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Isotope Systematics of Contaminant Leads in Monterey Bay

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■ Isotopic compositions of stable lead (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) were utilized to identify a lead slag deposit as the principal source of contaminant lead in Monterey Bay. This point source had been indicated by anomalously high lead concentrations (e.g., 1826 μg/g) in native mussels (*Mytilus californianus*) near that deposit, which were orders of magnitude above the base-line concentration of the species (0.5 μg/g). Subsequent analyses revealed that the lead concentrations of both transplanted mussels (*M. californianus*) and intertidal sediments were positively correlated with their proximity to the slag deposit. Complementary lead isotopic compositions substantiated those empirical correlations by demonstrating that the slag was the predominant source of contaminant lead in both the mussels and the sediments. Analyses of the digestive tracts of mussels from the slag deposit indicated that ingested slag particulates accounted for their elevated lead concentrations, while analyses of their gonads indicated that dissolved lead from other industrial sources was also being bioaccumulated by passive adsorption on exposed surfaces. Therefore, this study has demonstrated the potential of lead isotope systematics both to identify sources of lead contamination in marine organisms and to trace its biogeochemical cycle in the marine environment.

Introduction

Exceptionally elevated lead concentrations were detected in mussels (*Mytilus californianus*) from Monterey Harbor in the southern end of Monterey Bay, CA (Table I). Some of those concentrations (e.g., 1826 μg/g dry weight) were more than 3 orders of magnitude greater than the base-line concentration (0.5 μg/g dry weight) of the species (*1*). While there were no major waste water discharges into the harbor to account for the anomalously high lead concentations, geographic gradients in the elemental concentration of mussels indicated a point source origin within the harbor. This was substantiated by isotopic composition analyses, which traced the elevated lead concentrations in the mussels to an industrial lead slag deposit.

Isotopic composition analyses were required to identify the slag as the principal source of contaminant lead in the harbor because of the numerous sources of contaminant lead in the northeast Pacific. Different aeolian inputs account for over 95% pf the lead in offshore surface waters (*2–4*), and other industrial inputs add to the lead burdens of coastal waters (*5*, *6*). The multiplicity of those lead inputs precluded an unqualified identification of one principal source of contaminant lead with only lead concentration analyses. Therefore, complementary lead isotopic composition analyses were required to confirm the principal source of contaminant lead, utilizing the stable isotope ratio technique (*7*).

While the potential of this technique in environmental research has been recognized for several years (*8–10*), there have been very few applications of it in the marine environment. Contamination problems, which have plagued accurate measurements of lead concentrations in seawater (*2*), have also prevented accurate measurements of lead isotopic compositions in seawater until recently (*11*). Measurements of lead in marine organisms have been limited by the same problems of contamination (*12*). Moreover, the utility of lead isotopic composition measurements in marine environmental research was not fully recognized until the previously cited studies of C. C. Patterson and his associates had demonstrated (a) the magnitude of lead contamination in the marine environment and (b) the distinct isotopic compositions of contaminant leads in seawater and marine sediments. Some of those studies have been reviewed by Faure (*13*). Since most of them had been located in the northeast Pacific, they facilitated this initial study of lead isotope systematics in Monterey Bay.

Table I. Lead Concentrations (μg/g Dry Weight) of Native Mussels (*M. californianus*) in Monterey Bay

location (station)[a]	geographic coordinates	lead concn ($x \pm s$)
Point Pinos (411)	36° 38′ 27″ N 121° 55′ 46″ W	3.18 ± 1.03
Asilomar (413)	36° 38′ 10″ N 121° 55′ 34″ W	3.43 ± 0.92
Pacific Grove (414)	36° 38′ 18″ N 121° 55′ 46″ W	3.23 ± 0.65
Lovers Point (415)	36° 37′ 36″ N 121° 54′ 47″ W	16.7 ± 2.5
Hopkin's Marine Station (416)	36° 37′ 20″ N 121° 54′ 05″ W	10.0 ± 2.4
Coast Guard jetty (420.2)	36° 36′ 34″ N 121° 53′ 23″ W	91.7 ± 10.1
slag deposit (421.1)[b]	36° 36′ 23″ N 121° 53′ 35″ W	1826
restaurant wharf (421.2)	36° 36′ 20″ N 121° 53′ 29″ W	58.0 ± 24.4
commercial wharf (421.3)[c]	36° 36′ 21″ N 121° 53′ 20″ W	5.80 ± 0.64

[a] California State Water Resources Control Board Mussel Watch Station identification number (*15*). [b] Only one native mussel was present at the slag deposit site for the March 1984 collection. [c] Bay mussels (*M. edulis*) were collected and analyzed at the commercial wharf site (421.4).

Methods

Established procedures (*1–5*, *14*) were utilized to collect samples (mussels, seawater, and sediments) from Monterey Harbor and adjacent sites within the bay. Those sites are identified in Figure 1 by their California State Mussel Watch identification numbers (*15*). Corresponding geographic coordinates and landmark names are listed in Table I.

In addition to the collections of native mussels, other mussels were transplanted to some of the sites for subsequent collections and analyses. This was necessitated by

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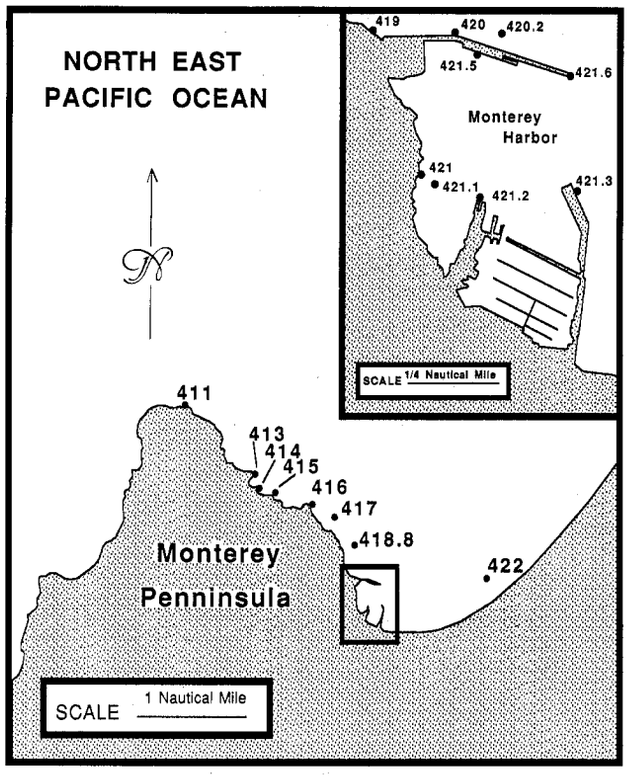

Figure 1. Lead concentration and isotopic composition sampling sites in Monterey Bay.

the limited distribution of mussels within the harbor (e.g., only one native mussel was found at the lead slag site in the March 1984 collection). The transplants were made with established procedures (*16*). All of the transplants were obtained from Bodega Head, CA (38° 18′ 42″ N, 123° 04′ 07″ W), where mussels have homogeneously low lead concentrations (0.87 ± 0.38 μg/g). This precluded problems of endemic physiological or genetic differences in lead metabolism among the transplanted organisms (*16*).

Two sets of transplants were made. An initial 18-week transplant (5/84 to 9/84) was made to substantiate the lead concentration gradient observed in the native mussels. A second 18-week transplant (9/84 to 2/85) was made to further substantiate the lead concentration gradient, obtain complementary lead isotopic composition data, and determine the distribution of contaminant lead within the mussels.

The distribution of contaminant lead within the mussels was determined by analyses of discrete tissues. Undepurated digestive tracts were analyzed to establish whether the mussels were contaminated by lead associated with ingested sediments, as observed in some intertidal organisms (*17*). Gonads were analyzed to establish whether the mussels were contaminated by dissolved lead that was adsorbed on their outer surfaces, as observed in other intertidal organisms (*18*).

Elemental concentrations were measured by graphite furnace atomic absorption spectrophotometry with standard procedures developed for the national mussel watch program (*1*). With one exception, this included analyses of three separate homogenates of 15 mussels, with an average shell length of 60 mm, from each site. (As previously noted, only one native mussel was available at the slag deposit site for the March 1984 collection rather than the 45 mussels collected for analyses at the other sites.) Previously detailed statistical analyses of the variance in elemental concentrations obtained with these homogenates have demonstrated a resolution of 20% differences in elemental concentrations of *M. californianus*

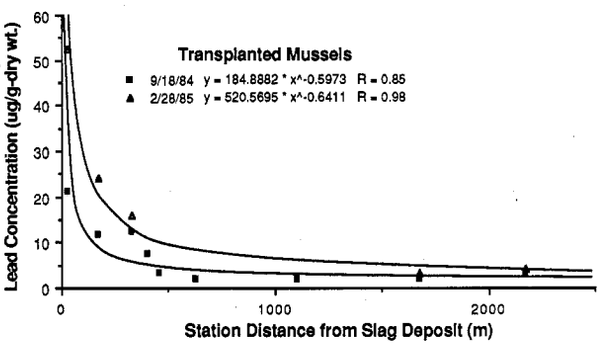

Figure 2. Correlations between lead concentrations in mussels transplanted in Monterey Bay and their proximity to a lead slag deposit.

from different populations (*19*). The separate tissue analyses were also made with homogenates to obtain comparable resolution. Each analysis was made in triplicate with matrix modification techniques and methods of addition, as in the national mussel watch program (*1*). Concurrently analyzed lead concentrations of NBS oyster tissue (SRM 1566), orchard leaves (SRM 1521), and bovine liver (SRM 1577a) were within 5% of their certified values.

Isotopic compositions were measured by thermal ionization mass spectrometry, following established digestion and concentration procedures (*3–5, 11*). Isotopic compositions of the mussels and their tissues were determined with homogenates of 15 individuals, as in the elemental analyses. Ionizations were accomplished at approximately 1200 °C, after the volatization of refractory hydrocarbons. Measurements were taken with total ion currents of 5×10^{-12} to 5×10^{-11} A. These were calibrated with concurrent measurements of the NBS common lead isotopic composition standard (SRM 981). The fractionation correction, which was derived from 20 separate analyses of SRM 981, was 0.12 ± 0.02% per mass unit. Errors based on the 95% confidence interval on the measurement precision were $^{206}Pb/^{204}Pb$ = 0.1%, $^{206}Pb/^{207}Pb$ = 0.05%, and $^{206}Pb/^{208}Pb$ = 0.1%. Coefficients of variation of eight analyses of subsamples from one homogenate of 15 mussels from the slag deposit site were $^{206}Pb/^{204}Pb$ = 0.3%, $^{206}Pb/^{207}Pb$ = 0.2%, and $^{206}Pb/^{208}Pb$ = 0.1%.

Results and Discussion

Lead Concentrations. Elemental concentrations of native mussels indicated that the slag deposit was the principal source of contaminant lead within the harbor. Lead concentrations of the native mussels within the study area (Table I) ranged from 3.2 μg/g at the relatively distant sites to 1826 μg/g in the one mussel at the slag deposit site (Figure 2). The latter concentration is believed to be the highest concentration ever reported for *M. californianus*. Subsequent analyses of the tissues of transplanted mussels, which are discussed later, indicated that some of that lead was in detrital sediments within the digestive tracts of the organisms rather than biologically accumulated lead within their tissues.

Other elemental concentrations (Ag, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Se, and Ti) of the native mussels were not above base-line levels (*1*), with the exception of zinc (*15*). Concentrations of zinc increased from a base-line level of 118 μg/g in mussels at relatively distant sites to 1128 μg/g in the one mussel at the slag deposit site. Concentrations of lead and zinc in native mussels within Monterey Harbor also were positively correlated ($p < 0.05$, simple linear correlation). This covariance further indicated that the slag was the principal source of lead contamination, since (a) the slag had high concentrations of zinc and (b) other point sources of contaminant lead (e.g., waste water out-

Table II. Lead Concentrations (μg/g Dry Weight) of Transplanted Mussels (*M. californianus*) in Monterey Bay

location (station)	transplant period	lead concn ($x \pm s$)
Monterey Bay Aquarium (417.0)	5/84 to 9/84	1.75 ± 0.35
Monterey Charthouse (418.8)	5/85 to 9/84	1.95 ± 0.13
Monterey Charthouse (418.8)	9/84 to 2/85	2.96 ± 0.38
outer Coast Guard jetty (420.2)	5/84 to 9/84	1,85 ± 0.01
slag deposit (421.1)	5/84 to 9/84	21.1 ± 0.4
slag deposit (421.1)	9/84 to 2/85	50.4 ± 5.2
restaurant wharf (421.2)	5/84 to 9/84	11.9 ± 2.2
restaurant wharf (421.2)	9/84 to 2/85	24.6 ± 3.7
commercial wharf (421.3)	5/84 to 9/84	7.38 ± 0.71
commercial wharf (421.3)	9/84 to 2/85	12.1 ± 0.4
Coast Guard docks (421.5)	5/84 to 9/84	12.3 ± 2.9
Coast Guard docks (421.5)	9/84 to 2/85	16.9 ± 1.9
end Coast Guard jetty (421.6)	5/84 to 9/84	3.13 ± 0.69
Holiday Inn (422.0)	5/84 to 9/84	3.09 ± 0.22
Holiday Inn (422.0)	9/84 to 2/85	3.91 to 0.31

falls) are often sources of other elemental contamination.

Geographic gradients in the lead concentrations of the transplanted mussels substantiated the lead gradient in the native mussel data (Table II). The highest lead concentrations occurred in mussels at the slag deposit site, and elevated lead concentrations in mussels at the other sites were positively correlated ($p < 0.05$, simple linear correlations) with their proximity (in meters) to the slag deposit (Figure 2). Lead concentrations in mussels at the slag deposit increased from the base-line level (0.9 μg/g) to 21.1 μg/g during the initial transplant period (5/84 to 9/84), and they increased to 50.4 μg/g during the second transplant period (9/84 to 2/85). The systematically higher lead concentrations in mussels from the second transplant indicated temporal differences in the dispersion of slag detritus within the marine biosphere. This may have been associated with seasonal differences in weathering processes and tidal action.

Elemental concentrations of sediments in the harbor also indicated that the slag was the principal source of contaminant lead (*20*). Concentrations of sediments next to the slag deposit (5600 μg/g) were 3 orders of magnitude greater than the average background concentration of Monterey Bay intertidal sediments (1.3 μg/g). Contours of decreasing lead concentrations radiated out from the slag deposit, with secondary maxima occuring in low-energy areas of deposition (Figure 3).

In summary, lead concentration gradients in native mussels, transplanted mussels, and sediments all revealed correlations between elevated lead concentrations in the samples and their proximity to the slag deposit. However, those correlations were empirical since they did not demonstrate that the slag was the source of lead contamination. Additionally, temporal and spatial variations in the gradients indicated that there might be other principal sources of contaminant lead within the harbor. Temporal variations of lead concentrations in the transplanted mussels indicated that the elevated lead concentrations might be

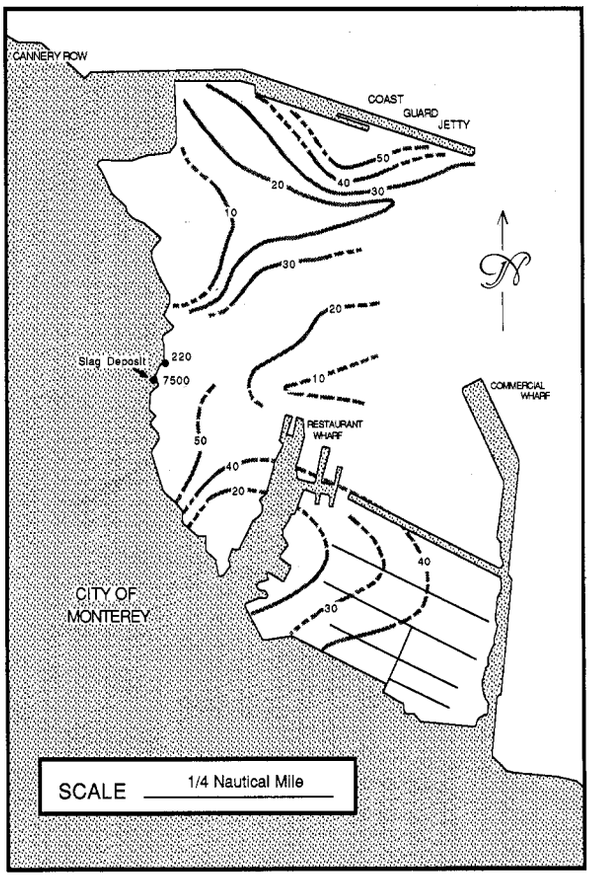

Figure 3. Contours of lead concentrations in surface sediments within Monterey Harbor, based on data of Youngerman (*20*).

due to seasonal inputs from other sources, such as surface runoff. Spatial variations in the sediment concentrations, with secondary maxima adjacent to the Coast Guard jetty, restaurant wharf, and commercial wharf, indicated that the elevated lead concentrations might also be due to inputs from other sources, such as marine operations and waste water discharges. Therefore, the following lead isotopic composition measurements were required to identify the principal source(s) of contaminant lead within the harbor.

Lead Isotopic Compositions. Lead isotopic compositions of the contaminated mussels, sediments, and slag (Table III) substantiated the preceding correlations between elevated lead concentrations and the slag deposit gradients. The $^{206}Pb/^{207}Pb$ ratios ($x \pm s$) of the ingots of lead slag (1.174 ± 0.001) were indistinguishable ($p < 0.05$, t test) from those of transplanted mussels ($^{206}Pb/^{207}Pb$ = 1.174 ± 0.001) at the slag deposit site. Isotopic compositions of the slag were also indistinguishable from those of contaminated intertidal sediments ($^{206}Pb/^{207}Pb$ = 1.173 ± 0.001) at the slag deposit site.

Isotopic compositions of other major sources of lead in the area (Table IV) contrasted with those of the most

Table III. Lead Concentrations (μg/g Dry Weight) and Isotopic Compositions of Gonads in Mussels (*M. californianus*) Transplanted in Monterey Bay and Digestive Tract of Mussels Transplanted at a Slag Deposit in the Bay

location (station)	Pb concn ($x \pm s$)	$^{206}Pb/^{204}Pb$ ($x \pm s$)	$^{206}Pb/^{207}Pb$ ($x \pm s$)	$^{206}Pb/^{208}Pb$ ($x \pm s$)
gonads				
slag deposit (421.1)	10.4 ± 1.1	18.65 ± 0.24	1.199 ± 0.004	0.4995 ± 0.0060
restaurant wharf (421.2)	2.6 ± 0.3		1.201 ± 0.006	0.4958 ± 0.0015
Coast Guard jetty (421.5)	4.2 ± 0.4	19.38 ± 0.05	1.222 ± 0.005	0.5168 ± 0.0033
Holiday Inn (422.0)	0.31 ± 0.03	18.90 ± 0.46	1.213 ± 0.005	0.4968 ± 0.0002
digestive tract				
slag deposit	108 ± 7	18.23 ± 0.08	1.173 ± 0.003	0.4851 ± 0.0023

Table IV. Lead Isotopic Compositions of Mussels (*M. californianus*) Transplanted in Monterey Bay

location (station)	$^{206}Pb/^{204}Pb$ ($x \pm s$)	$^{206}Pb/^{207}Pb$ ($x \pm s$)	$^{206}Pb/^{208}Pb$ ($x \pm s$)
Monterey Charthouse (418.8)	18.45 ± 0.07	1.180 ± 0.004	0.4830 ± 0.0009
slag deposit (421.1)	18.33 ± 0.05	1.174 ± 0.002	0.4814 ± 0.0005
restaurant wharf (421.2)	18.38 ± 0.02	1.177 ± 0.003	0.4828 ± 0.0007
Coast Guard jetty (421.5)	18.37 ± 0.03	1.174 ± 0.004	0.4820 ± 0.0010
Holiday Inn (422.0)	18.36 ± 0.10	1.176 ± 0.005	0.4819 ± 0.0011
Bodega Head (202.0)[a]	18.65 ± 0.07	1.193 ± 0.004	0.4860 ± 0.0010
Los Angeles Harbor (616.0)[b]	18.81 ± 0.08	1.202 ± 0.007	0.4902 ± 0.0011

[a] Initial isotopic composition of transplant mussels, which were all collected from the Bodega Head control site. [b] Isotopic compositions of native mussels from Los Angeles Harbor. These were measured to establish the existence of larger geographic gradients in mussels, which appear to be consistent with the geographic gradients in seawater (*11*).

Table V. Lead Isotopic Compositions of Lead Slag, Sediments, Grandiorite, and Intertidal (Unfiltered) Seawater in Monterey Bay

location (station)	$^{206}Pb/^{204}Pb$ ($x \pm s$)	$^{206}Pb/^{207}Pb$ ($x \pm s$)	$^{206}Pb/^{208}Pb$ ($x \pm s$)
lead slag			
lead ingots	18.31 ± 0.03	1.174 ± 0.005	0.4800 ± 0.0007
ferrous fragments	18.24 ± 0.05	1.168 ± 0.009	0.4783 ± 0.0008
glassy fragments	18.18 ± 0.05	1.167 ± 0.009	0.5060 ± 0.0009
sediments			
Monterey Charthouse (418.8)	17.40 ± 0.03	1.121 ± 0.001	0.4694 ± 0.0001
slag deposit (421.1)	18.30 ± 0.03	1.173 ± 0.001	0.4811 ± 0.0002
restaurant wharf (421.2)	18.49 ± 0.03	1.184 ± 0.002	0.4843 ± 0.0001
Coast Guard jetty (421.5)	18.41 ± 0.03	1.179 ± 0.002	0.4829 ± 0.0001
grandiorite			
slag deposit (421.1)	19.71 ± 0.06	1.256 ± 0.002	0.5060 ± 0.0001
unfiltered seawater			
slag deposit (421.1)	18.26 ± 0.08	1.180 ± 0.001	0.4844 ± 0.0010
Coast Guard jetty (420)	19.85 ± 0.37	1.253 ± 0.002	0.5180 ± 0.0010

contaminated mussels and sediments. The $^{206}Pb/^{207}Pb$ ratios of grandiorite outcroppings adjacent to the slag deposit (1.256), northeast Pacific seawater (1.19–1.22), and North American industrial lead aerosols (1.22) were all significantly ($p < 0.01$, t test) higher than those of the most contaminated mussels and sediments. Simple isotopic composition mixing models indicated that no combination of those other sources could account for more than 0.5% of the lead in the most contaminated mussels or sediments.

Lead Dispersion Patterns and Uptake Mechanisms. The dispersion of contaminant lead from the slag deposit appeared to be primarily a consequence of (a) weathering processes and tidal action, which degraded the slag and suspended the fine detritus, and (b) water circulation patterns, which regulated its dispersion. This was evidenced by the gradients in lead concentrations and isotopic compositions of mussels and sediments, which demonstrated that the slag was the predominant source of contamination within the harbor. It was also indicated by the contrasting isotopic compositions of unfiltered seawater from the slag deposit ($^{206}Pb/^{207}Pb$ = 1.180), which was similar to that of the slag, and of unfiltered seawater from the other side of the Coast Guard jetty ($^{206}Pb/^{207}Pb$ = 1.250), which was similar to that of the intertidal sediments formed by the decomposition of grandiorite (Table IV).

This dispersion mechanism was substantiated by the analyses of digestive tracts of transplanted mussels at the slag deposit (Table V). As previously noted, these indicated that suspended slag detritus was being directly ingested by the filter feeders. Lead concentrations of undepurated digestive tracts of transplanted mussels at the slag deposit (108 μg/g) were higher than the whole body concentrations (21 μg/g), and the amount of lead in the digestive tracts accounted for 92% of the lead in the organisms.

Contrasting isotopic compositions of the gonads revealed different lead uptake mechanisms might be predominant in those tissues (Table III). Simple isotopic composition mixing models indicated that less than 5% of the lead in the gonads was derived from slag lead. On the basis of characteristic $^{206}Pb/^{207}Pb$ ratios, the principal sources of lead in the gonads ($^{206}Pb/^{207}Pb$ = 1.20–1.22) were North American industrial leads, which are predominant in northeast Pacific coastal waters (*3–6*, *11*). This indicated that the lead accumulated in those tissues was adsorbed from seawater, which is consistent with other lead uptake studies (*12*, *18*).

However, variations in the gonad isotopic compositions correlated with the isotopic compositions of particulate leads. Lead concentrations of gonads in mussels from the slag deposit (10.4 μg/g) and restaurant wharf (2.6 μg/g) sites were high relative to those of mussels from the Holiday Inn site (0.31 μg/g), and their isotopic compositions ($^{206}Pb/^{207}Pb$ = 1.199–1.201) were closer to that of the slag lead ($^{206}Pb/^{207}Pb$ = 1.174) than those from the other sites. Lead concentrations of gonads in mussels at the Coast Guard jetty were also relatively high (4.2 μg/g), but their isotopic composition ($^{206}Pb/^{207}Pb$ = 1.222) was closer to that of the grandiorite ($^{206}Pb/^{207}Pb$ = 1.256) than to that of the slag. While these variations might be due to the metabolic bioaccumulation of particulate lead, they might also be due to contamination during the sampling procedures. Therefore, additional isotopic composition studies would be required to resolve the cycling of lead through these organisms, as well as the bioavailability of the slag lead to higher trophic levels.

Summary

Measurements of lead isotopic compositions in Monterey Bay demonstrated their potential to identify and trace the

biogeochemical cycles of different lead inputs to the marine biosphere. They confirmed the point source origin of elevated lead concentrations in marine organisms and sediments, which was empirically indicated by lead concentration gradients. Additional isotopic composition analyses of discrete tissues and unfiltered seawater samples demonstrated that the contaminant lead was accumulated in the bivalves by the ingestion of detrital particulates from that point source. Separate isotopic composition analyses of gonads from the mussels demonstrated that the lead in those tissues was primarily derived from seawater. Therefore, differences in the biogeochemical cycles of lead both within intertidal organisms and within tissues of those organisms were revealed by the isotopic composition measurements.

This initial application of lead isotope systematics in the marine biosphere was facilitated by the presence of a relatively unusual source of contaminant lead. The exceptionally high lead concentrations of the bivalves indicated that a unique source of contaminant lead was present within the harbor. Its point source origin allowed simple linear tracer studies with both concentration gradients and isotopic composition measurements. The distinctive isotopic composition of the contaminant lead precluded the need for elaborate mixing model calculations involving other potential contaminant sources. The presence of the contaminant lead in the particulate phase limited both its dilution by other leads in the environment and its form of bioavailability to marine organisms. This facilitated concurrent identifications of other sources of lead both within the bay and within discrete tissues of the organisms.

However, the applicability of lead isotope systematics in the marine biosphere is not limited to such apparently unique environments. Studies of lead isotopic compositions in coastal waters have previously distinguished inputs of (a) industrial aerosols, surface runoff, and sewage effluent in the Southern California Bight (*4*), (b) gasoline lead aerosols and lead mine tailings in coastal waters of British Columbia (*6*), and (c) inputs of different industrial aerosols in oceanic waters of the northeast Pacific (*3*, *4*, *21–23*). Other studies of lead isotopic compositions in sediments have distinguished different industrial lead inputs to estuaries and coastal basins (*14*, *24*, *25*). Additionally, a recent study has reconstructed the historical flux of industrial leads to the surface ocean utilizing lead isotopic compositions in corals (*26*). Therefore, these analyses have numerous applications in marine environmental research.

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Registry No. ^{204}Pb, 13966-26-2; ^{206}Pb, 13966-27-3; ^{208}Pb, 13966-28-4.

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