



Concentration and isotopic composition of dissolved Pb in surface waters of the modern global ocean

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Abstract

Several years have passed since the global phase-out of leaded petrol use. Nonetheless, emissions from anthropogenic activities remain the principal source of Pb to the oceans. The distribution of elemental Pb and its stable isotopes throughout the surface ocean provide information on the source and transport of these anthropogenic inputs. This study presents dissolved Pb concentrations and isotopic distributions from 110 surface water samples collected during the Malaspina 2010 Circumnavigation Expedition. Dissolved Pb concentrations ranged from 10 pM to 49 pM across the sampling stations covering all major ocean basins. The highest concentrations were found in the northeast Atlantic Ocean and the lowest in both the south Pacific and south Atlantic Oceans. Lead concentrations measured in the north Pacific Ocean, near Hawaii, were compared to previously published data from the same region. That comparison showed that Pb concentration has decreased ~40% since 1975, although the rate of decrease has slowed in the past two decades. The overall decline in concentration probably has been induced by the cessation of leaded gasoline use in North America. The temporal evolution of stable Pb isotopes in this region shows a shift from dominant North American-like composition in 1979 towards a more Asian-like composition in later years. More widely, the distribution of Pb and Pb isotopes measured in the Malaspina sample set of global surface waters were compared with previously published ratios of aerosols and other atmosphere-derived Pb sources from the countries surrounding the different ocean basins. This comparison identified the potential Pb sources to each ocean basin, providing new insights into the transport and fate of Pb in the oceans.

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1. INTRODUCTION

Lead (Pb) is a natural constituent of the Earth's crust that is commonly found in soils, plants, and even at trace levels in surface waters of the world ocean (e.g., [Chow and Patterson, 1962](#); [Boyle et al., 1986](#); [Pais and Jones,](#)

[1997](#); [Boyle et al., 2005](#)). For the past two centuries, however, anthropogenic Pb emissions to the atmosphere from high-temperature industrial activities (e.g., coal burning, cement production, smelting of Pb and other metals) and from the combustion of leaded gasoline have dominated over natural Pb emissions ([Nriagu, 1979](#); [Boyle et al., 2014](#)). Global natural Pb emissions are estimated to be 2×10^6 kg/year ([Nriagu, 1989](#)) while anthropogenic Pb emissions are 3.6×10^6 kg/year ([Liang and Mao, 2015](#)). The

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oceans receive much of these Pb emissions and provide a sensitive recorder of their changes over time and space.

Spatial and temporal variability of Pb fluxes to the surface ocean have been studied directly from seawater measurements (e.g., Schaule and Patterson, 1981; Boyle et al., 1986, 2005) as well as indirectly from Pb measurements in corals (Desenfant et al., 2006; Inoue et al., 2006; Kelly et al., 2009; Lee et al., 2014) and sediments (Trefry et al., 1985; Veron et al., 1987; Hamelin et al., 1990). In general, these previous studies have shown that in surface waters of some oceanic basins such as the Atlantic Ocean, the concentration of Pb increased rapidly with the onset of the industrial revolution and the combustion of leaded gasoline, and then decreased quickly after the phase-out of leaded gasoline in North America and Europe in the late 1970s and early 1980s (Shen and Boyle, 1988; Wu and Boyle, 1997; Shotyk et al., 2005; Kelly et al., 2009).

In addition to increasing the concentration of Pb in the ocean, anthropogenic inputs have also modified the stable Pb isotopic composition of seawater. Many different types of ore deposits and other anthropogenic sources of Pb have distinct isotopic signatures that depend on when and where they were formed. Radiogenic isotopes ^{206}Pb , ^{207}Pb , and ^{208}Pb are products of radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , respectively. Their abundances in Pb ores and minerals varies due to the different U and Th decay constants and initial concentrations. Therefore, depending on the age of formation and the initial U and Th concentrations, the Pb isotope ratios of rocks and minerals can differ significantly from one location to another (Dickin, 1995; Komárek et al., 2008). The isotopic composition of Pb is not affected by physical or chemical fractionation processes, so since different sources of Pb have their own isotopic signature, it is possible to identify the source of Pb by matching the Pb isotopic composition of seawater with that of potential sources (e.g., Sangster et al., 2000; Komárek et al., 2008). Source apportionment can even be quantified in cases where all isotopically distinct sources of Pb can be characterized (e.g., Atwood, 2013). Altogether, the combination of Pb concentrations and isotopic signatures provides a powerful tool for interpreting changes in anthropogenic Pb inputs and sources to oceanic surface waters.

Although in the last three decades significant advances have been made in documenting the Pb distribution and isotopic composition of oceanic waters (e.g., Flegal et al., 1984; Shen and Boyle, 1988; Veron et al., 1994; Wu et al., 2010; Noble et al., 2015; Bridgestock et al., 2016), our understanding of the sources and transport of anthropogenic Pb is still limited due to the lack of data from many oceanic regions. So far, Pb concentrations and isotope ratios have been most studied in the North Atlantic Ocean, with some data from the North Pacific and North Indian Ocean (e.g., Sañudo-Wilhelmy and Flegal, 1994; Gallon et al., 2011; Lee et al., 2015). Other areas of the world's oceans have remained largely uncharacterized.

Surface water samples collected during the Malaspina 2010 Circumnavigation Expedition (MCE), which covered all of the world's major marine basins, provide an opportunity to fill this gap. The main objective of this study is to

determine the concentration and isotopic composition of dissolved Pb from surface waters collected in different oceanic basins during the MCE. These measurements comprise one of the most globally comprehensive surveys to date of current Pb levels in the surface ocean, providing an opportunity to build on the work of previous oceanographic campaigns and improve our understanding of some understudied areas of the world ocean. Furthermore, the data provide the basis for evaluating the evolution of Pb concentration over time in selected ocean regions where historical data are available. Finally, the geographical gradients in Pb isotopic composition make it possible to consider how potential sources of Pb differ for the different oceanic basins sampled during the MCE.

2. MATERIALS AND METHODS

2.1. Malaspina circumnavigation expedition

Surface water samples were collected during the MCE aboard the R/V *Hespérides* from December 2010 to July 2011 (Fig. 1 and Table S1 in the supporting information). The MCE consisted of six oceanic transects: (1) a meridional transect from Cadiz, Spain, to Rio de Janeiro, Brazil (Stations 19–36), from December 2010 to January 2011, (2) a transect from Brazil to Cape Town, South Africa (Stations 37–51), from January to February 2011, (3) a transect in the Indian Ocean from South Africa to Perth, Australia (Stations 52–69), from February to March 2011, (4 & 5) two transects in the Pacific Ocean, from Auckland, New Zealand, to Honolulu, Hawaii (Stations 70–86), from April to May 2011, and from Hawaii to Panama (Station 87 to 110), from May to June 2011, and (6) a final transect back to Spain across the subtropical Atlantic, from Cartagena de Indias, Colombia to Cartagena, Spain (Stations 1 to 18), from June to July 2011.

2.2. Collection and analysis of samples for Pb and Pb isotopes

Samples were collected using a Teflon tow-fish sampling system deployed at approximately 3 m depth utilizing established trace metal-clean techniques (e.g., Bruland et al., 2005; Berger et al., 2008). After sample collection, seawater was filtered on board through acid-washed 0.2 μm filter cartridges and acidified using Optima grade HCl to a $\text{pH} < 2$. Sample bottles containing dissolved samples ($< 0.2 \mu\text{m}$) were double bagged in polyethylene bags and shipped to the trace metal clean laboratories at the University of Southern California in Los Angeles, where 1 L of sample was pre-concentrated using the technique described in Bruland et al. (1985). Procedural blanks for this technique are $0.05 \pm 0.025 \text{ ng Pb}$ ($n = 33$). The amount of Pb extracted per sample ranged from 3 to 9 ng.

Levels of Pb were quantified by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) on a Thermo Element 2 HR-ICP-MS, using external calibration curves and an internal indium standard. The accuracy of our analytical procedure was verified by analysis of a certified seawater reference material (SRM), CASS-5, for

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