

HISTORICAL TRENDS OF STABLE LEAD ISOTOPES, MERCURY AND OTHER TRACE METALS IN MARINE BIVALVE SHELLS FROM THE CANADIAN ARCTIC

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ABSTRACT

The temporal trends of trace metals and stable Pb isotopes in seawater from the late Holocene to the 20th Century at four locations in the Canadian Arctic were reconstructed by analysing sequences of marine bivalve shells. At two high-latitude sites, Cornwallis Island and Axel Heiberg Island, the concentrations of Hg, Cd, Pb and other metals and the isotope ratios of Pb in shells in the early 1990s were similar to or lower than Holocene material, a finding consistent with modern seawater metals being derived solely from natural geological sources. However, at two lower-latitude sites in southeast Hudson Bay and Bradore Basin (Newfoundland), significant increases of Pb and, in one case, Hg occurred in modern (1970s) shells. Changes in Pb isotopes were consistent with the introduction of American industrial Pb (in Newfoundland), and Canadian or Eurasian industrial Pb (in Hudson Bay) into local seawater. These findings suggest that in the mid- to late-1970s, significant amounts of industrial Pb and Hg had entered parts of the sub-Arctic marine environment, but not the High Arctic.

INTRODUCTION

Metals in the Arctic environment, particularly Hg and Cd, continue to be the focus of scientific attention because of their presence in biota and humans at concentrations that may be of toxicological significance. People in the Canadian Arctic have higher average tissue concentrations of Hg than southern Canadians, and some traditional foods including marine animals contain concentrations of Hg and Cd that greatly exceed Canadian dietary intake guidelines (Outridge et al. 1994; Wagemann et al. 1996). However, the extent to which long-range industrial pollution is responsible for this situation is unclear, because the natural background levels of many trace metals may also be high in certain geological settings.

The objective of this study was to determine whether industrial emissions of Hg, Cd, Pb and other metals are detectable in modern Arctic seawater, by determining the historical trends of these metals in marine bivalve shells from the pre-industrial period to recent decades. Stable Pb isotope ratios were used to determine the possible origin of any “foreign” Pb. Mollusc shells are ideal for time trend reconstructions of seawater metals because they incorporate metals including Pb, Cd and Sr in direct proportion to their seawater concentrations (Hockett et al. 1997; Mashiotta et al. 1997), and are commonly present both live and buried in Holocene beach ridges throughout the Arctic.

Shells of various species were collected live and from raised beach ridges at four locations across the Canadian Arctic and sub-Arctic. These sequences included: *Mytilus edulis* in Bradore Basin, Newfoundland (50.47°N, 57.25°W), *M. edulis* at a site in southeast Hudson Bay (55.58°N, 77.33°W), *Mya truncata* and *Hitella arctica* near Resolute, Cornwallis Island (74.68°N, 94.83°W), and *H. arctica* and *Astarte borealis* in Expedition Fiord, Axel Heiberg Island (79.35°N, 91.17°W). The Holocene samples were dated by radiocarbon analysis of shells from the beach ridges, and were collected within one degree latitude/longitude of the modern samples; in most cases the collections were within a few kilometres.

METHODS

Shells were selected for their excellent state of preservation, specifically to avoid those with signs of surface erosion or encrustation that might denote post-depositional leaching or growth of carbonates due to groundwater. Samples for analysis were removed by cutting out complete radial sections with a dremel tool; separate sections were removed for analysis of Hg and for all other metals and Pb isotopes. Samples were cleaned by removing the periostracum and any adhering soil with a rotary hand-grinder, then immersing the shells successively in 10% HNO₃ and distilled-deionized water. Sample preparation and analysis were as described for trace elements and Pb isotopes by Outridge and Stewart (1999), and for Hg by Outridge et al. (in press). The instrumental techniques were: for Hg, the AMA-254 solid-sample Hg analyser (Milestone Instruments, Sorisole, Italy); and for other trace elements and Pb isotopes, the Elan 5000 ICP-MS (Perkin Elmer - SCIEX, Concord, Ontario).

RESULTS AND DISCUSSION

Shells of *Mytilus edulis* collected in Bradore Basin in 1923 and 1979-81 exhibited significant increases of Pb, Zn and Mo compared with several late Holocene samples (Table 1A). Concentrations of these metals were generally highest in 1923. However, Hg levels increased steadily with increasing age of the samples, a pattern consistent with post-burial diagenetic contamination. In southeast Hudson Bay, modern *M. edulis* shells again had significantly higher concentrations of Pb, and Hg was also elevated above Holocene levels (Table 1B). Modern Hg was 50-300% above Holocene concentrations, depending on the sample age.

The increased modern Pb levels were paralleled at both sites by significant changes ($P < 0.01$) in Pb isotope ratios (Fig. 1). In Bradore Basin, two different “foreign” Pb sources prevalent at different times are indicated by the different trend directions between the Holocene and 1923, and subsequently between 1923 and 1979-81. The latter shift was possibly due to the introduction of US industrial Pb from Mississippi Valley ores into local seawater. Long-range transported Pb from US industrial emissions, either deposited directly from the atmosphere or indirectly via North Atlantic seawater circulation, is a plausible source given its widespread distribution (Boutron 1995; Hamelin et al. 1997). Although no known industrial signature can account for the pre-1923 shift in isotopic values, this change may also be due to industrial Pb, given that significant pre-20th Century increases of Pb deposition were documented in the Greenland ice cap (Boutron 1995). In Hudson Bay, a different source of industrial Pb is likely. In this case the shift in isotopic composition is most likely due to either Canadian or Eurasian/European industrial emissions, which have similar isotopic signatures. The winter atmosphere in the Canadian High Arctic is dominated by Eurasian/European industrial Pb (Sturges et al. 1993), but its presence in the atmosphere over Hudson Bay is not documented.

In contrast to the lower-latitude sites, bivalve shells at both sites in the High Arctic exhibited no significant modern increases in trace metal concentrations (Table 1C-F), nor significant changes in Pb isotope ratios (data not shown). At all four sites, Cd concentrations in most shells were either below detection or not significantly different through time. In *H. arctica* at Resolute, a significant Cd increase was found in the 1983 sample but not in 1991.

Post-deposition diagenesis is unlikely to have created the positive increasing trends of metals observed at two sites. Groundwater conditions such as low pH which may have leached elements from buried Holocene shells would also have caused erosion of the shell matrix. This study was careful to avoid shells with obvious signs of surface deterioration. Absorption of elements from alkaline

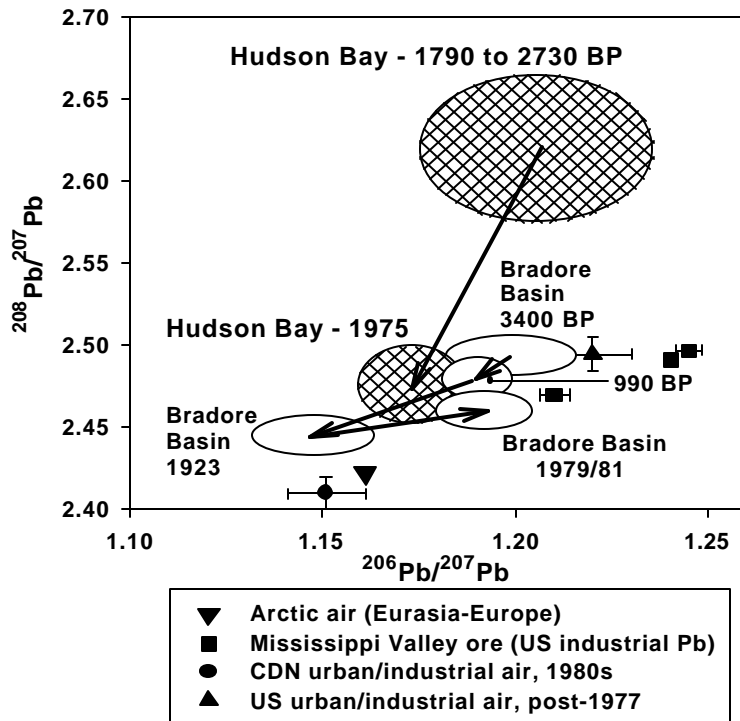


Fig. 1. Trends of Pb isotope ratios in *M. edulis* in SE Hudson Bay and Bradore Basin. (Ellipse axes or symbol and error bars represent mean \pm SD ratios. These industrial signatures are shown: Arctic air - Sturges et al. 1993; Mississippi Valley ores - Sangster et al. (in press); CDN and US air - Sturges and Barrie 1989)

western Canadian Arctic also exhibit significant increases of Hg over pre-industrial samples (Outridge, unpublished data), and show isotopic evidence of Eurasian Pb (Outridge et al. 1997). There was no good evidence of recently elevated Cd at any of the sites. The site-to-site differences in this study indicate that further locations must be surveyed to properly ascertain the degree and geographic extent of recent metal increases in the Arctic marine environment. Also, more recent samples from SE Hudson Bay and Bradore Basin are desirable to document the trends in Pb and Hg since the 1970s.

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groundwaters would have increased pre-industrial element concentrations, thereby increasing the risk of “false negative” errors, or at least reducing the difference between modern and Holocene shells. In either case, the increasing trends observed in Pb and Hg are likely to reflect real changes in shell metal concentrations through time.

The results suggest that seawater concentrations of Pb and, in one case, Hg were elevated in the mid- to late 1970s at the two southern latitude sites due to industrial contamination from either Eurasia or North America, while the concentrations at two High Arctic sites are presently similar to Holocene levels. The teeth of present-day beluga in the Mackenzie River Delta in the

Sturges WT, Hopper JF, Barrie LA, Schnell RC (1993) Atmos. Environ. 27A:2865-2871.
 Wagemann R, Innes S, Richard PR (1996) Sci. Tot. Environ. 186:41-66.

Table 1. Trace element concentrations in historical sequences of Arctic marine bivalve shells (Units: mean \pm SD μ g/g DW, except ng/g DW for Hg. Significant differences ($P<0.05$) indicated by different letters beside means. For *Mytilus* in Hudson Bay, Holocene samples were combined because of low replicate numbers. Bd = below detection; na = data not available)

DATE	Zn	Mo	Cd	Hg	Pb
(A) Species: <i>Mytilus edulis</i>		Location: Bradore Basin, Newfoundland			
1979-81 (N=7)	1.00 \pm 0.43 A	0.04 \pm 0.03 A	bd	0.3 \pm 0.1	0.35 \pm 0.10 A
1923 (N=5)	3.81 \pm 2.12 B	0.05 \pm 0.02 A	0.06 \pm 0.02	1.0 \pm 0.6	0.99 \pm 0.47 B
990 BP (N=7)	0.01 \pm 0.02 C	0.01 \pm 0.01 B	0.04 \pm 0.02	9.2 \pm 3.9	0.12 \pm 0.07 C
3400 BP (N=5)	0.01 \pm 0.02 C	bd B	0.01 \pm 0.02	8.8 \pm 5.8	0.08 \pm 0.02 C
9000 BP (N=5)	1.75 \pm 0.33 AB	0.02 \pm 0.02 B	0.02 \pm 0.03	17.0 \pm 11.9	0.14 \pm 0.06 C
(B) Species: <i>Mytilus edulis</i>		Location: SE Hudson Bay			
1975 (N=13)	0.05 \pm 0.09 A	0.010 \pm 0.01	bd	1.2 \pm 0.6 A	0.38 \pm 0.23 A
1790 BP (N=3)	0.26 \pm 0.18 B	bd	bd	0.3 \pm 0.1 B	0.17 \pm 0.17 B
2730 BP (N=4)	1.37 \pm 1.00	bd	bd	0.7 \pm 0.2	0.15 \pm 0.03
(C) Species: <i>Mya truncata</i>		Location: Resolute, Cornwallis Island			
1991 (N=10)	0.09 \pm 0.15 A	0.03 \pm 0.02 A	bd	8.8 \pm 9.0	0.26 \pm 0.10 A
6400 BP (N=6)	0.03 \pm 0.07 B	0.28 \pm 0.06 B	bd	21.3 \pm 16.2	0.07 \pm 0.03 B
8970 BP (N=4)	0.14 \pm 0.04 A	0.01 \pm 0.01 A	bd	1.4 \pm 0.9	0.50 \pm 0.26 C
(D) Species: <i>Hiatella arctica</i>		Location: Resolute, Cornwallis Island			
1991 (N=10)	0.32 \pm 0.08	0.01 \pm 0.01 A	0.18 \pm 0.08 A	0.92 \pm 0.86	0.47 \pm 0.35
1983 (N=3)	0.38 \pm 0.12	0.03 \pm 0.01 A	0.82 \pm 0.31 B	0.41 \pm 0.19	0.30 \pm 0.10
6400 BP (N=4)	0.31 \pm 0.33	0.14 \pm 0.09 B	0.10 \pm 0.13 A	2.49 \pm 2.06	0.16 \pm 0.20
7000 BP (N=5)	0.29 \pm 0.25	bd A	0.08 \pm 0.09 A	1.07 \pm 0.59	0.43 \pm 0.14
(E) Species: <i>Astarte borealis</i>		Location: Expedition Fiord, Axel Heiberg Island			

1991	na	na	0.12 ±0.10	0.08 ±0.06 A	0.35 ±0.12
5580 BP	na	na	0.24 ±0.06	0.37 ±0.17 B	0.41 ±0.18
7690 BP	na	na	0.15 ±0.11	0.42 ±0.13 B	0.21 ±0.06
7780 BP	na	na	0.19 ±0.15	0.67 ±0.32 B	0.30 ±0.16

(F) Species: <i>Hiatella arctica</i>	Location: Expedition Fiord, Axel Heiberg Island				
1991	na	na	0.22 ±0.05	0.23 ±0.07	0.60 ±0.21
7410 BP	na	na	0.24 ±0.09	0.53 ±0.46	0.57 ±0.42
