Stable Lead Isotopes Evidence Anthropogenic Contamination in Alaskan Sea Otters

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Introduction

Stable lead isotopes ($^{204}$Pb, $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb) in North Pacific oceanic surface waters demonstrate the predominance of industrial leads from North America and Asia (1–4). Those inputs have increased seawater lead concentrations 5–15-fold since preindustrial times (1, 2, 5), but the effects of that increase in high trophic level marine consumers are essentially unknown. Lead contamination of samples during collection, processing, and analyses has also invalidated many measurements of lead, confounding assessment of lead’s introduction and transport into the marine biosphere (6, 7). Models of lead transport through marine food webs indicate that lead is biodepleted relative to its biogeochemical analogue calcium (7, 8). Therefore, lead concentrations were projected to be lowest in top trophic level consumers (7), in contrast to some other trace elements (e.g., mercury) that are bioconcentrated in marine consumer organisms (9).

We adopted ultraclean techniques to measure lead in teeth of preindustrial and contemporary sea otters (Enhydra lutris) from Amchitka Island, AK. These analyses were conducted to determine if detectable changes in lead concentrations and isotopic compositions had occurred in top-level consumers corresponding to recent increases in lead in the North Pacific Ocean (1–4, 10, 11). This allowed us to assess the biodepletion model of lead transport through marine food webs (7, 8) and its susceptibility to perturbations by contaminant lead.

Lead can be characterized by its stable isotopic composition, since the relative natural abundance of these isotopes ($^{204}$Pb, $^{206}$Pb, $^{207}$Pb, and $^{208}$Pb) varies systematically with the geological evolution and age of the formation (12). This provides characteristic (but not necessarily unique) ratios that may be used to identify different lead sources (12).

Sea otters are unusual among marine birds and mammals in that they do not migrate (13) and are members of a nearshore, detritus-based food web (14). Their prey are obtained exclusively from local sources, and organic production in the ecosystem in which they live is derived largely from kelp and other macroalgae (15). Consequently, the composition of lead accumulated by sea otters reflects the ambient seawater lead incorporated by local primary producers, since there is no isotopic fractionation of lead within the biosphere (11).

Methods

Third postcanine or first molar teeth were obtained from five contemporary and five preindustrial sea otters from Amchitka Island, Aleutian Islands, AK (51°30' N, 179°00' E). Remains of the preindustrial sea otters were excavated from Aleut middens on Amchitka Island by O. J. Murie in 1937. Carbon-14 dating of a representative sample indicated an age of 1900 ± 230 years before present. The apparent $^{14}$C age may be biased to an older value by as much as 1000 years due to the assimilation of “old” carbon by the sea otter, but this would still substantially predate the onset of industrialization. Contemporary sea otter teeth were collected on Amchitka Island in 1986 and 1987. Teeth constitute a unique indicator of lead exposure because they accumulate lead over the life of the organism (16). In addition, they are resistant to contamination and post-mortem diagenetic alteration, relative to other tissues (17). This is because the inner dentine of buried teeth remains is isolated from the surrounding soil by a protective layer of enamel, which is very impervious to soil lead alteration (J. E. Ericson, personal communication).

Samples were processed and analyzed by ultraclean trace-metal techniques (17). Outer and inner (circumpulpal) tooth crown surfaces were ground down with an acid-cleaned tungsten carbide drill bit to obtain a non-contaminated sample (0.1–0.2 g) of dentine. Samples were rinsed repeatedly in dilute HNO₃ to remove any contaminant lead added during preparation (17) and then digested in concentrated HNO₃. Aliquots were removed for calcium determinations, and the remaining sample was further processed for lead by using a modified procedure of Tatsumoto (M. Tatsumoto, personal communication). Briefly, sample lead was converted to the bromide form in 1.2 N HBr and passed through a Teflon microcolumn loaded with AG-1 X8 200–400-mesh anion-exchange resin. Resin-bound lead was eluted with 8 N HCl, and aliquots were removed for lead concentration and isotopic composition analyses. Calcium concentrations were determined by flame atomic absorption spectrometry (AAS) using matrix modifiers. Lead concentrations were determined by graphite furnace AAS using standard additions and by isotopic dilution thermal ionization mass spectrometry. Lead isotopic compositions were determined by thermal ionization mass spectrometry (reported errors are ±2σ). The
fractionation correction for the latter analyses, which were derived from concurrent calibrations of SRM 981, was 0.12 ± 0.02%. Total cumulative lead blanks were <150 pg, based on the analyses of container, reagent, and procedural blanks. All reagents and containers (conventional polyethylene or Teflon) were prepared with the ultraclean procedures detailed by Patterson and Settle (18).

Lead concentrations are normalized to calcium since lead serves as a biologic analogue to calcium. Lead is transported intracellularly by essentially the same routes, and it is controlled by many of the same mechanisms responsible for maintaining calcium homeostasis in living systems (19). A total of 70–95% of a vertebrate’s body lead burden is localized in the skeletal tissue (20, 21), where concentrations increase with age and level of exposure to lead (22-24). Osseous tissue trace-element concentrations presented on a wet or dry weight basis can introduce analytical error and confound comparisons between samples due to differences in both mineral and nonmineral content between skeletal tissues and individuals sampled (25).

Results and Discussion

Sea otter lead burdens (expressed as $x \pm \sigma$ Pb/Ca atomic ratios) have not increased significantly ($P > 0.05$, t test) in the contemporary sea otters (4.4 ± 3.9 x $10^{-9}$) relative to their preindustrial counterparts (2.8 ± 1.6 x $10^{-9}$) based on this preliminary sampling (Table 1). This contrasts with measured order of magnitude increases in lead reported for western North Atlantic corals (26) and for humans (17), and similar estimated increases for pelagic tuna (6, 27) and for a remote terrestrial subalpine carnivore (28).

Those increases are attributed to atmospheric emissions of anthropogenic lead (3 x 10$^6$ kg year$^{-1}$), which are currently nearly 2 orders of magnitude greater than natural emissions (5, 29).

The absence of a significant increase in the Pb/Ca ratio of the contemporary sea otters compared to their preindustrial counterparts is attributed to the relatively small increase of lead in remote oceanic regions and the biodepletion of lead in marine food webs (Figure 1) (7, 8). Lead is passively enriched relative to calcium during the transfer of these elements from seawater to plants because lead is more strongly chelated on plant surfaces than is calcium, and because algae have a large surface area/volume ratio (7, 8). Lead is then biodepleted relative to calcium during subsequent transfers to consumer organisms (8, 27) because of a discrimination against lead in favor of calcium during the metabolic assimilation of these elements (8). The transfer of lead relative to calcium from seawater through the marine food web is nonlinear, and the biodepletion of lead apparently operates independently of the lead concentrations of food when they are within 100-fold of natural levels (8). This is evidenced in a simple coastal food web, where a 5-fold increase in Pb/Ca of food (algae) of a gastropod resulted in only a 3-fold increase in the Pb/Ca of its shell, and only a 50% increase in the Pb/Ca of its muscle (8).

The within group between sample variance is primarily attributed to individual differences in the accumulation of nonmineral lead emissions.
of lead due to otter age and diet. Lead exposure duration is a function of age, and lead exposure concentration is a function of diet. The effect of the latter variable on sea otter lead levels is illustrated by the lead biodepletion model (refs 7 and 8, Figure 1). This predicts that prey species occupying higher trophic levels will be more depleted of lead relative to calcium than lower trophic level organisms. Sea otters have highly individualized diets (30), and in addition to the typical prey of benthic invertebrates, sea otters at Amchitka Island consume kelp bed fishes. The extent of this piscivory also varies among individuals (31). Because most of the benthic invertebrates eaten by sea otters are herbivores (mainly sea urchins), the invertebrate feeders are essentially secondary consumers. However, since fish feed chiefly on a wide range of herbivorous, carnivorous, and detritivorous crustaceans (32), piscivorous sea otters are tertiary consumers or higher.

Although there has been no detectable increase in the lead content of contemporary sea otters, lead isotopic composition analyses indicate substantial changes in the source of lead in those animals. The lead isotopic ratios (Figure 2a, b) demonstrate that natural leads from the Aleutian arc (33) account for essentially all of the lead in preindustrial sea otters. The natural lead component is presumed to arise primarily from weathering of pliocene volcanic rocks in the Aleutian volcanic arc, with subsequent alluvial deposition along the coastal margin. The Aleutian arc lavas have distinct and contrasting lead isotopic compositions compared to volcanic rocks of the Pacific Ocean crust or the nearby Pribilof Islands (33), supporting the presumption of a primarily local (Aleutian arc) source of the natural lead assimilated by Amchitka Island sea otters.

Contemporary otters, in contrast, contain a mixture of Asian and Canadian industrial leads, with relatively minor amounts (<10%) of Aleutian arc leads. Asian industrial lead (207Pb/206Pb = 0.859 ± 0.007, 208Pb/206Pb = 2.12 ± 0.01) (M. Morozumi, personal communication) is introduced to waters of the Kuroshio current via aeolian deposition and transported across the North Pacific to the

Figure 2. (a) 207Pb/206Pb vs 204Pb/206Pb and (b) 206Pb/204Pb vs 207Pb/204Pb of preindustrial (●) and contemporary (●) sea otters from Amchitka Island, AK. Error bars in (a) are ±2σ. Error bars in (b) were omitted for clarity, although they were typically ±1.5× the symbol diameter for the contemporary sea otters and ±4× the symbol diameter for the preindustrial sea otters. Lead isotopic compositions of natural and anthropogenic sources are plotted for comparison: (O) natural Aleutian arc lead (33); (○) Japanese industrial lead (M. Morozumi, personal communication); (▲) western Canada industrial lead (1); (■) western United States industrial lead (40). The Northern Hemisphere reference line (---) (47) is included in (b) for reference.

Figure 3. Lead sources to Amchitka Island sea otters (206Pb/204Pb ratios). Leads in the preindustrial otters (2.04) were derived from natural weathering of the Aleutian arc lavas (2.04). In contrast, leads in the contemporary otters (2.09) were derived primarily from Asian (left arrow, 2.12) and western Canadian (right arrow, 2.07) industrial leads that were introduced into ocean surface waters via aeolian deposition.

Alaska Current (2–4). The Alaska Current skirts western North America, where it may entrain Canadian industrial lead \((^{207}\text{Pb}/^{206}\text{Pb} = 0.860, {^{208}\text{Pb}}/^{206}\text{Pb} = 2.07)\) (1), and then flows westward along the Aleutian arc as the Alaskan Stream (Figure 3) (34). Therefore, the isotopic composition of lead in contemporary otters is consistent with those of surface waters in the northeast Pacific Ocean, and with the projected dispersion of industrial lead aerosols.

Lead isotopic values within the preindustrial and contemporary sample groups are generally not significantly different \((P > 0.05, t\) test) because of the large errors calculated for most ratios. Those errors are dominated by the analytical blank correction \((117 \pm 58 \text{ pg of Pb; } {^{206}\text{Pb}}/^{204}\text{Pb} = 18.08 \pm 1.88, {^{207}\text{Pb}}/^{204}\text{Pb} = 15.27 \pm 0.82, \text{ and } {^{208}\text{Pb}}/^{204}\text{Pb} = 37.18 \pm 3.22)\), while the measured isotopic ratios were essentially unchanged. Use of this pooled blank, and propagation of its large error \((35)\), was considered the most conservative approach. Typical measurement errors \((\pm 2\sigma)\) for \({^{206}\text{Pb}}/^{204}\text{Pb}, {^{207}\text{Pb}}/^{204}\text{Pb}, \text{ and } {^{208}\text{Pb}}/^{204}\text{Pb}\) ratios were \(< \pm 0.08\%\) of the mean, while the errors on the more precise \({^{207}\text{Pb}}/^{206}\text{Pb} \text{ and } {^{208}\text{Pb}}/^{206}\text{Pb}\) ratios were \(< \pm 0.02\%\). After propagation of the pooled blank error value, the errors as reported were increased to approximately \(\pm 0.65\) and \(\pm 0.38\%)\), respectively. However, even these inflated errors do not preclude differentiation between leads accumulated by the contemporary and preindustrial sea otters.

United States industrial lead does not appear to measurably contribute to the lead isotopic compositions of the contemporary sea otter sample \((\text{Table I, Figure 2a,b})\). One possible exception to this is contemporary sea otter sample 2, which contains an isotopic composition closer to U.S. industrial lead, but most like the natural Aleutian arc leads. We have no explanation for this anomaly, other than to suggest it may be due to the intake of U.S. industrial lead and/or natural lead in the diet of the animal. This latter alternative is partly substantiated by the near identical lead isotopic composition of contemporary and preindustrial walrus teeth collected from animals that inhabited the St. Lawrence Island and southern Chukchi Sea regions (D. Smith, unpublished data). The isotopic composition of those preindustrial \({^{206}\text{Pb}}/^{204}\text{Pb} = 18.94 \pm 0.02, {^{207}\text{Pb}}/^{204}\text{Pb} = 15.62 \pm 0.02, \text{ and } {^{208}\text{Pb}}/^{204}\text{Pb} = 98.71 \pm 0.02\) and contemporary \({^{206}\text{Pb}}/^{204}\text{Pb} = 18.95 \pm 0.02, {^{207}\text{Pb}}/^{204}\text{Pb} = 15.61 \pm 0.02, \text{ and } {^{208}\text{Pb}}/^{204}\text{Pb} = 98.67 \pm 0.06\) samples is similar to the natural Aleutian arc leads and to North American continental deposit leads \({^{206}\text{Pb}}/^{204}\text{Pb} = 18.98 \pm 0.20, {^{207}\text{Pb}}/^{204}\text{Pb} = 15.63 \pm 0.04, \text{ and } {^{208}\text{Pb}}/^{204}\text{Pb} = 38.79 \pm 0.26\) (36). The absence of a change in lead isotopic composition between the preindustrial and contemporary walruses is attributed to the ingestion of relatively large amounts of natural sediment lead by those animals, who feed mainly on benthic invertebrates.

The exchange of soil lead is not considered to have significantly altered the lead composition of the preindustrial teeth. This is based on analogies with analyses by Ericson et al. (17), who reported minimal diagenetic alteration of tooth enamel of buried ancient Peruvian remains. The present analyses were also limited to dentine, which was physically isolated from the surrounding environment.

These sea otter data are relevant to concerns of lead toxicity because they demonstrate low lead levels and little or no postindustrial lead increase in a higher trophic level marine consumer. For comparison, levels reported here are 40–400-fold lower than those in teeth of children of the low-lead exposure group in a landmark study of asymptomatic lead toxicity (37). This does not eliminate cause for concern of lead contamination in marine mammals, since there may be no lower threshold concentration of lead toxicity (38). Additionally, analysis of contemporary sea otters from more industrialized regions is warranted, since the lead biodeposition process in marine mammals may be less efficient than in terrestrial mammals, for which the toxicity of lead is relatively well-known (39).

In summary, these data demonstrate that lead isotope systematics should be used to identify sources and transport routes of lead in the marine biosphere. If only lead concentrations had been determined in these sea otter teeth, it would have been incorrectly concluded that there was no measurable change in the lead accumulated by contemporary animals since preindustrial times. Finally, these data provide a means of deriving the occurrence of natural leads in the prehistoric oceans of high-latitude regions where there are no suitable calcite-containing macroinvertebrates.

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Measurements of Nitrous Acid inside Two Research Houses

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Continuous analyzers for NO, NO2, and HONO were used to study the production and decay of these gases in two indoor air quality research houses, using unvented gas space heaters and ranges as combustion sources. In agreement with previous studies, indoor HONO concentrations were elevated during unvented combustion. Peak (15-min) levels up to 100 ppb HONO and 24-h averages as high as 40 ppb were measured. The observed kinetics suggest the secondary formation of HONO, possibly as a result of heterogeneous reactions involving NO2, in addition to primary production of HONO during combustion.

Introduction

The production of nitrogen dioxide and other nitrogen oxides in combustion processes has for some time been recognized as a potential indoor air quality problem. Research efforts have indicated that concentrations of NOx indoors sometimes exceed outdoor concentrations in environments where unvented gas heating the cooking appliances are operating (1–6). Indoor concentrations are a function of both (indoor and outdoor) source and removal processes, such as air exchange, or chemical reactions.

Several recent laboratory investigations have identified surface materials commonly present indoors that react with NOx to reduce concentrations (7–10). These studies have primarily been limited to measurements of the gases NO2 and nitric oxide, and of nitrite and nitrate ions on the materials. One possible gaseous product of NO2 reactivity is nitrous acid. Preliminary results of one of these studies detected significant amounts of nitrous acid, probably resulting from heterogeneous reactions involving NO2 and the surface material (9).

Although little information exists with respect to HONO toxicity and typical indoor concentrations, HONO has been well studied as a reactant in photochemical smog production (11, 12). Photolysis of HONO (310 nm < λ < 390 nm) has been recognized as a major source of hydroxyl radical in the early morning hours (13–15). Outdoor (15-min average) HONO concentrations of 0.03–15.0 ppb have been measured, with the highest levels measured during predawn hours in heavily polluted urban areas. Typical outdoor concentrations in urban areas peak at less than 5 ppb (11, 15–18). An important formation pathway is suspected to be the heterogeneous reaction of NO2 with water to produce both HNO3 and HONO (19, 20).

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]  

Since a heterogeneous reaction mechanism for HONO production was thought to dominate in smog chambers and reaction vessel studies (21–23), Pitts and co-workers conjectured that NOx to HONO conversion would also occur in typical indoor environments, particularly in circumstances where indoor combustion appliances generated significant concentrations of NO2. In a preliminary study in a mobile laboratory, NO2 was injected into the laboratory air and HONO concentrations increased with first-order kinetics with respect to NO2, indicating the potential...