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Recent distribution of lead in the Indian Ocean reflects the impact of regional emissions

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Humans have injected lead (Pb) massively into the earth surface environment in a temporally and spatially evolving pattern. A significant fraction is transported by the atmosphere into the surface ocean where we can observe its transport by ocean currents and sinking particles. This study of the Indian Ocean documents high Pb concentrations in the northern and tropical surface waters and extremely low Pb levels in the deep water. North of 20°S, dissolved Pb concentrations decrease from 42 to 82 pmol/kg in surface waters to 1.5–3.3 pmol/kg in deep waters. South of 20°S, surface water Pb concentrations decrease from 21 pmol/kg at 31°S to 7 pmol/kg at 62°S. This surface Pb concentration gradient reflects a southward decrease in anthropogenic Pb emissions. The upper waters of the north and central Indian Ocean have high Pb concentrations resulting from recent regional rapid industrialization and a late phase-out of leaded gasoline, and these concentrations are now higher than currently seen in the central North Pacific and North Atlantic oceans. The Antarctic sector of the Indian Ocean shows very low concentrations due to limited regional anthropogenic Pb emissions, high scavenging rates, and rapid vertical mixing, but Pb still occurs at higher levels than would have existed centuries ago. Penetration of Pb into the northern and central Indian Ocean thermocline waters is minimized by limited ventilation. Pb concentrations in the deep Indian Ocean are comparable to the other oceans at the same latitude, and deep waters of the central Indian Ocean match the lowest observed oceanic Pb concentrations.

Indian Ocean | Pb content | anthropogenic emissions | GEOTRACES | lead

Although naturally occurring at trace levels throughout the environment, lead (Pb) in the modern ocean is dominated by anthropogenic sources (from leaded gasoline and high-temperature industrial activities). As such, it represents one of the great “global geophysical experiments” performed on the earth, comparable to fossil fuel CO₂, nuclear bomb fallout, and atmospheric trace gases: thus we have massively injected Pb into the surface ocean in a time- and space-dependent pattern, and we can now observe where and when it has gone. Although Pb concentrations in the open ocean are low and are not hazardous to marine life or humans, oceanic Pb illustrates the evolving extent of the human footprint upon the natural environment. The first valid oceanic Pb data were obtained for samples collected in 1976–1977 (1), and subsequently, there have been numerous studies documenting concentrations and isotope ratios of Pb in seawater (2–7). Most of these studies report data from the North Atlantic and North Pacific oceans. There has only been very limited information from elsewhere in the ocean, with almost no useful data from the entire Indian Ocean. Indian Ocean Pb data are crucial to understanding the impact of anthropogenic Pb on the global-scale environment because (i) large-scale economic development in recent decades and limited environmental regulation results in very high fluxes of Pb from the South Asian subcontinent into the Indian Ocean (8) and (ii) southern Asia and Oceania eliminated leaded gasoline later than other industrial

countries. Hence the flux of lead to the northern and central Indian Ocean during the past 20 y is likely to have been higher than elsewhere in the world. Here we present Pb concentration data from a Japanese GEOTRACES cruise in a north–south transect throughout the Indian Ocean that demonstrate that the surface of the Indian Ocean has higher Pb concentrations than representative sites in the North Atlantic and North Pacific oceans, despite very low concentrations in old deep waters with Southern Ocean sources.

GEOTRACES is an international program directed at understanding the global-scale distribution of trace elements and their isotopes in the marine environment (9). Here we show data from 11 stations from the 2009–2010 Japanese GEOTRACES transect in the Indian Ocean between 18°N and 65°S (Fig. 1). To our knowledge, this is the first study of Pb in the Indian Ocean with a detection limit capable of documenting the extremely low levels in the deep water of this basin that defines and refines the significance of the global Pb distribution.

Results and Discussion

Surface water Pb concentrations in the northern and central Indian Ocean (53–82 pmol/kg north of 20°S, Fig. 2) are now higher than in the central North Atlantic and North Pacific oceans near Bermuda and Hawaii (10, 11). Given no northern deep water formation and limited upper water ventilation, anthropogenic Pb in the Indian Ocean has not penetrated as deeply as in the Atlantic Ocean, where those waters influenced by anthropogenic emissions are carried to the north, cool and become dense in the winter, then circulate to the south at depth moving into the South Atlantic and Antarctic. In contrast, in the Indian Ocean there is insignificant cooling and limited transport of

Significance

Humans have altered the earth surface environment by massive injection of certain chemicals into our air and water. In some cases these injections are detrimental to environmental health and must be monitored to limit the damage (e.g., freons and the ozone layer); in other cases (e.g., freon dissolving into the ocean) there are no harmful consequences, but the chemicals are useful as tracers of ocean circulation patterns. Lead remains a major hazard when it is proximate to humans (e.g., plumbing, housepaint, and contaminated soils); in the open ocean, lead serves as an inadvertent experiment demonstrating how metals move through the marine environment. To our knowledge, this study is the first to examine the fate of human-injected lead in the Indian Ocean.

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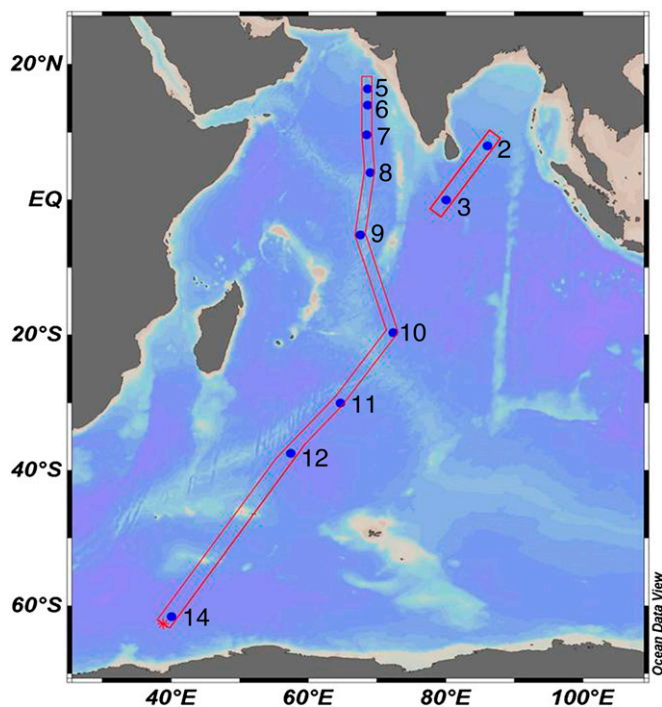


Fig. 1. Map showing station positions and indicating section segments.

northern waters to the south. In the northern Indian Ocean, both thermocline and intermediate water chlorofluorocarbon (CFC) concentrations are relatively lower, and CFC ages are older in the Bay of Bengal than in the Arabian Sea (12). In the upper waters, at a given density, CFC-derived ages increase and concentrations decrease from the south to north, with the lowest concentrations and oldest ages in the Bay of Bengal (13).

Dissolved Pb concentrations along the north-south transect exhibit strong vertical and horizontal gradients (Fig. 2). North of 20°S, dissolved Pb concentrations decrease from 42 to 82 pmol/kg in surface waters (with the highest concentration seen at 10°N in the Arabian Sea) to extremely low concentrations of 1.5–3.3 pmol/kg in deep waters. South of 20°S, surface water Pb concentrations further decrease from 21 pmol/kg at 31°S to 7 pmol/kg at 62°S. This surface Pb concentration gradient reflects a southward decrease in anthropogenic Pb emissions that are carried by atmospheric aerosols and deposited into the sea surface.

The southwest and northeast monsoons over the northern Indian Ocean drive strongly directional winds with a dominant period in wind stress variability of one year (14). For oligotrophic open-ocean upper waters the residence time of lead is around 2 y (15–20). Hence Pb concentrations that we observe for surface waters of the Arabian Sea and the Bay of Bengal derive from sources sampled by the mixture of the different atmospheric flows during the year. During winter (northeast) monsoon (November–February), the weak (~5 m/s) northeast trade wind brings cool, dry continental air, but during the summer (southwest) monsoon (June–September) the strong (~15 m/s) southwest wind brings humid maritime air into the Arabian Sea (21). The Arabian Sea has high salinity (usually in the range 35–37 practical salinity scale) due to excess of evaporation over rainfall. In contrast, the Bay of Bengal has much lower salinity due to the large influx of fresh water from river discharge and the high amount of rainfall. Wind directions over the Indian Ocean, which is the main forcing function, reverse twice during the year (22). Gaseous and particulate pollutants emitted by the Indian subcontinent and the South Asian region are transported over

the entire north Indian Ocean by the persistent northeastern low-level monsoonal flow, reaching as far south as 5–10°S (23, 24). Although southwest monsoon winds are stronger, atmospheric aerosol transport into the Arabian Sea during this time comes mostly from marine sources and from less industrialized areas in Africa. In the Arabian Sea, atmospheric trace element fluxes are one to two orders of magnitude larger than in the tropical and southern Indian Ocean (25). Our data show Pb surface concentrations for the Arabian Sea (stations 5–7) (60–82 pmol/kg) and in the Bay of Bengal (76 pmol/kg) that are significantly higher than in the western equatorial Indian Ocean, reflecting higher inputs by atmospheric deposition. Arabian Sea station 7 (10°N) has the highest surface lead concentration (82 pmol/kg) in the Indian Ocean.

The increase in lead concentrations at ~1,000 m for stations 11 and 12 (20–25 pmol/kg) with respect to the northern stations (10–15 pmol/kg) is in proximity to a salinity minimum attributable to the presence of the Antarctic Intermediate Water (AAIW). This is a low-salinity water mass that in the Indian Ocean sinks at around 45–55°S and spreads northward at a depth of 1,000–1,800 m. This feature disappears near a hydrographic front at 10°S (26), which is consistent with lower lead concentrations at 1,000 m (9 pmol/kg) for station 9 (5°S). A weak Pb maximum also corresponds to the salinity minimum at a depth of 800 m at station 10 (Figs. 2 and 3). These Pb maxima corresponding to middepth AAIW imply that the Pb supply to the surface water of the AAIW formation region ~20 y ago was higher than it is now.

Dissolved lead concentrations (1.5 pmol/kg) in the bottom water at 4,000 m at station 8 (4°N) are similar to that obtained in deep water at 7°S in the Pacific Ocean (6). Here, both sites are two-to-threefold lower than the lowest dissolved Pb concentration reported elsewhere for the world ocean. At station 14 (62°S), the closest station to Antarctica, there is scant vertical gradient, with lead concentrations between 4 and 7 pmol/kg at all depths except for a slight maximum of 13 pmol/kg at ~200 m.

Lead concentrations in old deep waters in the stations around and above the equatorial zone (1.5–3.3 pmol/kg) are lower than seen in contemporary Antarctic source waters. Two processes account for this observation: (i) although anthropogenic Pb fluxes to the Antarctic are low, they are not zero, and hence modern Pb concentrations are bound to be higher in the modern Antarctic than in the waters that sank centuries ago to form the present-day northern Indian deep waters and (ii) ²¹⁰Pb-²²⁶Ra studies have established that Pb is removed from the deep ocean on a time scale of decades to a century by “scavenging” onto sinking particulate matter and “boundary scavenging” onto bottom sediments (15–19, 27). Therefore it is expected that much of the Pb that may have been present in the north and central Indian Ocean deep waters at the time they sank from the surface will have been removed by scavenging by the time the water reaches the deep northern Indian Ocean. Abyssal waters of the Indian Ocean are occupied by Antarctic Bottom Water (AABW) with two significant flows. One flow originates from the Weddell Sea, filling the western basins of the Indian Ocean. The other flow originates from the Adelie Land coast/Ross Sea and fills the eastern basins (28, 29). Both waters flow northward, and in the northern basin, they gradually upwell to form the overlying Indian Deep Water (IDW), which occupies the depths between AAIW and AABW. Unlike AAIW and AABW, IDW is not formed in the Southern Ocean. Rather, it is a mixture of North Atlantic Deep Water carried from the Atlantic sector with AABW, forming Circumpolar Deep Water along the path into the Indian Ocean. The details of these two flow paths and mixing could create differences in the source Pb between the eastern and western Indian Ocean, which are not apparent in Pb

and the deep waters of the central Indian Ocean match the lowest Pb concentrations observed anywhere in the ocean, due to low initial Pb concentrations in the source waters and scavenging of Pb along the flow path. It should be expected that the continued evolution of human activities around the Indian Ocean will lead to a continuing evolution of the anthropogenic footprint of Pb on the ocean.

Materials and Methods

Sample collection information: samples were obtained during the Japanese Indian Ocean GEOTRACES cruise (KH-09-5, November to December 2009), which collected Pb samples from 11 stations from the Bay of Bengal, Arabian Sea, to the Antarctic Circumpolar Water (62°S, Fig. 1). Seawater samples for Pb analysis were collected from 11 stations using a conductivity temperature depth recorder carousel with an Epoxy-coated Al frame and Teflon-coated Niskin-X bottles (General Oceanics, 12 L-type), which were thoroughly cleaned by soaking in 1.5% Extran MA01 (EMD Millipore), 0.1M HCl, and high-purity water. Upon retrieval, Niskin-X bottles were transferred into a high-efficiency particulate air (HEPA)-filtered air “bubble,” and seawater samples were pressure-filtered through 0.2- μ m capsule filters (Pall Scientific, AcroPak 200). Filtered samples were acidified to pH 2.0 on board with clean HCl and shipped to Massachusetts Institute of Technology (MIT) for analysis.

Pb analysis: Total Pb concentration was analyzed by the nitrilotriacetic acid (NTA) isotope dilution-inductively coupled plasma mass spectrometry (ICPMS) method described by Lee et al. (11). Acid-leached 1.5-mL vials were used. The acidified seawater sample was poured into the vial, and 1.3 mL of the sample was pipetted out using a clean pipette tip. The 1.3-mL sample in the pipette tip was pipetted back into the same vial after quickly emptying the vial. The sample was then spiked with 25 μ L of stable ^{204}Pb isotope spike and left for a few minutes to establish equilibrium between added isotope spikes with their natural isotopes in the samples. Then the pH of the sample was adjusted

to pH = 5.3 using ammonium acetate buffer solution (pH = 7.9–8.0). Finally, 150 μ L of a NTA resin suspension (2,400 beads) were added to the vial, and it was shaken on an orbital table at 2,000 rpm for 4 d to allow the Pb and resin to bind. After 4 d, the sample vial was centrifuged (for 45 s at 14,500 rpm), and the overlying seawater was siphoned off carefully, leaving the resin beads at the bottom. The resin beads were then rinsed three times with high-purity H_2O to remove seasalt. In each rinse, the vial was filled with high-purity water, centrifuged down, and the supernatant was siphoned off. After rinsing, 150 μ L of 0.5 M HNO_3 were added to the vial, and then 2 d were allowed for Pb to be released into solution. The final solution was then brought to the ICPMS for measurement of the isotope ratio ($^{208}\text{Pb}/^{204}\text{Pb}$) of this solution (after on-peak zero acid blank correction) which is used to calculate the Pb concentration. Exactly 0.3 mL of low-Pb seawater were used to determine the procedure blank. At least three replicates of each sample were measured. Above the detection limit, the precision of the data are about 3%, based on a long-term standard with 32 pmol/kg. The detection limit (3σ of the SD of low-concentration samples) is about 1.5 pmol/kg. By comparison, of the only other publications reporting Pb data from the Indian Ocean, one only reported data as low as 0.01 nM (30), a concentration that exceeds that found in 40% of the samples in this dataset (Dataset S1), and the other publication only plotted overlain profiles from some stations in a supplementary figure with no discussion of the data (31).

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- Schaule BK, Patterson CC (1981) Lead concentrations in the northeast Pacific: Evidence for global anthropogenic perturbations. *Earth Planet Sci Lett* 32(1):304–312.
- Boyle EA, Chapnick SD, Shen GT (1986) Temporal variability of lead in the western North Atlantic. *J Geophys Res* 91(C7):8573–8593.
- Flegal AR, Itoh K, Patterson CC, Wong CS (1986) Vertical profile of lead isotopic compositions in the north-east Atlantic. *Nature* 321:689–690.
- Helmers E, Rutgers van der Loeff MM (1993) Lead and aluminum in Atlantic surface waters (50°N to 50°S) reflecting anthropogenic and natural sources in the eolian transport. *J Geophys Res* 98(C11):20261–20263.
- Alleman LY, Veron AJ, Church TM, Flegal AR, Hamelin B (1999) Invasion of the abyssal North Atlantic by modern anthropogenic lead. *Geophys Res Lett* 26(10):1477–1480.
- Wu J, Rember R, Jin M, Boyle EA, Flegal AR (2010) Isotopic evidence for the source of lead in the North Pacific abyssal water. *Geochim Cosmochim Acta* 74(16):4629–4638.
- Gallon C, et al. (2011) Asian industrial lead inputs to the North Pacific evidenced by lead concentrations and isotopic compositions in surface waters and aerosols. *Environ Sci Technol* 45(23):9874–9882.
- Flegal AR, Gallon C, Ganguli PM, Conway CH (2013) All the lead in China. *Crit Rev Environ Sci Technol* 43(17):1869–1944.
- SCOR Working Group (2007) GEOTRACES—An international study of the global marine biogeochemical cycles of trace elements and their isotopes. *Chem Erde* 67(2):85–131.
- Boyle EA, Bergquist BA, Kayser RA, Mahowald N (2005) Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA: Temporal variability and an intermediate water hydrothermal plume. *Geochim Cosmochim Acta* 69(4):933–952.
- Lee JM, et al. (2011) Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. *Anal Chim Acta* 686(1–2):93–101.
- Fine RA, et al. (2008) Decadal ventilation and mixing of Indian Ocean waters. *Deep Sea Res Part I Oceanogr Res Pap* 55(1):20–37.
- Haine TWN, Watson AJ, Liddicoat MI, Dickson RR (1998) The flow of Antarctic Bottom Water to the southwest Indian Ocean estimated using CFCs. *J Geophys Res* 103(C12):27637–27653.
- Shetye SR, Gouveia AD, Shenoi SSC (1994) Circulation and water masses of the Arabian Sea. *Proc Indiana Acad Sci* 103(2):107–123.
- Bacon MP, Spencer DW, Brewer PG (1976) $^{210}\text{Pb}/^{226}\text{Ra}$ and $^{210}\text{Po}/^{210}\text{Pb}$ disequilibria in seawater and suspended particulate matter. *Earth Planet Sci Lett* 32(2):277–296.
- Nozaki Y, Thomson J, Turekian KK (1976) The distribution of ^{210}Pb and ^{210}Po in the surface waters of the Pacific Ocean. *Earth Planet Sci Lett* 32(2):304–312.
- Cochran JK, Bacon MP, Krishnaswami S, Turekian KK (1983) Po-210 and Pb-210 distributions in the central and eastern Indian Ocean. *Earth Planet Sci Lett* 65(2):433–452.
- Chung Y, Finkel R (1987) Pb-210 in the western Indian Ocean: Distribution, disequilibrium, and partitioning between dissolved and particulate phases. *Earth Planet Sci Lett* 85(1–3):28–40.
- Turekian KK, Graustein WC, Cochran JK (1989) *Chemical Oceanography*, eds Riley JP, Chester R (Academic Press, London), Vol 10, pp 51–81.
- Kim G, Hussain N, Scudlark JR, Church TM (2000) Factors influencing the atmospheric depositional fluxes of stable Pb, ^{210}Pb and ^7Be into Chesapeake Bay. *J Atmos Chem* 36(1):65–79.
- Rengarajan R, Sarin MM (2004) Atmospheric deposition fluxes of ^7Be , ^{210}Pb and chemical species to the Arabian Sea and Bay of Bengal. *Indian J Mar Sci* 33(1):56–64.
- Vinayachandran PN, Shankar D, Kurian J, Durand F, Shenoi SSC (2007) Arabian Sea mini warm pool and the monsoon onset vortex. *Current Science* 93(2):203–214.
- Satheesh SK, Moorthy KK, Murthy BVK (1998) Spatial gradients in aerosol characteristics over the Arabian Sea and Indian Ocean. *J Geophys Res* 103(D20):26183–26192.
- Tindale NW, Pease PP (1999) Aerosols over the Arabian Sea: Atmospheric transport pathways and concentrations of dust and sea salt. *Deep Sea Res Part II Top Stud Oceanogr* 46:1577–1595.
- Saager PM (1994) The biogeochemical distribution of trace elements in the Indian Ocean. *Proc Indiana Acad Sci* 103(2):237–278.
- Tchernia P (1980) *Descriptive Regional Oceanography* (Pergamon Press, Oxford).
- Spencer DW, Bacon MP, Brewer PG (1981) Models of the distribution of Pb-210 in a section across the north equatorial Atlantic Ocean. *J Mar Res* 39(1):119–138.
- Gordon AL, Tchernia PL (1972) Waters of the Continental Margin off Adélie Coast, Antarctica. *Antarctic Oceanography II: The Australian–New Zealand Sector*, Antarctic Research Series, ed Hayes E (AGU, Washington, D.C.), pp 59–69.
- Mantyla AW, Reid JL (1995) On the origins of deep and bottom waters of the Indian Ocean. *J Geophys Res* 100(C2):2417–2439.
- Morley NH, Statham PJ, Burton JD (1993) Dissolved trace metals in the southwestern Indian Ocean. *Deep Sea Res Part I Oceanogr Res Pap* 40(5):1043–1062.
- Vu HTD, Sohrin Y (2013) Diverse stoichiometry of dissolved trace metals in the Indian Ocean. *Nature Sci Rep* 3:1–5.