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Anthropogenic Lead Emissions in the Ocean

The Evolving Global Experiment

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Boyle group at sea deploying the "weather-vaning" trace element sampler.

ABSTRACT. We review the current distribution of lead and lead isotopes in the ocean with regard to the evolving pattern of human emissions during the past decades and centuries.

INTRODUCTION

Humans have increased the flux of reactive lead (Pb) into Earth's surface environment by more than a factor of 10, as Caltech lead-research pioneer Clair Patterson, co-workers, and associates pointed out in several cutting-edge publications (e.g., Murozumi et al., 1969; Shirahata et al., 1980; Schaule and Patterson, 1981; Flegal and Patterson, 1983). As such, this activity is, in the spirit of Roger Revelle's words, one of the great "large scale geophysical experiments" whereby the human race alters the global environment and waits to observe the consequences (Revelle and Suess, 1957). Fortunately for the marine environment, lead emissions have not been high enough to cause harmful consequences in the open ocean. However, human and continental ecosystem health suffers the negative consequences of Pb emissions from a variety of sources that include lead-soldered cans; drinking water from Pb-contaminated plumbing; lead components of paint on houses and other structures; paint scrapings and leaded gasoline consumption that contaminates soils, including playgrounds and agricultural areas; and acute impacts from smelting, metal refining, and acid mine drainage (Nriagu and Pacyna, 1988). Studies of the fate of Pb in the open-ocean environment can be used to study ocean metal transport and reactivity, just as harmless ocean fluorocarbons are used to trace and quantify ocean physical transport. Studies of the evolution of the anthropogenic Pb transient in the ocean can also serve as an analogue

for other anthropogenic pollutants.

Pb is a volatile element at high temperatures; it can be emitted as an atomic vapor when Pb-containing materials are heated to these temperatures. Pb is also emitted as reactive PbBrCl compounds upon the combustion of leaded gasoline. At low temperatures, Pb is not stable as a gas, and Pb atoms attach to the surfaces of, or react chemically with, fine atmospheric aerosol particles (Cziczo et al., 2009). These particles are dispersed by the global atmospheric transport system and can travel to remote regions of Earth before they are deposited on land or the ocean surface (Reuer and Weiss, 2002). The residence time of atmospheric particles is short. Studies of the natural radioisotope ^{210}Pb (Bacon et al., 1976; Nozaki et al., 1976) show that the residence time of Pb in the low-productivity waters of the central ocean gyres is about two years. Thus, surface water Pb concentrations tend toward a steady state with atmospheric deposition fluxes during the previous few years, and Pb concentrations in surface waters tend to follow recent deposition rates of contaminated atmospheric aerosols.

Patterns of lead production and utilization have been changing during the past two centuries, particularly for leaded gasoline consumption (Figure 1). As a result, we expect to see large temporal changes in Pb distribution in the ocean as anthropogenic sources wax and wane and ocean circulation carries lead far from its deposition site.

Pb AND Pb ISOTOPE SPATIAL AND TEMPORAL VARIABILITY

During the last 10 years, the authors of this study have obtained Pb concentration and isotope ratio data from high-quality samples from almost all of the major ocean basins (North and South Atlantic, North and South Pacific, and Indian Ocean, including the Southern Ocean), with the exception of the Arctic Ocean. Most of these data are yet to be published. Although we will include a nod to recent literature, in the following discussion, any unreferenced data are from our yet-to-be-published work, and published work from our labs or others will be cited specifically. We will briefly summarize this work, showing that the impact of evolving anthropogenic Pb emissions on time scales of years through centuries can be seen in the Pb and Pb isotope composition of the marine environment, either directly in seawater measurements or through the use of archive proxies that reflect past Pb changes in the ocean. As a result of the pervasive nature of Pb contamination during sampling and analysis and the very low concentrations (sub-nanomolar) occurring in the ocean, there were no successful measurements of Pb in seawater prior to 1976 (Schaule and Patterson, 1981). So, it is only in the past four decades that we have direct observations on the evolution of anthropogenic Pb in the ocean. This period has seen reductions in Pb emissions in some regions (Japan, North America, and Europe) and rising Pb emissions in other regions (e.g., Southeast Asia). But, the history of significant environmental lead pollution extends throughout at least the past 200 years, and studies of Pb in annually banded corals (e.g., Kelly et al., 2009) and laminated sediments (e.g., Lima et al., 2005) help provide century-scale perspective to three decades of seawater data. Our MIT lab has strived to develop highly efficient methods for the analysis of seawater Pb concentrations (Lee et al., 2011) and Pb isotope ratios (Reuer et al., 2003; Boyle et al., 2012) in small samples.

The North Atlantic Ocean was the region most heavily impacted by early industrializing economies, and

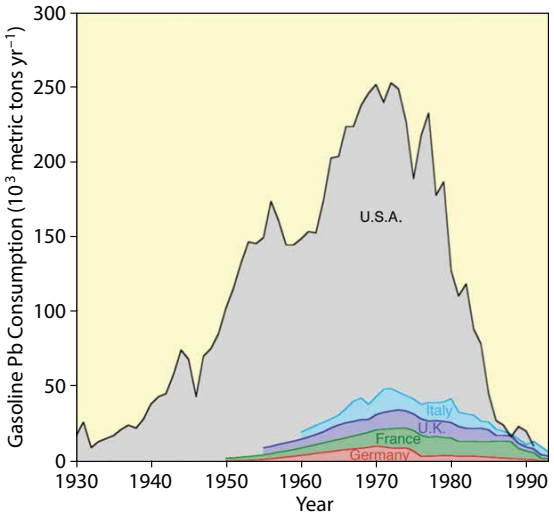

Figure 1. Gasoline lead consumption in the USA, Germany, France, United Kingdom, and Italy from 1930 through 1993. Note that the four European countries plotted account for ~ 70% of Western Europe gasoline consumption.

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there are far more studies of Pb in the North Atlantic Ocean than elsewhere. Beginning with the work of Schaule and Patterson (1983, on samples collected in 1979) through many other studies (Boyle et al., 1986; Shen and Boyle, 1987, 1988; Helmers et al., 1990, 1991; Helmers and van der Loeff, 1993; Veron et al., 1993, 1994, 1999; Hamelin et al., 1997; Wu and Boyle, 1997; Alleman et al., 1999; Weiss et al. 2003; Desfenant et al., 2006), we have significant information on the spatial and temporal variability of Pb in this ocean basin. Combining surface seawater observations near Bermuda with annually banded coral data, the century-scale temporal variability of Pb in the surface waters of the western North Atlantic can be seen in the data of Kelly et al. (2009) (Figure 2). This work combines data from three corals from the North Rock reef northeast of Bermuda island with annually averaged seawater data from near Bermuda from 1979–2000 (Hydrostation S, Bermuda Atlantic Time Series [BATS], and Bermuda Testbed Mooring, [BTM]).

Combined with data from another coral from the Southern Preserve, close to shore southeast of Bermuda island (see map in Kelly et al., 2009, data not shown here), we can describe Pb evolution in the western North Atlantic surface waters. Pb in surface waters began to rise from about 10 pmol kg^{-1} at the beginning of the nineteenth century with the development of the US Upper Mississippi Valley lead district in the mid-1800s (Heyl et al., 1959) and the US industrial revolution, reaching a plateau of about 80 pmol kg^{-1} in the 1920s. Seawater Pb concentrations began to soar in the late 1940s (Figure 2) with the end of World War II, rising US prosperity ("two cars in every garage" that ran on leaded gasoline), and, eventually, European prosperity. Bermuda surface ocean lead levels peaked at more than 200 pmol kg^{-1} in the 1970s. The US Clean Air Act of 1970 mandated catalytic converters to reduce atmospheric pollution, which required removal of tetraethyl Pb from gasoline because it poisoned the catalysts (Nriagu, 1989). Since then, western North Atlantic Pb concentrations have fallen continuously (Figure 2), with the lowest surface water Pb concentrations observed so far (17 pmol kg^{-1}) seen during the US GEOTRACES North Atlantic Transect cruise in November 2011 (recent work of authors Noble and Boyle).

There is some spatial coverage of surface water Pb concentrations in the Atlantic Ocean. For example, during the period from 1986–1993 (Figure 3), the highest surface Pb concentrations during the past three decades occur in the subtropical gyre, downwind of both US and some European emissions. The atmosphere and North Atlantic Drift current carry that Pb northward where it is driven by wind (Ekman) pumping into the thermocline and winter cooling driving dense deepwater formation during winter. South of the subtropical/tropical boundary (~ 20°N), Pb concentrations in the 1989–1995 period rapidly decrease to less than 20 pmol kg^{-1} and occur at similar low levels all the way into the South Atlantic (e.g., Helmers and van der Loeff, 1993). Though not shown in Figure 3, there is an unusual peak in Pb concentration that occurs in the Atlantic coastal waters of southern Spain, where acid mine drainage from the Rio Tinto and Rio Odiel deliver water with Pb concentrations a million times more than measured in Atlantic surface waters (e.g., see van Geen et al., 1997). These high Pb levels flow into the Mediterranean Sea in the northern branch of the Gibraltar inflow (recent

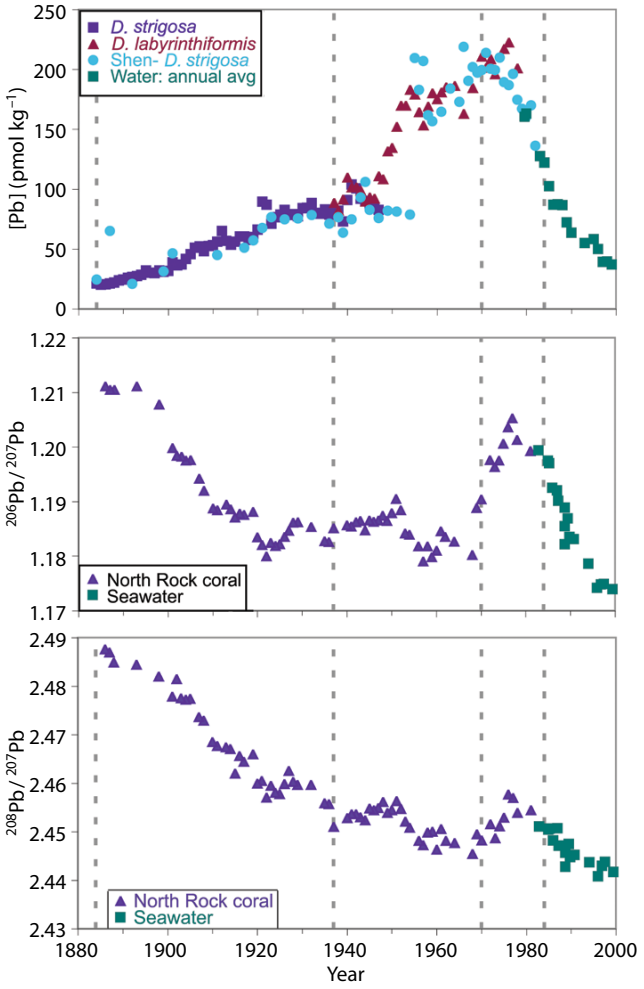

Figure 2. Pb concentration and isotopic composition of Bermuda surface waters for the past 120 years (Kelly et al., 2009). Squares (1979–2000) represent annual averages of data from water samples. The other data are from three different coral cores, with Pb concentrations estimated from coral Pb/Ca converted by a partition coefficient as described by Kelly et al. (2009).

work of author Moos and author Boyle's lab). Mediterranean surface water data from the 1980s shows very high values, up to 500 pmol kg^{-1}, and in 1982 the values from the deep Mediterranean that contribute to the Mediterranean Outflow at Gibraltar are ~ 250 pmol kg^{-1} (recent work of author Moos and colleagues).

Thermocline ventilation and deep-water formation bring surface waters into the ocean's interior. In the North Atlantic, thermocline ventilation occurs on time scales of years in the uppermost ocean to perhaps a century at 1,000 m (Jenkins, 1998). Near Bermuda, Pb profiles have been collected at roughly five-year intervals during the past 30 years (Figure 4). Waters that sank decades ago when surface Pb concentrations were an order of magnitude higher are found at mid-depths, with a maximum occurring at ~ 400 m depth in 1979, deepening to 1–2 km in 2011. In addition to purely surface boundary/advective-driven changes, it is likely that a component of the decrease in water column Pb is driven by scavenging onto sinking particles. The GEOTRACES program has obtained detailed sections of Pb in the Atlantic (GEOTRACES tracks GA02, GA03, and GA10; see map at http://www.bodc.ac.uk/geotraces/cruises/section_maps/atlantic_ocean). A Pb maximum of > 60 pmol kg^{-1} is seen at ~ 1,000 m in the eastern North Atlantic in chlorofluorocarbon (CFC)-containing waters.

US gasoline dominantly used tetraethyl lead from the Ethyl Corporation that mainly relied on US Pb sources (with a $^{206}Pb/^{207}Pb$ ratio typically > 1.17), whereas Europe dominantly used tetraethyl Pb from Associated Octel Ltd. that derived from Australian, Swedish, and Moroccan sources (with a $^{206}Pb/^{207}Pb$ ratio typically < 1.15; see Grousset et al., 1994). The Pb isotope ratio of North Atlantic surface waters reflects the relative mixture of US and European sources, depending on total emissions, atmospheric wind patterns, and proximity. Westerlies dominate mid-latitude winds, and the United States used several times more Pb than Europe (Figure 1); hence, for a long time, high US $^{206}Pb/^{207}Pb$ ratios dominated the North Atlantic (Weiss et al., 2003). But, as the United States phased

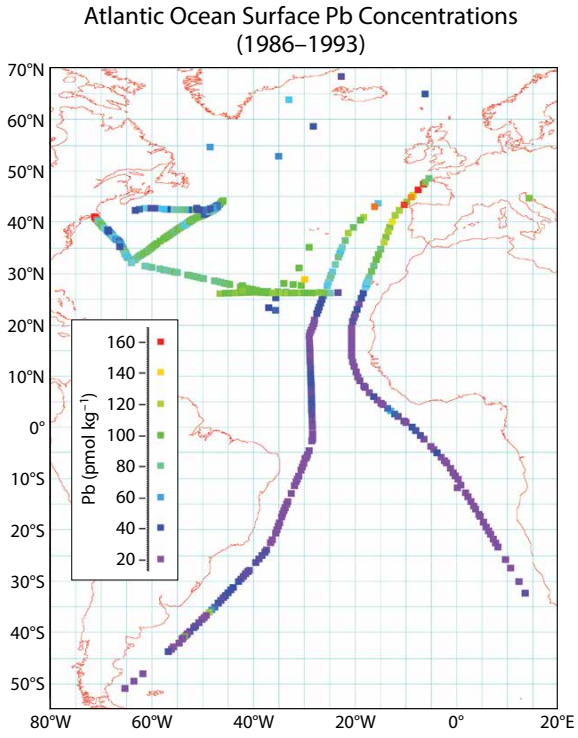

Figure 3. Pb data from the surface Atlantic Ocean from samples collected between 1986 and 1993. "Hot" colors are high Pb concentration and "cool" colors are low Pb concentration. The two long north-south data tracks are from Helmers and van der Loeff (1993). Northernmost data (> 50°N) are from Veron et al. (1999). The rest of the data are yet-to-be-published Massachusetts Institute of Technology (MIT) data from cruises in which the authors have participated.

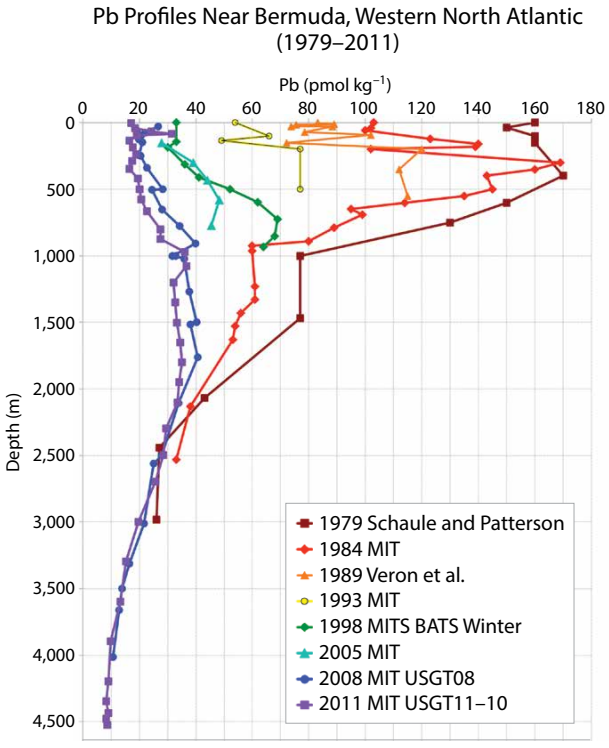

Figure 4. Pb concentration data from profiles collected near Bermuda, 1979–2011. Data are from the MIT lab, except for 1979 data from Schaule and Patterson (1983) and 1989 data from Veron et al. (1993). USGT refers to US GEOTRACES cruises. Key to data sources: 1979 Schaule and Patterson = Schaule and Patterson (1983). 1984 MIT = Shen and Boyle (1987). 1989 Veron et al. = Veron et al. (1993). Other profiles up to 2008: Lee et al. (2011). MIT USGT11-10 = recent work of author Noble and colleagues.

out leaded gasoline faster than Europe (with a crossover in total Pb gas utilization in the early 1990s), the $^{206}Pb/^{207}Pb$ ratio decreased in North Atlantic surface waters (Figure 2), and this lead reduction influenced the upper ocean through thermocline ventilation (Figure 5).

Other factors affected surface Atlantic Pb isotope composition in previous decades. In 1973, a fire in the baghouse (dust-filtering system) at the Bunker Hill Pb smelter in Idaho, which produced 25–30% of US lead the time, resulted in particulate emissions that contaminated the city of Kellogg, Idaho, and nearby communities with 1,000 tons of Pb and other toxic elements during a one-year period (Landrigan and Baker, 1981; Miller, 2000). The smelter shut down and became a US Environmental Protection Agency Superfund site. This Idaho smelter Pb had a lower $^{206}Pb/^{207}Pb$ ratio (~ 1.15) than other US Pb sources (mainly Mississippi Valley), so the Pb isotope ratio of lead and leaded gasoline increased in the mid-1970s after the smelter was shut down. The consequence for rising Pb isotope ratios in US emissions is clearly illustrated in coral data (Figure 2). Another major influence on the Pb isotope record was the dominance of Upper Mississippi Valley lead in the middle of the nineteenth century. This deposit was easily worked and close to major water transport networks, so it was the all-but-exclusive source of Pb in the United States at that time (Lima et al., 2005). The smelting procedure (open charcoal fires) was rudimentary, with no emission controls. The emissions were transported downwind, and the influence of this Pb can be seen in sediments of the Great Lakes (Graney et al., 1995), Chesapeake Bay (Marcantonio et al., 2002), and offshore Rhode Island (Lima et al., 2005), as well as in sediments from Canadian lakes in Quebec (Gobeil et al., 2013). This source of Pb has an unusual Pb isotope composition ($^{206}Pb/^{207}Pb$ ~ 1.33 and $^{208}Pb/^{207}Pb$ ~ 2.51), so its influence also can be seen in Bermuda coral records (Kelly et al., 2009). Its dominance as the US Pb source diminished in the latter nineteenth and early twentieth centuries, leading to decreasing $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios into the early decades of the twentieth century.

As a result of the evolving Pb isotope ratio of North Atlantic lead, some periods exhibit a unique Pb isotope ratio. For example, the Bermuda surface water $^{206}Pb/^{207}Pb$ ratio was ~ 1.19 and the $^{208}Pb/^{207}Pb$ ratio was ~ 2.46 in the 1920s, which is the only time in the past 150 years where these ratios co-occurred. Hence, we have been able to identify lead that sank from the surface of the North Atlantic Ocean in the 1920s in deep eastern Atlantic Ocean waters and in deep western South Atlantic waters near Rio de Janeiro.

There are fewer data on Pb in the North Pacific Ocean than in the North Atlantic, although it is still more data than is available elsewhere in the world. Schaule and Patterson (1981) obtained the first valid oceanic Pb data on samples collected in 1976. They observed Pb concentrations in surface samples near Hawaii of ~ 65 pmol kg^{-1}. By the late 1990s, Pb concentrations near Hawaii had declined by a factor of two (Boyle et al., 2005). But the situation in the Pacific is not as simple as in the North Atlantic, where Pb emissions have been declining steadily for decades in almost all of the surrounding countries. Pb emissions by China and Southeast Asian countries have been increasing (dominantly derived from coal combustion, because Pb gasoline has not been used in China for the past 15 years; Flegal et al., 2013). Although there is scant older data for comparison, Pb concentrations in the surface waters of the western North Pacific are quite high compared to those in the east (Gallon et al., 2011). To the extent that data are available in deep profiles from the North Pacific, any change in Pb concentration in the central North Pacific appears confined to the upper few hundred meters (Boyle et al., 2005, and confirming observations from SAFe and

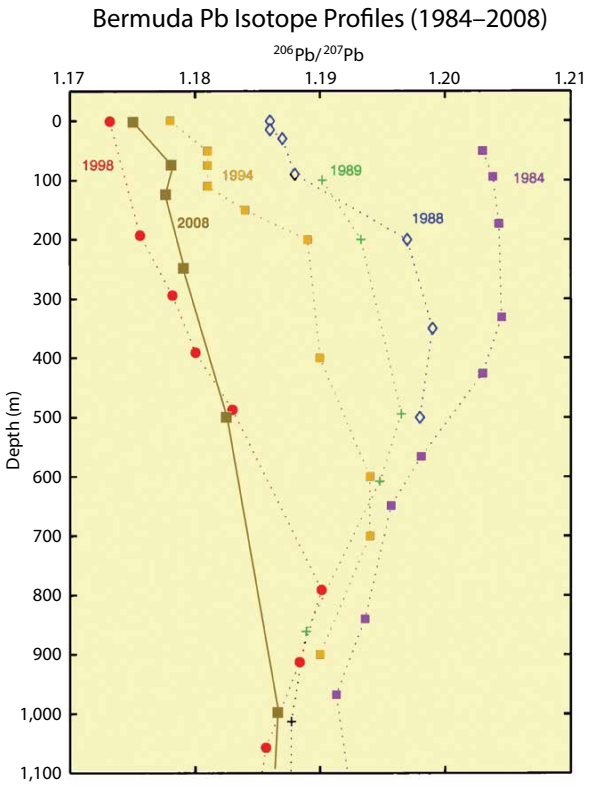

Figure 5. Pb isotope data from the upper 1,100 m from profiles near Bermuda, 1984–2008. Data from 1984 are from Shen and Boyle (1988), 1988 data from Sherrell et al. (1992), 1989 data from Veron et al. (1993), 1998 data from Reuer (2002) and Reuer et al. (2003), and 2008 data from Boyle et al. (2012).

GEOTRACES data in the eastern North Pacific [Wu et al., 2010; Ken Bruland, UC Santa Cruz, *pers. comm*., 2009, 2010; recent work of author Boyle's lab]).

Data from the South Pacific Ocean are sparse; the only published data available are from the equatorial zone of the western South Pacific (Flegal and Patterson, 1983; Wu et al., 2010), and author Boyle's MIT laboratory has two yet-to-be-published profiles from the tropical southeastern Pacific. These profiles show Pb concentrations of 13–23 pmol kg^{-1} in the surface waters, decreasing to ~ 4 pmol kg^{-1} in the deep waters.

Pb concentrations from samples obtained during the 2009–2010 Japanese Indian Ocean GEOTRACES expedition and analyzed at MIT (International GEOTRACES track GI 04) show that the northern and central Indian Ocean now have higher surface Pb concentrations (40-80 pmol kg^{-1}) than the North Atlantic near Bermuda and the North Pacific near Hawaii. This is a result of the spurt of economic growth and industrialization in this region, as well as a late phasing out of leaded gasoline compared to other parts of the world. The deep northern Indian Ocean has possibly the lowest seawater Pb concentration ever observed, 2 pmol kg^{-1}. This is probably the combined result of century-scale age (relative to the surface), plus scavenging of Pb along the flow path. Interestingly, there is a near-constant offset of the Pb isotope ratios throughout the water columns between the Bay of Bengal and Arabian Sea, even though the concentrations are the same. Because the deep waters of both basins have similar ultimate origins in the Southern Ocean, some process along the way must change the isotopic composition without altering the Pb concentration. This is a novel observation that needs further study.

In the nearby Persian Gulf, seawater Pb concentrations range from ~ 100 pmol kg^{-1} near a major city to 30 pmol kg^{-1} elsewhere. Peak and phaseout of anthropogenic Pb in recent decades is observed in coral core records (recent work of author Zhao and colleagues).

Pb concentrations in the Indian Ocean sector of the Southern Ocean are relatively uniform and low, 5–12 pmol kg^{-1}. The Pb isotope ratio of the deep Southern Ocean profile is $^{206}Pb/^{207}Pb$ 1.18–1.19, suggesting that a significant fraction of the Pb may be of natural crustal origin (~ 1.20, because anthropogenic Pb aerosols in the Southern Hemisphere are $^{206}Pb/^{207}Pb$ ~ 1.16 or lower; Bollhöfer and Rosman, 2000).

CONCLUSIONS

Human emissions of Pb into the atmosphere have altered the Pb concentration and isotope composition of a large fraction of the ocean. Pb levels in surface waters have been changing in line with regional emissions, with North Atlantic Pb levels increasing from ~1830 to ~1975 and decreasing since then. Pb concentrations in the Atlantic thermocline reflect the decreasing surface water concentrations of the ventilating waters. Pb has decreased near Hawaii, but increased emissions from China paint a different story in the western Pacific. Recent economic development and a late phaseout of leaded gasoline in India, Indonesia, China, and some other southern Asian countries have led to relatively high concentrations in the northern and central Indian Ocean. The isotope composition of deep Antarctic waters in the Indian sector may indicate a significant contribution of natural crustal Pb in addition to recent anthropogenic sources.

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