



Dynamic variability of dissolved Pb and Pb isotope composition from the U.S. North Atlantic GEOTRACES transect



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ABSTRACT

This study presents dissolved Pb concentration and isotopic composition distributions from GEOTRACES GA03, the U.S. North Atlantic Transect. Pb in the ocean is primarily derived from anthropogenic sources and Pb fluxes into the North Atlantic Ocean have been steadily decreasing following the phase-out of alkyl leaded gasoline usage in North America and Europe between 1975 and 1995. A compilation of dissolved Pb profiles from three stations occupied repeatedly during the last three decades reveals a dramatic decrease in concentrations within the surface layers and the thermocline maxima, although elevated concentrations greater than 60 pmol/kg are still observed in the center of the North Atlantic gyre where ventilation timescales are longer than at the western boundary. The evolution of stable Pb isotopes at these stations shows a shift from dominantly North American-like composition in surface waters in the early 1980s towards a more European-like composition in later years. The most recent shallow signatures at the Bermuda Atlantic Time Series station (BATS) show an even more recent trend returning to higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios after the completed phase-out of leaded gasoline in Europe, presumably because recently deposited Pb is more strongly influenced by industrial and incineration Pb than by residual alkyl leaded gasoline utilization. In surface waters, trends toward a more prominent European influence are also found in the middle of the basin and toward the European coast, coincident with higher concentrations of surface dissolved Pb. Scavenging of anthropogenic Pb is observed within the TAG hydrothermal plume, and it is unclear if there is any significant contribution to deep water by basaltic Pb leached by hydrothermal fluids. In the upper water column, many stations along the transect show Pb concentration maxima at ~ 100 m depth, coincident with a low $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic signature that is typical of European emission sources. Although Pb ores from the United States historically tend to carry $^{206}\text{Pb}/^{207}\text{Pb}$ signatures > 1.17 (Hurst, 2002), subsurface signatures as low as 1.1563 in $^{206}\text{Pb}/^{207}\text{Pb}$ were observed in this feature. This signature appears to be carried westward within saline Subtropical Underwater (STUW), that ventilates from the Central Eastern part of the North Atlantic Subtropical Gyre where the lowest surface isotope $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are observed. Along the western boundary, deep water masses of different ages carry distinct isotope ratios corresponding to their respective times of ventilation. Finally, a low $^{206}\text{Pb}/^{207}\text{Pb}$ signature in bottom water along the Eastern margin suggests that there may be some mobilization of European-derived anthropogenic Pb from recent surface deposits on the ocean floor.

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1. Introduction

The evolving distribution of Pb within the ocean provides a case study of the far-reaching footprint of humans on the environment. In the recent past, the North Atlantic Ocean was historically the most strongly affected basin, receiving a large atmospheric flux of Pb during the last several decades from industrial activities and especially from leaded gasoline utilization in the US and Europe.

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Most of the Pb in the oceans is derived from anthropogenic sources with leaded gasoline being the largest source during its peak utilization, and high temperature industrial processes such as coal burning, smelting, and incineration also contributing to this flux (Nriagu, 1979). Pb reaches the ocean through the advection and deposition of fine atmospheric aerosols, and many studies have focused on characterizing the Pb isotopic signature of aerosols and rain from different source regions that affect the North Atlantic Basin (Hamelin et al., 1997; Véron et al., 1998, 1992; Véron and Church, 1997; Kumar et al., 2014; Erel et al., 2007; Church et al., 1990). Changes in the flux of Pb to the ocean over time have been recorded by incorporation into sediments, corals, and snow (Schaule and Patterson, 1983; Trefry et al., 1985; Shen and Boyle, 1988; Véron et al., 1987; Hamelin et al., 1990; Boyle et al., 1994; Callender and Van Metre, 1997; Reuer et al., 2003; Kelly et al., 2009). The consequences of these fluxes on the Atlantic Ocean Pb distribution have been documented in several publications (Boyle et al., 1986; Shen and Boyle, 1988; Helmers et al., 1990, 1991; Helmers and van der Loeff, 1993; Véron et al., 1993, 1994, 1999; Hamelin et al., 1997; Wu and Boyle, 1997; Alleman et al., 1999; Weiss et al., 2003). During the past 200 years, the evolution of Pb in surface waters of the Western North Atlantic has shown a steady increase in concentration during the industrial revolution and a rapid rise after the introduction of alkyl leaded gasoline in the 1920s followed by a dramatic decrease after the phaseout of Pb gasoline usage in the 1970s and 1980s (Shen and Boyle, 1988; Desenfant et al., 2006; Kelly et al., 2009). The changing surface concentrations are injected into the ocean interior by thermocline ventilation and deepwater formation, and elevated concentrations are still found in intermediate level waters that were injected during previous decades when North Atlantic surface Pb concentrations were an order of magnitude higher than today (Boyle et al., 1986; Alleman et al., 1999; Véron et al., 1999). Early work has shown that the majority of Pb delivered to the Atlantic Ocean interior occurs through lateral ventilation of thermocline waters rather than through vertical processes (Boyle et al., 1986; Shen and Boyle, 1988). During the past four decades, as both the US and Europe have phased out the usage of alkyl leaded gasoline, Pb concentrations in the ocean surface and interior have decreased dramatically. This decrease is driven both by the decreased flux of Pb into the oceans and by scavenging onto sinking particles within the water column. The Pb residence time is ~ 2 years in oligotrophic surface waters and decades to a century in deeper waters (Bacon et al., 1976; Nozaki et al., 1976). In surface waters, steady-state balance is achieved between input and particle uptake, therefore surface water Pb tracks inputs. It is not known whether shallow Pb removal occurs by active biological uptake or passive scavenging onto particle surfaces, but in deeper waters, it is attributed to passive scavenging.

In tandem with Pb concentration distribution, the stable Pb isotopic composition can be used to delimit time and space dependent inputs to the ocean, constraining different sources and different periods of Pb deposition. This is possible because there will be no significant interference from stable isotopic fractionation during industrial processing or in the environment in comparison to very large differences resulting from distinctive radiogenic signatures of Pb ores. Although stable isotope fractionations have been reported for some heavy stable isotopes (e.g. Tl, Rehkamper et al., 2002; Hg, Bergquist and Blum, 2007), these fractionations are at most only a few parts per thousand, whereas naturally-occurring radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ isotope signatures can vary by more than 300 parts per thousand. Lead ores contain distinctive isotopic ratios because of the temporal evolution of their parent rock U and Th reservoirs (Doe, 1970), and atmospheric and oceanic Pb inputs have changed both temporally and spatially (Schaule and Patterson, 1981, 1983). Hence, temporal and spatial

source aspects of Pb transport through the ocean can be traced. The temporal evolution of Pb isotope ratios of sources can allow for determination of Pb transit times from the surface to the deep ocean (Alleman et al., 1999; Véron et al., 1999), and the naturally-occurring radioisotope ^{210}Pb enhances our ability to constrain Pb behavior on a decadal scale (Bacon et al., 1976; Turekian, 1977; Boyle et al., 1986; Shen and Boyle, 1988). Because Pb is affected by many processes that influence other trace metals (atmospheric deposition, biological uptake, and abiotic scavenging), the study of Pb not only elucidates anthropogenic contamination but also helps constrain processes that move other metals through the ocean.

This manuscript presents results from the US North Atlantic GEOTRACES Transect GA03 and examines how the distributions of Pb have changed with time by comparing these results to previous occupations of three stations. This expedition was a part of the International GEOTRACES Program, whose goal is to map the world oceans for trace elements and isotopes in order to improve our understanding of biogeochemical cycling and circulation in the ocean (www.geotraces.org).

2. Methods

Samples were collected from GEOTRACES track GA03, referred to as the U.S. GEOTRACES North Atlantic Transect (USGT-NAT), that took place in two legs, aboard the R/V *Knorr* (USGT10, Oct. 14, 2010–Nov. 3, 2010; USGT11, Nov. 4, 2011–Dec. 14, 2011; Chief Scientists: William Jenkins, Ed Boyle, and Greg Cutter). The first leg (USGT10) departed from Lisbon, Portugal and sampled Mediterranean Outflow Water (MOW) at Station USGT10-01, followed by an approximately meridional transect southwards to 21°N (Station GT10-08, Fig. 1). Because of ship malfunction, the cruise was terminated after a short zonal transect was completed across the Mauritanian Upwelling along 17.4°N (Stations USGT10-09 to USGT10-12), sampling the northern edge of the low oxygen waters there and concluding at 24.5°W , Station TENATSO (USGT10-12). The second leg (USGT11) departed from Woods Hole, MA and sampled 7 stations along Line W to the Bermuda Atlantic Time Series station (BATS, Station USGT11-10, Fig. 1). Stations were then occupied at approximately 3° spacing across the basin alternating between full depth sampling of the water column (even numbered stations) and intermediate sampling to 1000 m (odd numbered stations). Full depth stations during the two legs consisted of either 24 (“full” stations) or 36 (“super” stations) depths, and shallow stations consisted of 12 depths. A surface towed fish was also deployed and an additional surface sample was taken for each station. The second leg concluded with a re-occupation of Station TENATSO (USGT11-24).

2.1. Trace metal sampling techniques

Samples were collected using the ODU GEOTRACES Carousel (Cutter and Bruland, 2012), and were filtered through $0.2\ \mu\text{m}$ Acropak capsule filters in the GEOTRACES clean van. The carousel was used to collect samples from surface to near bottom waters, and an additional sample was collected from a surface towed “fish” at each station. Pre-conditioned, teflon-coated Go-Flo sampling bottles (General Oceanics, Miami, FL) of 12 L capacity were deployed on a polyurethane powder-coated aluminum rosette with titanium pylons and pressure housings (Sea-Bird Electronics, Inc., Bellevue, WA) attached to a Kevlar, non-metallic conducting cable. For more information regarding carousel deployment, please refer to the GEOTRACES Cookbook, located on the GEOTRACES Program website (www.GEOTRACES.org). After retrieval of the carousel, Go-Flo bottles were moved to the U.S. GEOTRACES Program class-100 trace metal clean van, and pressurized with HEPA filtered air for sampling in

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