anemic appearance of the gills of some species of Antarctic fish until the 1950s. At that time it was noticed that members of the Channichthyidae were white, as a result of which they were called 'white-blooded fish' or 'icefish'. The blood of channichthyids is devoid of hemoglobin, although small numbers of nonfunctional erythrocytes have been described in a few species.

Initial consideration was given to determine whether, because channichthyids do not possess scales, cutaneous respiration might be a major factor in oxygen uptake. However, the absorptive area and vascularization relative to the gills mitigated against that mechanism. Alternatively it was thought possible that channichthyids possessed either a more efficient oxygen utilization mechanism or else lowered oxygen requirement. This second consideration was being examined at a time when the concept of metabolic cold adaptation was under discussion.

Studies on oxygen uptake rates indicated that channichthyids utilized oxygen at a slightly lower rate as compared with equivalent red-blooded notothenioids. In the absence of hemoglobin, the oxygen-carrying capacity of channichthyid blood is only about one tenth that of red-blooded fish. Two mechanisms are possible to compensate for this effect; either channichthyid blood is circulated at a much faster rate or there is much more of it in the system. The latter has proven to be the case and channichthyid blood takes up 8–9% of the total volume of the fish (two to four times that of other

teleosts), the heart rate and blood pressure are low but the stroke volume and resultant cardiac output are large. To reduce the resistance to flow the capillaries are larger than in other teleosts.

Even though the hemoglobinless condition is clearly effective it is a feature that confines the fish to areas of high oxygen tension such as are present in Antarctic waters. Experimental studies have demonstrated that channichthyids are particularly sensitive to hypoxia, indicating that in their natural habitat the oxygen saturation is always consistently high.

See also

Antarctic Circumpolar Current. Current Systems in the Southern Ocean. Weddell Sea Circulation.

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ANTHROPOGENIC TRACE ELEMENTS IN THE OCEAN

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Introduction

Human activities have increased the fluxes of several chemical elements into the ocean above natural levels. Despite convincing evidence for this enhancement of elemental fluxes (see Further Reading section for references relevant to the discussion in this article), there is only one element – lead (Pb) – where abundant evidence proves that open-ocean seawater concentrations are substantially higher than they were in preindustrial times. For a few other elements – e.g. cadmium (Cd) and mercury (Hg) – there is some evidence suggesting a detectable anthropogenic impact (or models indicating that an anthropogenic enhancement must exist even if it has not been observed). For most other elements, the size of the oceanic reservoir of these elements overwhelms relatively large anthropogenic fluxes, and it may require centuries of further inputs before the human impact can be discerned.

Anthropogenic Lead in the Ocean

Sampling and analysis for Pb have been difficult because of low concentrations and abundant con-

tamination sources: lead paint, lead weights, and gasoline exhausts. The latter source is now substantially reduced, so perhaps the current Pb contamination problem is less serious than it was in the 1980s.

Patterson and co-workers were the first to call attention to the overwhelming anthropogenic augmentation of Pb fluxes into the environment, particularly that resulting from alkyl leaded gas utilization. Patterson's evidence began with the demonstration that Pb deposition in remote Greenland snows had increased by two orders of magnitude. In the late 1970s/early 1980s, his laboratory obtained the first valid data (uncontaminated and properly analyzed) for the vertical distribution of Pb in water sample profiles from the North Atlantic, North Pacific, and South Tropical Pacific (**Figure 1**). These data demonstrated that the highest concentrations of Pb occurred in the surface ocean and that concentrations decreased with increasing depth in the water column. At that time, the highest Pb concentrations were found in the North Atlantic Ocean (160×10^{-12} moles kg^{-1} at the surface de-

creasing to 26×10^{-12} moles kg^{-1} at 3000 m water depth). The high Pb concentrations in this basin are emitted from the major industrial nations surrounding the basin. Lower Pb concentrations were seen in North Pacific surface waters (60×10^{-12} moles kg^{-1} at the surface decreasing to 5×10^{-12} moles kg^{-1} at 3500 m depth), and the lowest concentrations in the south tropical Pacific (20×10^{-12} moles kg^{-1} at the surface decreasing to 4×10^{-12} moles kg^{-1} at 4000 m). In Patterson's view, this evidence proved the anthropogenic origin of Pb in the modern ocean.

The lead industry attempted to discredit Patterson's evidence on environmental Pb pollution by many spurious arguments. Although they were not clever enough, they might have attempted to discredit Patterson's interpretation of his oceanic Pb data by pointing out that similar comparative concentration variations occur for aluminum (Al) in the ocean, even though oceanic Al is entirely of natural origin. Al is released from terrestrial dusts blown into the ocean and 'scavenged'
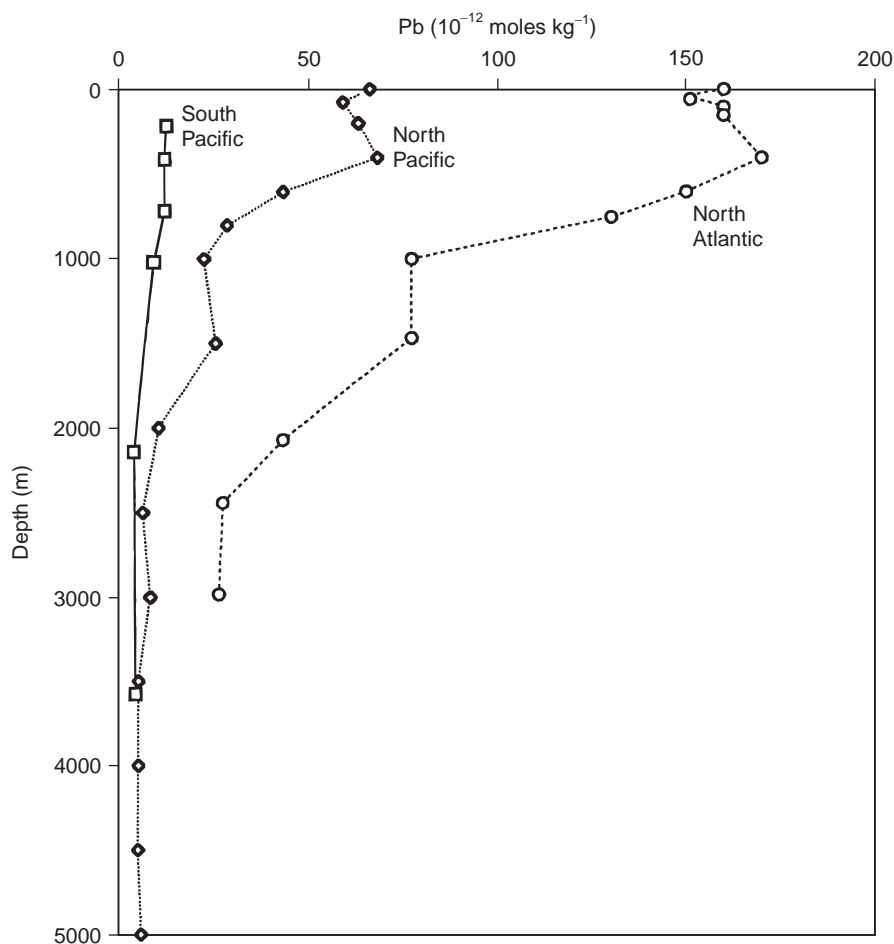

Figure 1 Oceanic Pb profiles obtained by Patterson and co-workers on samples collected between 1976 and 1981.

onto sinking biologically produced particles that remove it from the deep ocean. Therefore Al is high in the surface ocean, highest downwind of major dust sources such as north-west Africa, and lowest in the South Pacific because of low dust inputs to the surface and cumulative scavenging in the deep waters.

Lead was phased out of gasoline in the USA (followed soon by Canada and Japan, and somewhat later by western Europe and a few other countries) beginning in 1970 when the US Environmental Protection Agency mandated emissions controls on gasoline exhausts. Originally, controls on lead emissions were not the goal of the regulations; the regulations were formulated to minimize emissions of hydrocarbons, nitrogen oxides, and carbon monoxide. As it turned out, the technological fix for those problems was to use catalytic converters on the exhaust stream, and the activity of the catalysts was destroyed by lead exhausts. Hence leaded gasoline could not be used with catalytic converters, and regulations mandated the elimination of leaded gasoline. Later, regulations specifically directed at minimizing lead emissions into the environment were also enacted.

Changing leaded gasoline utilization patterns offer an opportunity to establish that Pb decreases in the ocean in response to the decreasing Pb emissions from leaded gasoline. Pb gas utilization increased from its introduction in the 1920s until the 1970s, then decreased rapidly – resulting in nearly complete elimination from the USA by 1990 and from western Europe by the turn of the century (**Figure 2**).

Surface waters of the ocean should respond within a few years to changes in fluxes from the atmosphere, and the upper layers of the ocean should respond on decadal timescales. These expectations are based upon the penetration of the nuclear bomb tritium into the ocean and natural radioisotope ^{210}Pb (half-life 22.3 years). Studies of tritium penetration show that surface waters ventilate the upper thermocline of the ocean on a timescale of several years to several decades. ^{210}Pb is supplied to the ocean from wind-blown aerosols which have acquired ^{210}Pb from the decay of the radioactive noble gas ^{222}Rn. ^{222}Rn is released into the atmosphere as a decay product of naturally occurring crystal ^{238}U which decays in several stages to the immediate parent of ^{222}Rn, ^{226}Ra. The flux of ^{210}Pb out of the atmosphere has been measured at numerous sites, therefore the flux of ^{210}Pb into the ocean can be estimated reasonably well. In the surface ocean, ^{210}Pb is rapidly scavenged from sea water by newly formed biological material whose residues eventually sink out of the surface waters carrying ^{210}Pb. The steady-state concentration of ^{210}Pb in the mixed layer of the ocean is thus determined by a balance between ^{210}Pb supply from the atmosphere and ^{210}Pb removal by sinking particles. The time constant for this process is estimated by dividing the measured surface water ^{210}Pb reservoir by the flux of ^{210}Pb from the atmosphere. The rate of removal varies with the rate of biological activity, but in typical open-ocean 'deserts' such as the Sargasso Sea, ^{210}Pb is removed from surface waters every 2 years. Thus as the flux of anthropogenic lead from the atmosphere decreases, the concentration of lead in surface waters should follow this decrease with a 2 year lag.

Decreasing concentrations of Pb in surface waters of the Atlantic Ocean have been documented by observations from 1979 until the present (**Figure 3**). The decreasing concentration of Pb in the upper layers of the ocean is also observed (**Figure 4**), with a slower response in the deeper waters that are replaced on decadal timescales. These decreases are seen in other parts of the Atlantic and North Pacific as well. This evidence amply demonstrates that the phasing out of leaded gasoline in the USA has been closely followed by decreases of the Pb concentration of the ocean on the appropriate timescale.

In the period before direct observations of Pb in the ocean, the response of oceanic Pb to earlier changes in emissions are documented by the Pb content of reef-building corals. Corals precipitate calcium carbonate skeletons with annual variations in their density that can be counted in the same way as tree rings, hence providing a chronology of the time of deposition. In corals from near Bermuda, concentrations of Pb increased from very low levels in the 1880s to higher levels in the 1920s, in pace with the emissions of Pb from high temperature industrial activities (smelting, coal combustion, etc.) (**Figure 5**). With the introduction of leaded gasoline, Pb increased far more until the mid-1970s, when coralline Pb began to decrease with the phasing out of leaded gasoline, confirming the picture provided by direct observations in this period.

Other information on the sources and dispersion of anthropogenic lead can be derived from the stable isotope ratios of lead (e.g. ^{206}Pb/^{207}Pb) which vary from one mining source to another because of differing Pb/U and Pb/Th for geological sources of lead. In particular, US leaded gasoline for many years had a ^{206}Pb/^{207}Pb ratio of > 1.20, whereas European leaded gasoline was < 1.15. Eventually anthropogenic Pb will be removed from the water column and reside in marine sediments, and there is already evidence from surficial sediments of the

North Atlantic Ocean for significant quantities of anthropogenic Pb.

Anthropogenic Mercury in the Ocean

Volatile mercury (Hg) and organomercury compounds are emitted from the land into the atmosphere naturally from wildfires, volcanoes, and microbial activity. Mercury is emitted into the atmosphere by humans as a result of high temperature processes (e.g. smelting, coal combustion, incineration) combined with commercial uses of elemental mercury (e.g. thermometers, batteries), as well as disposal of mercury-laden wastes (e.g. from gold mining operations) that are then converted into volatile forms in the environment. Estimates indicate that the anthropogenic mercury emissions from the land into the atmosphere exceeded natural sources by approximately a factor of three during the past century, not nearly so large as the Pb emission enhancement, but nonetheless substantial. A large fraction of this Hg is carried over great distances by the atmosphere and deposited into the ocean.

As for Pb, contamination is a major problem in Hg sampling and analysis (perhaps even more so), because Hg^0 is volatile and broken mercury thermometer residues exist in most chemical laboratories.

Evidence for anthropogenic perturbation of the oceanic Hg reservoir is less straightforward than it is for Pb. Observations in the modern Atlantic marine atmosphere show that the Northern Hemisphere has two- to three-fold higher Hg concentrations
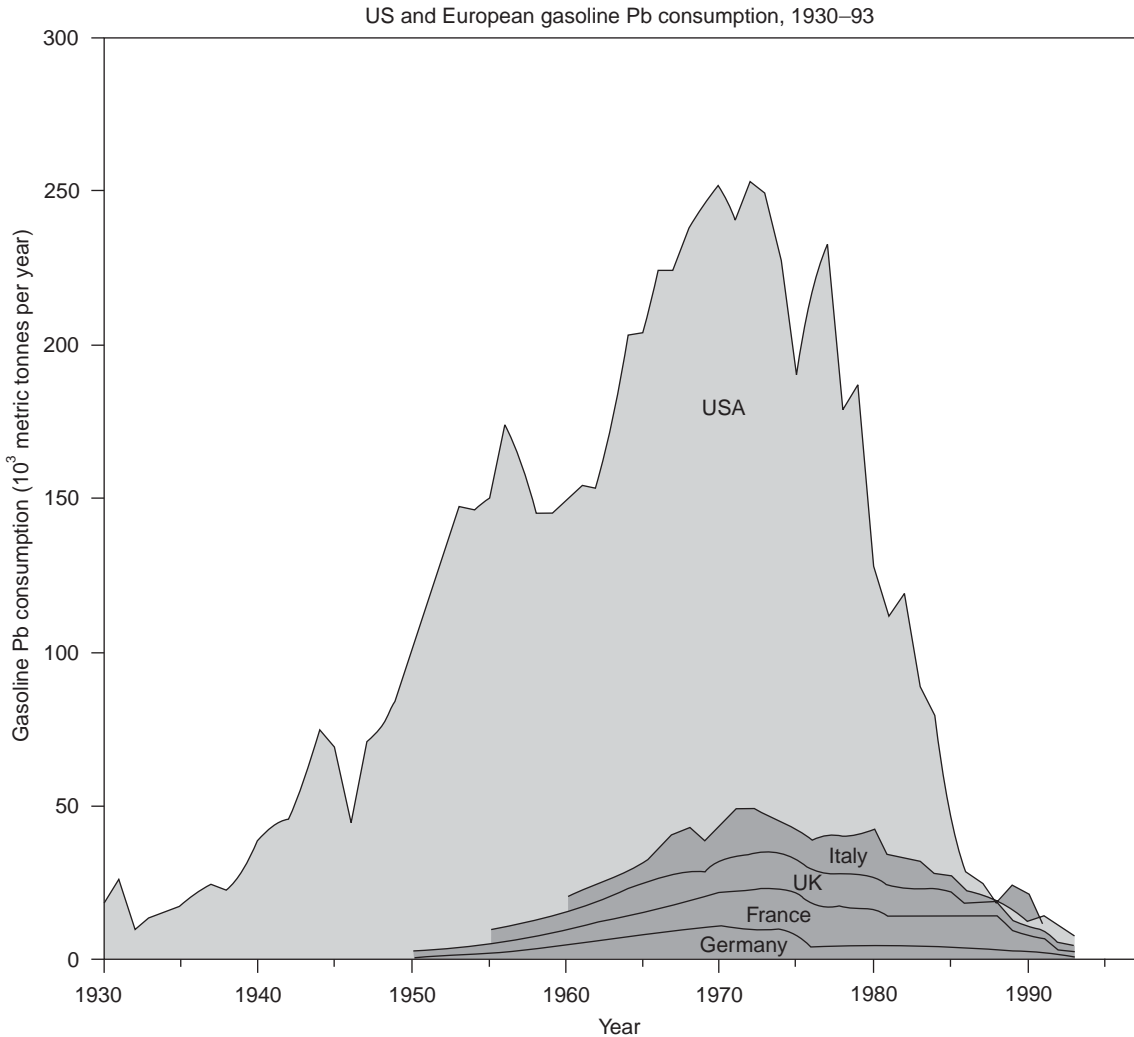

Figure 2 Alkyl Pb gas consumption, 1930–93. Four European countries (accounting for 70% of EC gasoline consumption) stacked to compare with the much higher US consumption.

than the Southern Hemisphere, as might be expected for an anthropogenic source. However, land area is also higher in the Northern Hemisphere, and it is likely that even natural emissions are higher in the Northern Hemisphere, so observation of an inter-hemisphere difference does not by itself prove anthropogenic perturbation. Measurements of Hg in sea water have attempted to determine elemental (Hg^0), organometallic (e.g. CH_3Hg, $(CH_3)_2Hg$), and 'reactive' forms (ionic and inorganically complexed Hg, organically complexed Hg, and labile organic and particulate Hg). Reported Hg concentrations range from 10^{-11} to 10^{-9} moles kg^{-1}. There are no direct seawater measurements or indirect seawater indicators such as corals which have yet documented an anthropogenic enhancement, although it has been estimated that Hg concentrations in the surface ocean have increased from 0.5 to 1.5 pmol kg^{-1} during the past century.

Other Anthropogenic Elements in the Ocean

Several other elements have had significant anthropogenic enhancements of global fluxes, but in most cases, the size of the oceanic reservoir of the elements is too large for an observable shift in open-ocean concentrations. A two- to three-fold increase in the concentration of cadmium (Cd) has been observed in corals near Bermuda during the past century. However, the concentrations of Cd in surface waters near Bermuda are low even today (certainly $< 10^{-11}$ moles kg^{-1} and sometimes as low as 10^{-12} moles kg^{-1}; because concentrations in deep waters are two or three orders of magnitude higher, the oceanic reservoir is large compared with the anthropogenic enhancement of Cd in surface waters. Although concentrations of Zn in corals were not measured, a similar anthropogenic enhancement of emissions to the atmosphere may well have caused slight enhancements to the Zn concentrations of the surface ocean, but evidence of such an increase has not been reported.

Because of the use of tributyl tin as a stabilizer in PVC plastic (hence an incineration source for inorganic Sn) and as an antifouling agent in marine paints, there has been some interest in the fate of anthropogenic Sn in the oceanic environment. Inorganic Sn is very low in the surface waters of the Sargasso Sea ($\sim 3 \times 10^{-12}$ moles kg^{-1}). Tributyl tin
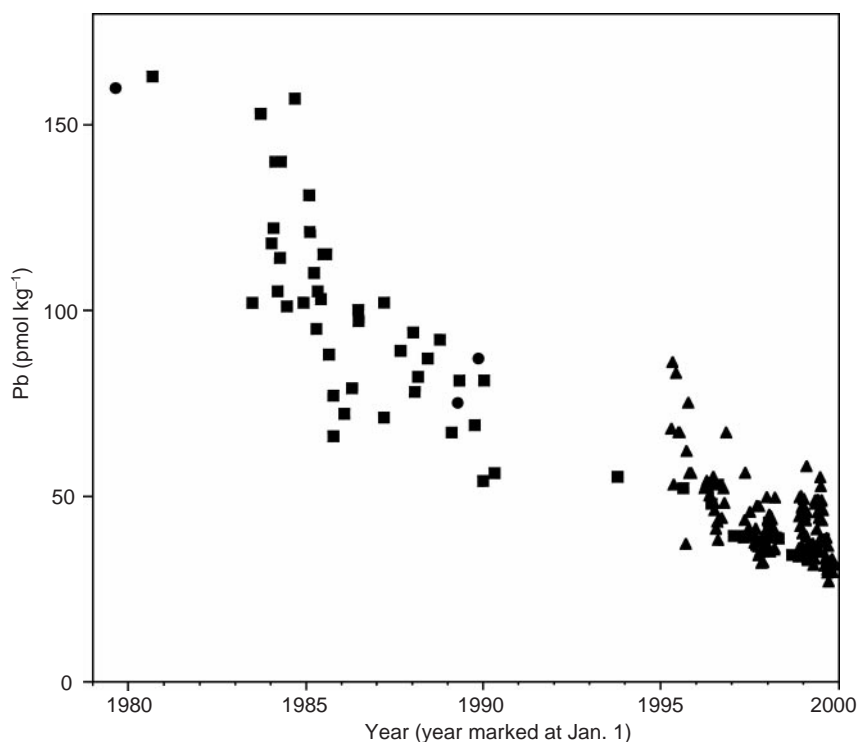

Figure 3 Pb in Bermuda surface waters, 1979–99. Squares (near surface waters) and triangles (40–50 m depth) are samples collected and analyzed by the MIT group (see Wu and Boyle 1997 for data through 1996; 1997–2000 from Boyle *et al.*, unpublished); circular symbols are samples collected and analyzed by Schaule and Patterson (1981) and Veron *et al.*, (1993).
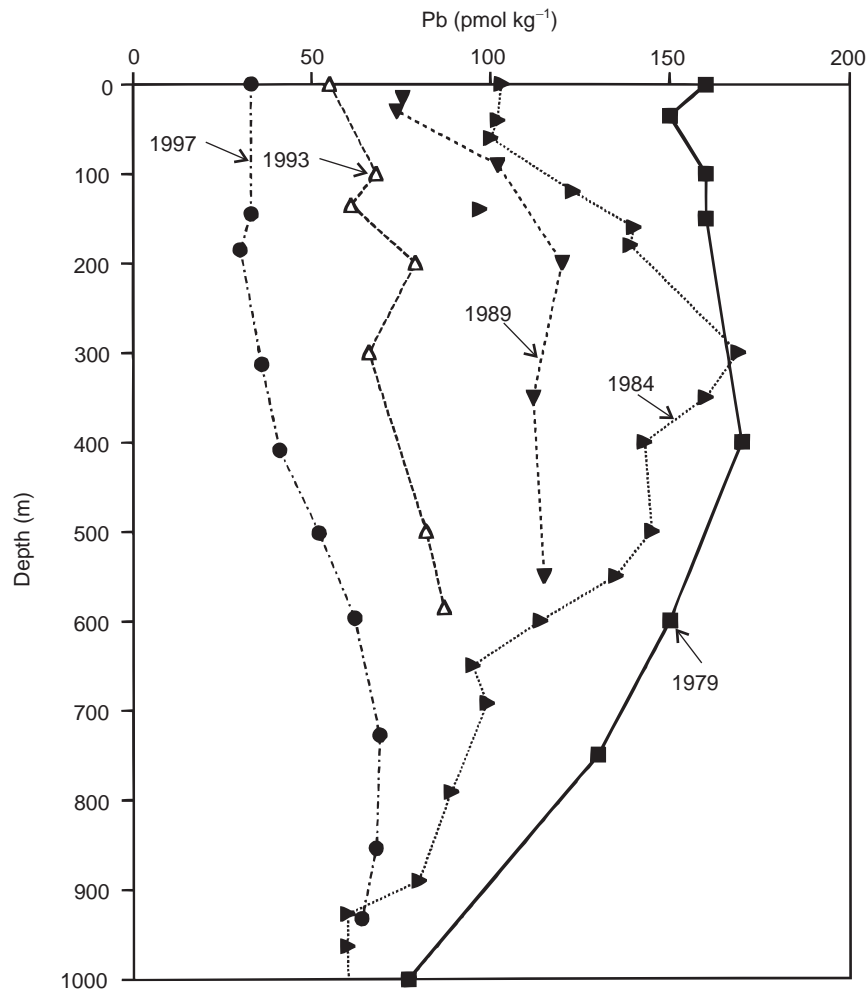
Figure 4   Pb in ocean profiles in the Sargasso Sea near Bermuda: 1979 data from Schaule and Patterson (1983); 1984 data from Boyle *et al.* (1986); data from Veron *et al.* (1993); 1993 data from Wu and Boyle (1997); 1997 data (Wu and Boyle, unpublished).

has been observed in enclosed harbors, but not in the open ocean.

On the whole, however, the size of the ocean precludes major enhancements of oceanic trace metal concentrations. Even where the enhancement is clear, such as for Pb, the concentrations are quite low and there is no reason to suppose that these enhancements pose a threat to marine biota.

Anthropogenic Trace Metal Enhancements in Coastal Waters and Embayments

As opposed to minimal evidence for anthropogenic trace metal contamination of open-ocean waters, it is clear that major impacts on the trace metal chemistry of coastal sea water have occurred and that these have sometimes had serious consequences.

The discharge of untreated industrial and human wastes into coastal waters, and the release of toxic metals and metal compounds from antifouling paints have clearly increased metal concentrations in shallow ocean waters in many coastal regions.

One of the most notorious examples of coastal pollution was in Minimata Bay, Japan where from the 1930s until the 1960s a chemical company dumped tonnes of mercury, which contaminated the bay sediments. This Hg pollution entered the marine food chain. Thousands of people developed severe neurological symptoms as a result of eating Hg-contaminated fish. This is perhaps the most extreme example where pollution in the marine environment has demonstrably harmed humans directly.

More recently, it has been demonstrated that high Cd, Zn, Cu, and Pb concentrations in Atlantic coastal waters of southern Spain have risen by many
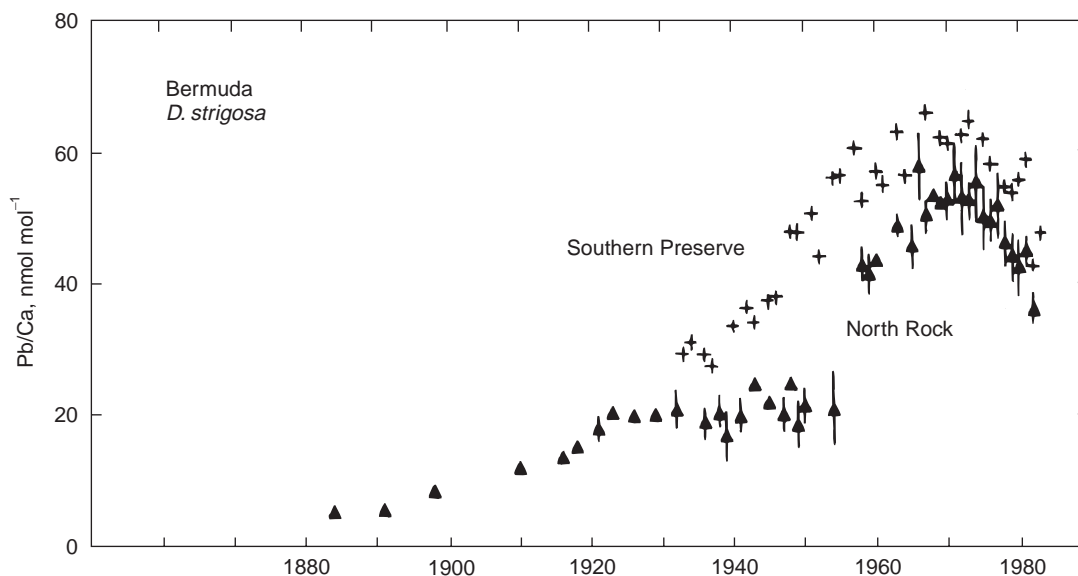
Figure 5 Pb in corals near Bermuda in annually laminated layers deposited between 1880 and 1997 (Shen and Boyle, 1987).

orders of magnitude due to acid mine drainage from the Rio Tinto massive sulfides. As yet, little is known about any human health effects from this trace element pollution, although the region has an active coastal fishing industry.

There is too much detail in the many local examples to discuss here, but there is little doubt that many coastal embayments proximate to big cities have elevated metal levels, and that an understanding of the consequences of this pollution is still being developed. Unfortunately, proper measurement capabilities did not exist until the past two decades, so there is usually no direct evidence for the degree of enhancement of dissolved metals relative to preindustrial times. One exception to this situation is in San Francisco Bay, where the anthropogenic enhancement of dissolved cadmium has been documented by measuring the Cd content of benthic foraminifera.

An anthropogenic impact on metals in coastal marine sediments has been demonstrated repeatedly. Lead has been shown to be enriched in coastal sediments. Even more exotic elements such as silver (photography) and osmium (electron microscopy) are enriched in the sewage of some cities and can be traced from their source.

Conclusions

The anthropogenic dominance of lead in the open-ocean environment has been conclusively demon-strated. Although there is evidence that the fluxes of other elements to the ocean have been enhanced to a significant degree, there is less direct evidence documenting their enhancements in the open-ocean environment. Coastal waters and sediments near major cities show large enhancements in several trace metals.

See also

Metal Pollution. Radioactive Wastes. Refractory Metals. Transition Metals and Heavy Metal Speciation.

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