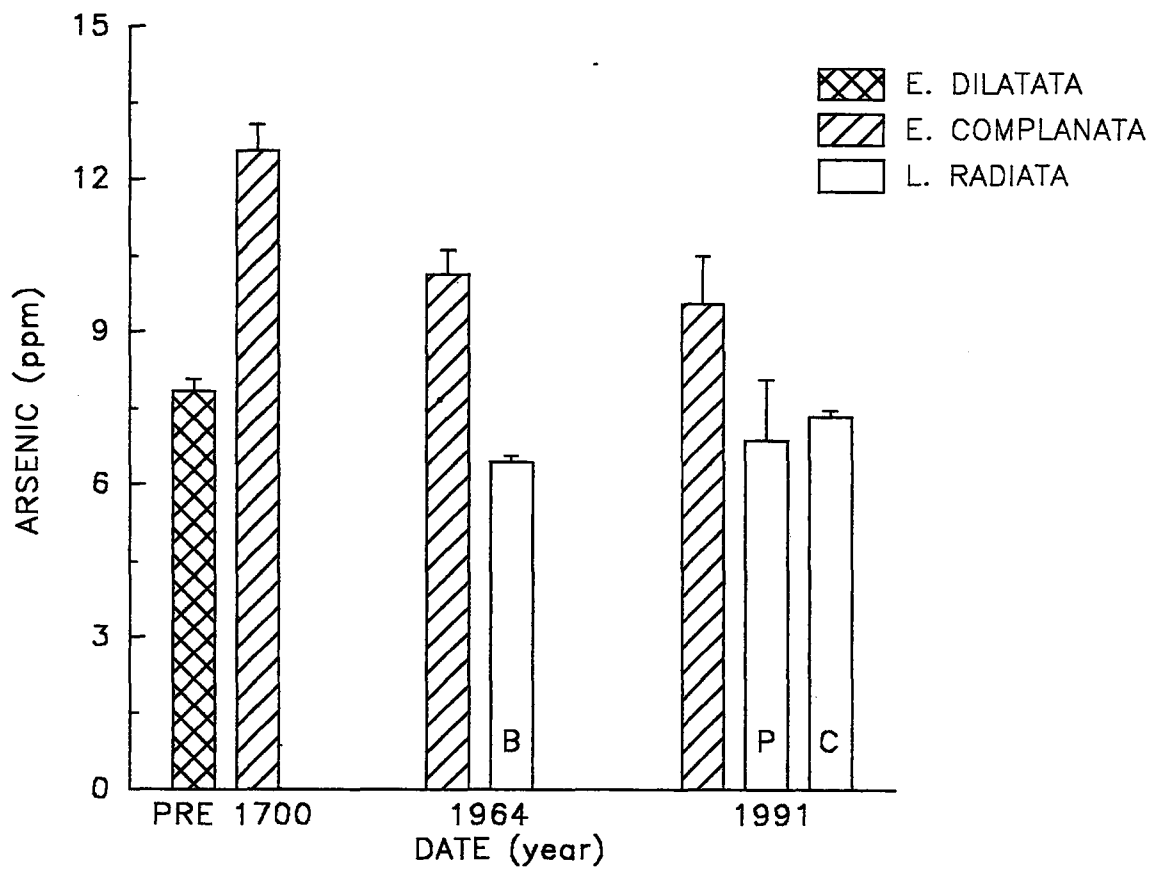
**FIGURE 6.** Arsenic concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte

(P) Port Colborne

(C) Cleveland, Ohio





**TABLE 4:** Mean arsenic concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

	...PRE-1700...		.....1964.....		.....1991.....		
[As]:	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	7.9	12.6	10.1	6.4	9.6	6.9	7.4
STE	0.2	0.5	0.5	0.1	0.9	1.2	0.1
n	6	5	7	7	5	7	6

**PRE-1700:** ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

**1964:** ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

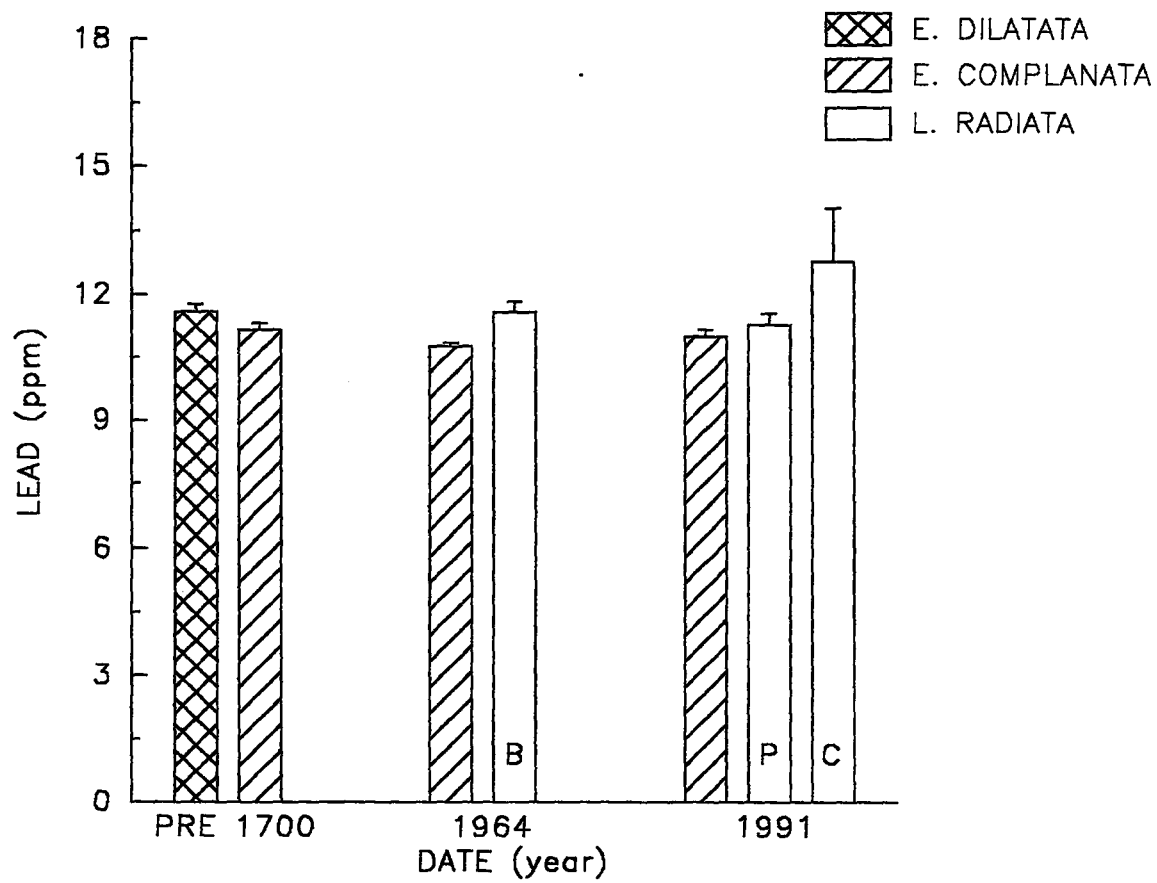
**1991:** ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio

**FIGURE 7.** Lead concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte

(P) Port Colborne

(C) Cleveland, Ohio



**TABLE 5:** Mean lead concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

[Pb]:	...PRE-1700....		.....1964.....		.....1991.....		
	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	11.6	11.2	10.8	11.6	11.0	11.3	12.8
STE	0.2	0.2	0.1	0.3	0.2	0.3	1.3
n	6	5	7	7	5	7	6

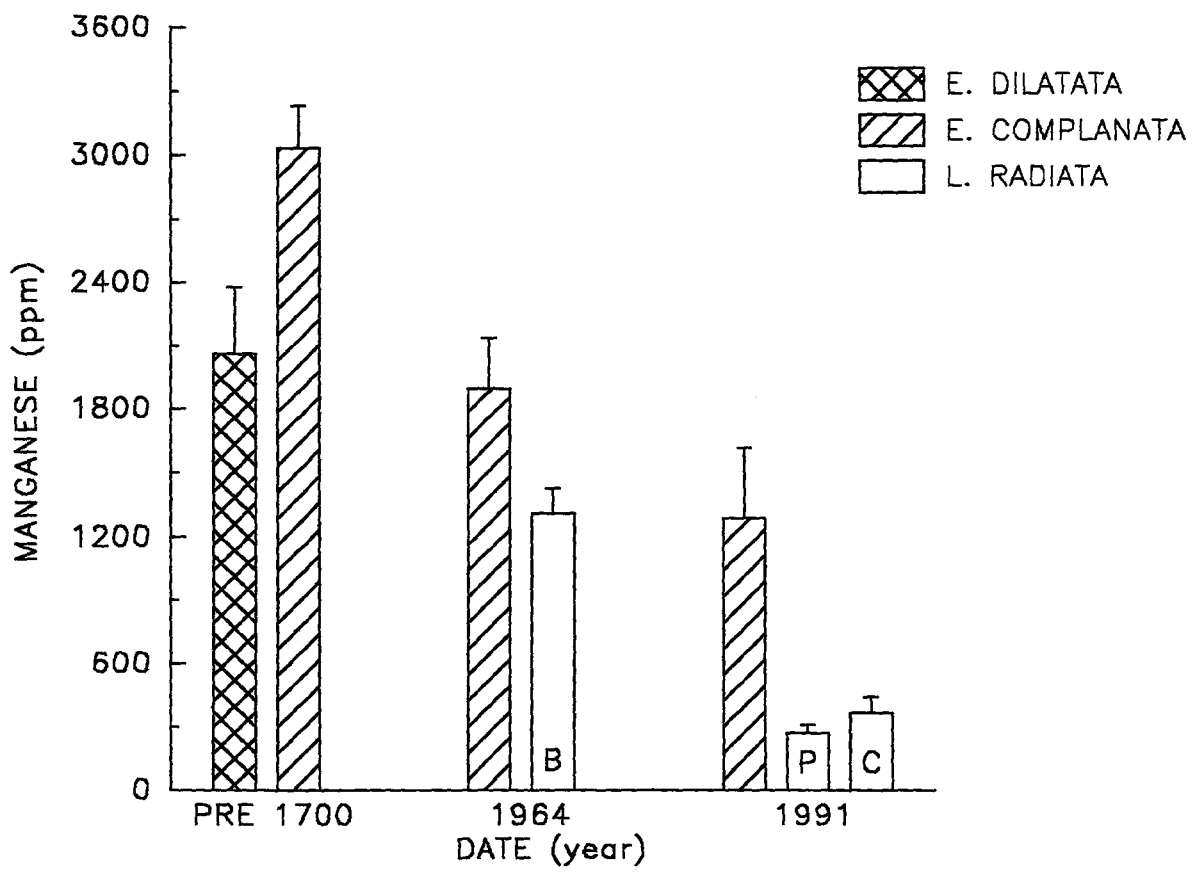
PRE-1700: ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

1964: ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

1991: ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio

**FIGURE 8.** Manganese concentrations (ppm) determined in fossil and modern bivalve mollusc shells. Each bar represents the mean value of the sample group. The vertical lines across the bars represent the standard error values ( $\pm$  STE).

*Lampsilis radiata siliquoidea*: (B) Bay of Quinte  
(P) Port Colborne  
(C) Cleveland, Ohio



**TABLE 6:** Mean manganese concentrations (ppm) determined in fossil and modern bivalve mollusc shells.

Standard Error ( $\pm$  STE)

	...PRE-1700....		.....1964.....		.....1991.....		
[Mn]:	ED (ppm)	EC (ppm)	ECQ (ppm)	LQ (ppm)	ECK (ppm)	LP (ppm)	LC (ppm)
MEAN	2058.7	3032.6	1893.3	1309.3	1288.9	268.9	365.0
STE	317.9	198.6	240.5	118.1	325.5	36.6	75.6
n	6	5	7	7	5	7	6

PRE-1700: ED *Elliptio dilatata*, all sites combined  
 EC *Elliptio complanata*, all sites combined

1964: ECQ *Elliptio complanata*, Bay of Quinte  
 LQ *Lampsilis radiata siliquoidea*, Bay of Quinte

1991: ECK *Elliptio complanata*, Barry's Bay  
 LP *Lampsilis radiata siliquoidea*, Port Colborne  
 LC *Lampsilis radiata siliquoidea*, Cleveland, Ohio



## DISCUSSION

### METAL UPTAKE IN BIVALVE MOLLUSC SHELLS

Historical change in environmental metal concentrations of the Great Lakes region was not reflected as a *simple* change in shell metal concentrations of freshwater bivalve mollusc shells. This study used ICP-MS to analyze fossil and modern bivalve shells, collected from in and around Lake Ontario and Lake Erie, for the following trace metals: Cu, Ni, Zn, As, Pb, and Mn. Regardless of date, shell sample groups revealed the following: a higher affinity for Mn, by three orders of magnitude, than for Cu, Ni, As, and Pb; a higher affinity for Zn, by one order of magnitude, than for Cu, Ni, As, and Pb; no significant differences in Cu, Ni, and Zn levels with time.

#### Pre-1700 Metal Levels as Background

Analysis of bivalve shells revealed a decrease in some metal levels, but no increases, despite a historical increase in environmental metal levels. *Elliptio complanata* shells were obtained from both pre-industrial and post-industrial sites. Higher mean concentrations of As, Pb, and Mn were measured in the fossil shells than in the modern shells. No change was detected in mean Cu, Ni, and Zn concentrations through time. These results corroborate with the findings of Tevesz, Mansoff, Frank, and McCall (1989): one cannot assume pre-industrial shells will necessarily possess lower trace metal concentrations than modern shells; one cannot assume the natural background, or baseline, data provided by these shells will be necessary and/or useful to prove environmental loading.

### Variability Between Species and Genera

The fossil shells analyzed in this study include two distinct species from the same genera, *Elliptio dilatata* and *Elliptio complanata*. For individual metal values of each sample see APPENDIX I and APPENDIX II. Although from different archaeological sites, shells of various pre-industrial dates had to be combined to make up two sufficiently large sample sets for statistical analyses. We can safely combine these samples into larger groups because there was no anthropogenic input of metals into any of these pre-industrial sites.

The As and Mn concentrations were both higher in the *E. complanata* than in the *E. dilatata*. None of the other metal concentrations differed between these two species. These results suggest that *E. complanata* may have a higher affinity for As and Mn than *E. dilatata*. A previous investigation of Mn in freshwater bivalve shells combined fossil *Lampsilinae* fragments, dated at 950-1000, without concern for species identification (Tevesz, Mansoff, Frank, and McCall, 1989). The Mn measures obtained from such a group may not be reliable since the *Lampsilinae* fragments may have included different species from this one genera. Just as distinct *Elliptio* species may have differing affinities for individual metals, any distinct species among the *Lampsilinae* fragments may have differing affinities for individual metals.

The 1964 shells analyzed in this study include two different species from different genera, *Elliptio complanata* and *Lampsilis radiata siliquoidea*. For individual metal values of each sample see APPENDIX II and APPENDIX III. Both groups of shells were obtained from the same site, the Bay of Quinte. This area is noted for heavy metal contamination, in 1964 as well as today.

The As and Mn concentrations are higher, and the Pb concentration is lower, in the *E. complanata* than in the *L. radiata siliquoides*. None of the other metal concentrations differed between these two species. These results suggest that *E. complanata* may have a higher affinity for As and Mn, but a lower affinity for Pb, than *L. radiata siliquoides*.

The 1991 shell groups analyzed in this study are less reliable for comparisons between *E. complanata* and *L. radiata siliquoides* because they are from different sites, each representing different levels of metal contamination. For individual metal values of each sample see APPENDIX II and APPENDIX III. The *E. complanata* are from Barry's Bay, a site less inundated with metal pollutants than Lake Erie, where the *L. radiata siliquoides* were obtained from. Nevertheless, the general pattern of *E. complanata* having a higher affinity for As and Mn, but a lower affinity for Pb, than *L. radiata siliquoides* is suggested: As is higher in the *E. complanata* than in the *L. radiata siliquoides* from Cleveland, Ohio; the Mn is higher in the *E. complanata* than in the *L. radiata siliquoides* from both groups; Pb means tend to be lower in the *E. complanata* than in the *L. radiata siliquoides* from both groups, although not significantly so (Table 5). Analysis of larger sample sizes per group may be necessary for more statistically significant results (Tevesz, Mansoff, Frank, and McCall, 1989).

Other researchers have questioned how comparable trace element data from different species of bivalve molluscs may be (Forester, 1981; Bourgoin, 1987a), and some have experimented to investigate this issue (Duncan, Tevesz, and Towns, 1987; Tevesz, Mansoff, Frank, and McCall, 1989).

## Metal Uptake vs Environmental Levels

Evidence of post-industrial metal contamination of lakes Ontario and Erie has been found in coastal sediments (Kemp and Dell, 1976). Among the trace metals detected in the sediments of these freshwater bodies, Pb, Zn, Cu, and Mn were highly enriched in the modern sediments. With the exception of Mn, all enrichments were attributed to anthropogenic inputs. Analysis of trace metal concentrations in bivalve mollusc shells, from in and around lakes Ontario and Erie, did not reveal metal enrichment signatures corresponding to dates of intense urbanization and industrialization of this region.

Across time and regardless of species, no significant differences were found between shell Cu, Ni, and Zn levels, and any changes in Pb levels were minute. Previous investigations have found that Cu, Ni, Zn, and Pb were significantly higher in the periostracum of modern *E. complanata* than in their inorganic prismatic shell layer (Dermott and Lum, 1986). This study revealed similarly low metal levels for *E. complanata*, *E. dilatata*, and *L. radiata siliquoidea*. Further investigation is necessary to determine if Cu, Ni, Zn, and Pb have a greater affinity to the periostracum of the latter two species. Such results would suggest that the periostracum, rather than the inorganic shell layer, of these freshwater bivalves might be a better bioindicator of environmental contamination for these metals. If such is the case, comparisons with fossil bivalves would not be reliable since fossils rarely possess an intact periostracum.

Fossil shells, of both *E. complanata* and *E. dilatata*, were richer in As, Pb, and Mn than were modern shells from contaminated environments. Previous investigators have reported similarly higher Mn concentrations

(Tevesz, Mansoff, Frank, and McCall, 1989). Some investigators have proposed that sediment Mn-oxides and Fe-oxyhydroxides may control the dissolved trace metal concentrations to which the bivalve mollusc soft tissues are exposed (Tessier, Campbell, Auclair, and Bisson, 1984). Analysis of the soft tissues of *E. complanata* revealed that low Mn levels corresponded to high Cu and Cd levels, and high Mn levels corresponded to low Cu and Cd levels (Hinch and Stephenson, 1987). Possibly, these competitive or protective effects of Mn and Fe also influence shell trace metal concentrations. In this study, no such correlations could be detected between Mn and Cu, or any other metals. Further investigations, with larger sample sizes per group of each species, are necessary to discover whether or not Mn and Fe play such a role in freshwater bivalve mollusc shells.

Modern shells, of both species *E. complanata* and *L. radiata siliquoidea*, did not reflect environmental metal levels. The *E. complanata* from the Bay of Quinte did not reveal higher metal levels than those from Barry's Bay, even though the latter site received less metal contamination. Previous investigations have suggested that metal levels in the shells of *E. complanata* may not directly correspond to environmental levels (Dermot and Lum, 1986). However, the *L. radiata siliquoidea* from the Bay of Quinte revealed higher Mn concentrations than both Lake Erie sites, and higher Ni and lower As concentrations than the Cleveland, Ohio site. These results are likely attributable to environmental metal differences among the three sites sampled. Further investigations would help assess the effectiveness of *L. radiata siliquoidea* shells, over those of *E. complanata*, as indicators of environmental metal levels.

## SUMMARY AND CONCLUSIONS

In this study, ICP-MS was used to analyze freshwater bivalve mollusc shells for the following trace metals: Cu, Ni, Zn, As, Pb, and Mn. Fossil and modern shells were collected from in and around Lakes Ontario and Erie. Fossil shells, obtained from pre-1700 sites, included *Elliptio dilatata* and *Elliptio complanata*. Modern shells, obtained from both high- and low-contamination sites, included *Elliptio complanata* and *Lampsilis radiata siliquoidea*.

Historical change in environmental metal concentrations of the Great Lakes region was not reflected as a *simple* change in shell metal concentrations of freshwater bivalve molluscs. Regardless of date, shell trace metal levels revealed a high affinity for Zn and Mn. Despite anthropogenic inputs during the post-industrial periods, the modern shells contained lower concentrations of As, Pb, and Mn than the fossil samples. No significant changes were detected in the Cu, Ni, and Zn concentrations through time, regardless of species. These results support the suggestion that one cannot assume fossil shell samples from pre-industrial times will necessarily possess low, or baseline, trace metal concentrations (Tevesz, Mansoff, Frank, and McCall, 1989).

Shell metal analyses is neither applicable for all metals, nor for all bivalve mollusc species (Forester, 1981; Bourgoin, 1987a; Duncan, Tevesz, and Towns, 1987; Tevesz, Mansoff, Frank, and McCall, 1989). Distinct species, wether of distinct or like genera, may possess different affinities for certain metals. Concentrations of As and Mn were generally higher, while Pb was generally lower, in *E. complanata* than in *E. dilatata* and *L. radiata siliquoidea*. The *E. complanata* shells seem to have a

higher affinity for As and Mn, but a lower affinity for Pb, than both the *E. dilatata* and the *L. radiata siliquidea* shells.

Across time and regardless of species, little or no significant differences were found between shell Cu, Ni, Zn, and Pb levels. These metals have a greater affinity for the periostracum rather than the inorganic prismatic shell layer of *E. complanata* (Dermott and Lum, 1986). Further investigations are necessary to determine if such is also true for *E. dilatata* and *L. radiata siliquidea*. In such a case, the periostracum would be a closer representation of environmental contamination than the aragonitic shell layer, for these metals.

No clear correlations could be detected between Mn and any other metals. Mn and Fe are suspected of playing a protective and competitive role in the uptake of metals in soft tissues of *E. complanata* (Tessier, Campbell, Auclair, and Bisson, 1984; Hinch and Stephenson, 1987). Further investigations are necessary to determine if Mn and/or Fe influence metal uptake in the shells of freshwater bivalve molluscs.

Among the modern shells the *E. complanata* showed no differences in metal concentrations between samples from high- and low-contamination sites, while the *L. radiata siliquidea* showed changes in Ni, As, and Mn concentrations among the same sites. *L. radiata siliquidea* may be more representative of environmental metal concentrations than *E. complanata*.

Historical increase in environmental metal concentrations in the Great Lakes Basin was not *directly* reflected in shell metal concentrations of indigenous freshwater bivalves. Further trace metal studies of freshwater shells, and periostracum, are necessary to decipher the connection between environmental input and mollusc uptake.

## REFERENCES

- Bertine KK, Goldberg ED. Trace elements in clams, mussels, and shrimp. *Limnol Oceanogr* 1972; 17: 877-884.
- Botts L, Krushelnicki B. The Great Lakes: an Environmental Atlas and Resource Book. Toronto and Burlington: Environment Canada, 1987.
- Bourgoin BP. A rapid and inexpensive technique to separate the calcite and nacreous layers in *Mytilus edulis* shells. *Marine Environ Res* 1988; 25: 125-129.
- Bourgoin BP. *Mytilus edulis* shells as environmental recorders for lead contamination. PhD thesis, Geology Department, McMaster University, Hamilton, ON. 1987a; 138 pp.
- Bourgoin BP. Trace Metal Concentration in Fossil and Recent Shells of the Arctic Infaunal Bivalve, *Mya truncata* L. In: Crick RE, ed. Origin, Evolution, and Modern Aspects of Biomineralization in Plants and Animals, First Edition. New York: Plenum Press, 1987b: 385-392.
- Bourgoin BP, Risk MJ. Historical changes in lead in the Eastern Canadian Arctic, determined from fossil and modern *Mya truncata* shells. *Sci Total Environ* 1987; 67: 287-291.
- Clarke AH. The Freshwater Molluscs of Canada: Natural Museum of Natural Sciences. Ottawa: National Museums of Canada, 1981.
- Czarnecki JM. Use of the pocketbook mussel, *Lampsilis ventricosa*, for monitoring heavy metal pollution in an Ozark stream. *Bull Environ Contam Toxicol* 1987; 38: 641-646.
- Deer WA, Howie RA, Zussman J. Carbonates. In: An Introduction to Rock Forming Minerals, Twelfth Impression. London: Longman Group Ltd, 1980: 473-503.
- Dermott RM, Lum KR. Metal concentrations in the annual shell layers of the bivalve *Elliptio complanata*. *Environ Pollut (Ser B)* 1986; 12: 131-143.
- Duncan WFA, Tevesz MJS, Towns RLR. Use of fingernail clams (*Pisidiidae*) and x-ray fluorescence spectrometry for monitoring metal pollution in Contwoyto lake, NWT. *Water Poll Res J Canada* 1987; 22: 270-279.
- Ferris N. Buttons I Have Known. In: Fox WA, ed. Studies in Southwestern Ontario Archaeology, Occasional Publications No 1. London: Ontario Archaeological Society Inc, 1986.
- Forester A. Unionacean clams as indicators of persistent substances in fresh water. In: Stokes PM, ed. Ecotoxicology and the Aquatic Environment, International Association on Water Pollution Research. Toronto: Pergamon Press Ltd, 1981: 37-42.



- Hayton A, Hollinger D, Tashiro C, Reiner E. Biological monitoring of chlorinated dibenzo-dioxins in the rainy river using introduced mussels (*Elliptio complanata*). Chemosphere 1990; 20: 1687-1693.
- Hinch SG, Stephenson LA. Size- and age-specific patterns of trace metal concentrations in freshwater clams from an acid-sensitive and a circumneutral lake. Can J Zool 1987; 65: 2436-2442.
- Kemp ALW, Dell CI. A preliminary comparison of the composition of bluffs and sediments from Lakes Ontario and Erie. Can J Earth Sci 1976; 13: 1070-1081.
- Kennedy WJ, Taylor JD, Hall A. Environmental and biological controls on bivalve shell mineralogy. Biol Rev 1969; 44: 499-530.
- Russel RW, Gobas FAPC. Calibration of the freshwater mussel, *Elliptio complanata*, for quantitative determination of hexachlorobenzene and octachlorostyrene in aquatic systems. Bull Environ Contam Toxicol 1989; 43: 576-582.
- Servos MR, Malley DF, Mackie GL, LaZerte BD. Lack of bioaccumulation of metals by *Elliptio complanata* (bivalvia) during acidic snowmelt in three south-central Ontario streams. Bull Environ Contam Toxicol 1987; 38: 762-768.
- Shen GT, Boyle EA. Determination of lead, cadmium and other trace metals in annually-banded corals. Chem Geol 1988; 67: 47-62.
- Taylor JD, Kennedy WJ, Hall A. Environmental and biological controls on bivalve shell mineralogy. Biol Rev 1969; 44: 499-530.
- Tessier A, Campbell PGC, Auclair JC, Bisson M. Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc *Elliptio complanata* in a mining area. Can J Fish Aquat Sci 1984; 41: 1463-1472.
- Tevesz MJS, Frank SA, McCall PL. Interspecific differences in manganese levels in freshwater bivalves (research note). Water, Air, & Soil Pollut 1989; 47: 65-70.

## APPENDIX I

Species: *Elliptio diltata*

1580-1600 CE: Mannen

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
EDM1	5.7	6.0	10.8	135.2	7.5	11.5	2988.0
EDM2	5.9	4.5	11.3	73.2	7.2	11.7	936.0

1520-1540 CE: Cleveland

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
EDC1	6.2	4.4	12.6	87.2	7.6	11.4	1295.4
EDC2	6.2	7.5	14.2	44.4	8.2	12.3	2473.7

900-940 CE: Van Besien

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
EDVB1	7.4	9.5	9.2	0.9	8.8	11.2	2381.5
EDVB2	6.8	7.8	10.8	184.4	7.7	11.4	2277.8

Mannen & Cleveland & Van Besien:		[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
	MEAN	6.6	11.5	88.9	7.9	11.6	2058.7
	STE	0.8	0.7	25.7	0.2	0.2	317.9

## APPENDIX I I

Species: *Elliptio complanata*

1991 CE: Barry's Bay, Kamaneskeg Lake

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
ECK1	7.8	7.9	12.5	25.2	12.4	10.7	1737.6
ECK2	7.2	6.1	8.0	36.5	7.6	11.6	1696.0
ECK3	7.8	9.4	11.3	23.9	11.2	11.1	1489.9
ECK4	8.1	3.3	2.3	34.9	8.1	10.8	1.1
ECK5	8.2	6.9	9.4	152.9	8.5	10.8	1520.2
	MEAN	6.7	8.7	54.7	9.6	11.0	1288.9
	STE	1.0	1.8	24.7	0.9	0.2	325.5

1964 CE: Bay of Quinte (Cat #26229)

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
ECQ1	9.0	4.5	9.1	3.6	8.5	10.7	1178.1
ECQ2	8.9	5.0	8.3	73.0	9.0	10.6	2261.6
ECQ3	8.6	4.7	7.8	31.6	9.6	10.8	1876.6
ECQ4	10.2	5.9	17.9	7.6	11.2	11.0	3104.1
ECQ5	9.2	5.7	10.2	6.7	9.7	10.6	1646.0
ECQ6	8.8	3.8	9.6	6.4	11.2	10.7	1798.2
ECQ7	8.8	17.3	11.3	20.2	11.9	11.1	1388.4
	MEAN	6.7	10.6	21.3	10.1	10.8	1893.3
	STE	1.8	1.3	9.4	0.5	0.1	240.5

Species: *Elliptio complanata*

1630-1651 CE: Hamilton

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
ECH1	7.8	8.5	12.3	47.0	12.4	11.2	2567.2
ECH2	6.8	17.4	11.3	145.0	13.3	11.4	3481.1
ECH3	8.5	5.6	10.9	33.8	14.1	11.5	3008.4

1320 CE: Gunby

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
ECG1	7.0	4.6	10.6	4.6	11.3	11.1	2623.3
ECG2	5.0	7.5	12.4	15.6	11.7	10.6	3483.0

Hamilton & Gunby combined:		[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
MEAN		8.7	11.5	49.3	12.6	11.2	3032.6
STE		2.3	0.4	25.0	0.5	0.2	198.6

## APPENDIX III

Species: *Lampsilis radiata siliquoidea*

1991 CE: Cleveland, Ohio

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
LC1	5.9	5.5	4.7	19.5	7.2	19.0	259.1
LC2	5.3	7.9	5.9	21.7	7.9	12.1	296.5
LC3	5.5	9.0	5.4	23.3	7.0	11.2	176.3
LC4	5.9	6.3	5.6	23.9	7.3	12.3	526.1
LC5	5.8	6.1	12.1	37.2	7.4	11.2	274.4
LC6	5.9	5.7	10.7	8.3	7.3	10.9	657.5
	MEAN	6.8	7.4	22.3	7.4	12.8	365.0
	STE	0.6	1.3	3.8	0.1	1.3	75.6

1991 CE: Port Colborne

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
LP1	5.1	7.9	7.7	24.5	7.3	12.8	297.1
LP2	6.0	5.0	5.0	22.1	7.9	10.9	446.6
LP3	5.0	6.1	4.2	19.7	6.9	10.7	221.5
LP4	4.6	5.4	5.4	26.3	7.0	11.2	163.6
LP5	5.0	9.2	15.4	20.8	12.3	11.3	228.9
LP6	4.6	7.0	11.7	15.2	1.5	10.8	328.5
LP7	4.3	7.2	12.4	18.9	5.3	11.2	196.1
	MEAN	6.8	8.8	21.2	6.9	11.3	268.9
	STE	0.6	1.6	1.3	1.2	0.3	36.6

Species: *Lampsilis radiata siliquoidea*

1964 CE: Bay of Quinte (Cat #26230)

SITE & BIVALVE ID	VALVE LENGTH (cm)	[Cu] (ppm)	[Ni] (ppm)	[Zn] (ppm)	[As] (ppm)	[Pb] (ppm)	[Mn] (ppm)
LQ1	9.2	6.5	9.6	12.6	5.9	12.0	1537.4
LQ2	9.7	5.4	11.1	9.9	6.5	12.2	1497.8
LQ3	9.9	6.5	9.0	56.0	6.2	11.3	972.8
LQ4	8.8	4.7	9.5	52.6	6.5	11.2	1703.9
LQ5	8.5	5.1	10.7	14.8	6.2	11.2	849.5
LQ6	9.5	9.2	11.9	15.2	6.8	12.5	1208.7
LQ7	9.2	5.0	10.7	42.7	6.9	10.6	1395.0
	MEAN	6.1	10.4	29.1	6.4	11.6	1309.3
	STE	0.6	0.4	7.7	0.1	0.3	118.1