

Lead Sources to the Amundsen Sea, West Antarctica

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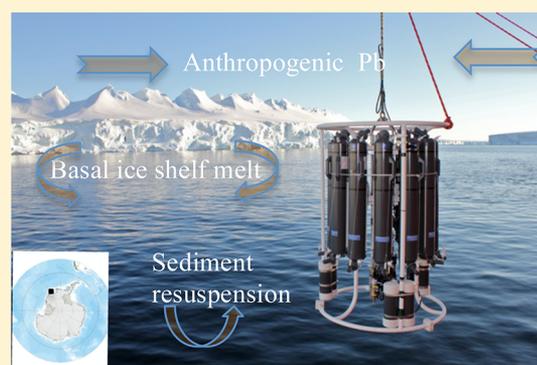
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S Supporting Information

ABSTRACT: The global prevalence of industrial lead (Pb) contamination was exemplified decades ago by the predominance of anthropogenic Pb in samples of Antarctic surface ice and in Southern Ocean surface waters. Decreases in environmental Pb contamination corresponding with the near-global phase-out of leaded automobile gasoline beginning in the 1970s have since been observed. Measurements of Pb concentration in snow and ice core samples from Antarctica show that recent fluxes of industrial Pb to Antarctica have similarly declined. Here, we present measurements of Pb concentrations and isotopic compositions in seawater and surface sediments from the Amundsen Sea continental shelf including the Amundsen Sea Polynya. Both sets of measurements show that most (~60–95%) of the Pb at our sites, at the time of sampling, is natural in source: that is, derived from the weathering of Antarctic continental rocks. These fluxes of natural Pb then become entrained into polynya waters either from sediment resuspension or from the transport of sediment-laden glacial melt waters to the polynya.



INTRODUCTION

The global prevalence of environmental lead (Pb) contamination was first revealed by detection of industrial Pb in polar and other remote regions over five decades ago.^{1–4} Since then, subsequent studies have documented decreases in industrial Pb in some of those regions, associated with global efforts to reduce industrial Pb emissions. The most notable of these studies systematically chronicled decreases in Pb concentrations and changes in Pb isotopic composition in the North Atlantic that are consistent with the phase out of leaded gasoline in both North America and Europe.^{5–7} Data on the concentration and isotopic composition of Pb measured in snow and ice core samples from Antarctica indicate that fluxes of anthropogenic Pb to that continent have similarly declined.^{8–10} Consequently, a reasonable expectation is that industrial Pb concentrations have also measurably decreased in the Southern Ocean following the virtual elimination of leaded gasoline in the Southern Hemisphere. We tested this hypothesis in the Amundsen Sea, a shelf region of West Antarctica in the Southern Ocean (Figure 1a), where we measured both Pb concentrations and Pb isotope compositions of seawater and sediments.

Climate change has the potential to further alter Pb inputs to the Southern Ocean, particularly along the West Antarctic sector where the effects of global climate change are especially pronounced. Glaciers that drain into the Amundsen Sea Embayment are among the world's fastest dischargers of ice into the ocean.¹¹ This region is especially important because the West Antarctic ice sheet is mainly grounded below sea level and is therefore sensitive to changes in ocean circulation resulting in increased heat delivery to the submerged ice sheet.¹² This effect has been documented by the recently accelerated thinning of ice shelves and by grounding line retreat in the Amundsen Sea Embayment regions.^{11,13} Basal melting of ice shelves has been attributed to the increased presence of relatively warm Circumpolar Deep Water (CDW) that floods the network of deep, glacially carved troughs on the continental shelf, eroding the ice shelves from their underlying cavities.¹⁴ With the accelerated melting of this relatively old ice, it is expected that the flux of preindustrial (natural) Pb to the

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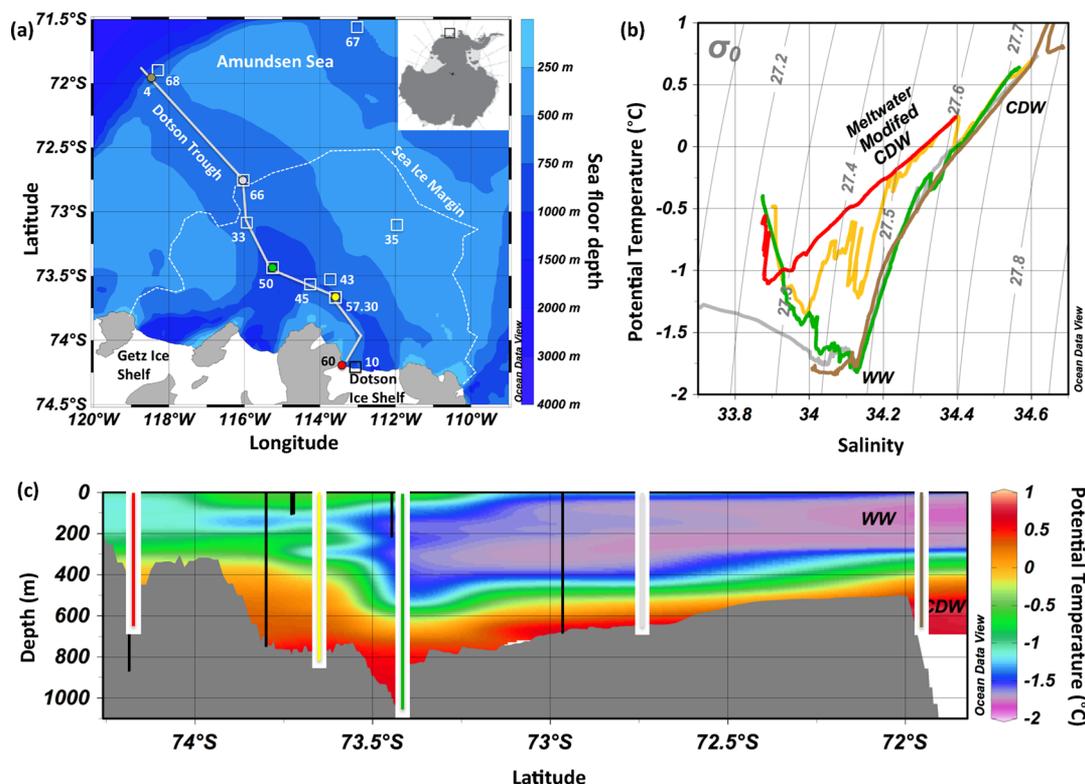


Figure 1. Study site. (a) Station locations of the PbIC measurements, indicating where water (filled circles) and sediment (squares) samples were taken. Blue shading indicates bathymetric depth (darker is deeper). The white dotted line delineates the northern extent of the Amundsen Sea Polynya as observed in January 2011. Inset: Antarctic map showing Amundsen Sea location. (b) Potential temperature–salinity (θ – S) plot (with density anomaly isopycnals, σ_0) showing the four PbIC (water) stations: 4 (brown), 66 (gray), 50 (green), and 57.30 (yellow) and, for reference, the ice shelf outflow station (red). The water column is characterized by two main water masses, in the upper water column, Winter Water, and at depth, Circumpolar Deep Water (CDW). Surface waters show variable temperature and salinity, depending on the amount of in situ sea ice melt and subsequent solar warming. (c) Latitude–depth section (location indicated in (a) by bold white line), showing potential temperature in degrees Celsius. The vertical colored lines indicate the location and depth of CTD casts taken at the four stations listed above; the vertical black lines indicate additional CTD casts used to create the latitude–depth section plot. Vertical profiles that extend deeper than the indicated sea floor (in gray) result from spatial averaging of the bathymetry in the east–west direction.

Amundsen Sea will increase in the coming years. Conversely, in the Amundsen Sea sector surface ablation of the ice sheet is not expected to increase dramatically in the near future as increasing air temperatures are still below zero for most of the year.¹⁵ Consequently, remobilization of industrial Pb from surface melt is not expected to increase significantly in this region but could be of greater relative importance in other regions of Antarctica such as the Western Antarctic Peninsula where increases in air temperature over at least the last 65 years¹⁶ have resulted in increased surface melt duration and extent at these lower latitudes.¹⁵

The objective of this study was to determine the relative proportions of natural Pb vs anthropogenic Pb in the Amundsen Sea sector of the Southern Ocean. To this end, we analyzed dissolved Pb concentrations and Pb isotope compositions (PbIC) of water and sediment samples collected from the Amundsen Sea Polynya (ASP), a recurring area of seasonally open water bounded by sea ice and the continental coast. Most of the samples were collected from the Dotson Trough area and within the ASP (Figure 1).¹⁷

MATERIALS AND METHODS

Regional Setting. The Amundsen Sea continental shelf spans about 315000 km² and extends approximately 300 km in an east–west direction. The continental shelf bathymetry is

deeper inshore than offshore and is characterized by several north–south glacially cut troughs that can be as deep as 1500 m at the coast (e.g., Figure 1a).¹⁴ Relatively warm and salty CDW (Figures 1b and c), which flows within the Antarctic Circumpolar Current (ACC) in close proximity to the Amundsen Sea continental shelf break, appears to gain direct access to the continental shelf at the outer trough locations.¹² Along the coast there are several floating ice shelves overlying these deep trough areas, where CDW is observed at depth (Figure 1).^{14,18} Recent reports have also indicated the presence of glacial meltwater at depth in the Dotson Trough area¹² and throughout the ASP area.¹⁹

Sample Collection. Seawater and sediment samples were collected during the NBP 10–05 ASPIRE cruise (13 Dec 2010–12 Jan 2011) aboard the icebreaker *Nathaniel B. Palmer* as detailed in the Supporting Information.¹⁷ In brief, seawater samples were collected along a transect that extended from the Amundsen Sea continental shelf break south to the open waters of the ASP (Figure 1). Water samples were collected using 12 L Teflon-lined externally closing Niskin bottles (Ocean Test Equipment, Ft. Lauderdale, FL) mounted on a noncontaminating CTD-Rosette deployed on a coated aramid cable. The Niskin bottles were removed from the rosette and subsampled inside a positive pressure (class 1000) trace metal clean lab container. Water samples for dissolved Pb measurements were

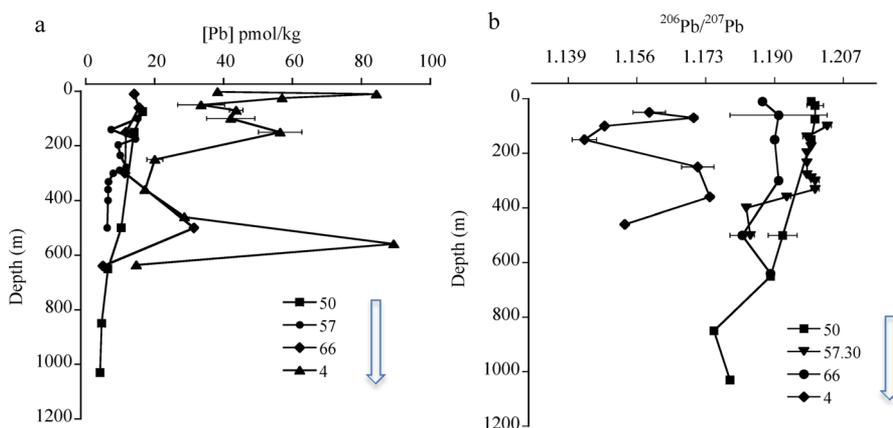


Figure 2. Vertical profiles of Pb concentration (a) and $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic composition (b) for water sampled from four stations on the Dotson Trough shown in Figure 1a. Error bars for Station 4 Pb concentration profile (a) on five data points from 50 to 250 m depth represent the difference about the mean of analyses performed at University of California Santa Cruz and Rutgers University. The arrow next to the legend indicates increasing station distance from the continent.

pressure-filtered through a precleaned $0.2\ \mu\text{m}$ capsule filter (Acropak 200, Pall) into low-density polyethylene trace metal clean bottles. Seawater samples were then immediately acidified to $\sim 24\ \text{mM}$ of HCl (Fisher Optima grade).

Surface sediment samples were collected from the sea floor using a Smith McIntyre grab sampler, and only samples where the surface water interface appeared undisturbed were taken. The upper 3–5 cm were collected and homogenized before subsampling.

Wet sediments were stored frozen until further processing. In the shore laboratory, sediments were dried at $60\ ^\circ\text{C}$ for ~ 2 days and manually powdered using an acid-cleaned agate pestle and mortar.

Sample Analysis. Most of the Pb concentration and all of the PbIC measurements were performed on a Thermo ELEMENT XR magnetic sector high-resolution inductively coupled plasma mass (HR-ICP-MS) at the Institute of Marine Sciences at UC Santa Cruz. Dissolved Pb concentration was measured using an online resin column extraction method.²⁰ Seawater extraction blanks ($24\ \text{mM}$ HCl), determined using a chelating resin column extraction coupled online to the HR-ICP-MS analysis,²⁰ were $1.9\ \text{pmol}\ \text{kg}^{-1}$ ($n = 14$), and the limit of detection (3 times the standard deviation of the blank) was $3.3\ \text{pmol}\ \text{kg}^{-1}$. Concurrent analyses of seawater reference materials showed reasonable agreement between our analyses and Pb data reported by others (Table S1).

Additional samples from Station 4 (separate subsamples from the same Niskin bottles) were analyzed for Pb concentrations at Rutgers University using an automated preconcentration system and a Thermo ELEMENT-1 HR-ICP-MS instrument in order to show replication of results by an independent method in an independent laboratory. Process blanks determined by preconcentrating equivalent volumes of ultra-pure deionized water (acidified with HCl) were $0.8 \pm 0.2\ \text{pmol}\ \text{kg}^{-1}$ (average of 17 analytical sessions, with several blanks each) for a calculated limit of detection of $0.5\ \text{pmol}\ \text{kg}^{-1}$. Analyses of international reference seawater samples gave values indistinguishable from the reported consensus values (Table S1).

Sediment samples were dried, and $\sim 0.1\ \text{g}$ was leached using 10 mL of freshly prepared aqua regia (trace metal grade) in Savillex PFA (Perfluoroalkoxy) vials. Samples were refluxed on a hot plate set at $180\ ^\circ\text{C}$ for 9 h. The residue was dissolved in

$1.5\ \text{M}$ HNO_3 , swirled vigorously, and heated for 1 h at $130\ ^\circ\text{C}$. After cooling, the leachate was decanted and analyzed. This protocol was chosen because aqua regia or dilute acid extraction removes the Pb fraction sorbed onto ferro-manganese oxides, mineral surfaces, and organic debris,^{21,22} which is most similar to the phase association of Pb remobilized in seawater by resuspended sediments. Concurrent leaching of three reference material sediments had 80–97% recovery compared to their total certified Pb content, indicating this leach method recovered most of the sedimentary Pb (Table S3). Sediment leaching blanks (aqua regia) were $0.4\ \mu\text{g}\ \text{kg}^{-1}$ ($n = 4$), 0.007–0.015% of sample leachate concentrations.

For isotope analyses, 0.2–1.0 L of seawater was preconcentrated to bring the total Pb concentration to at least $1\ \mu\text{g}\ \text{kg}^{-1}$ and then analyzed as previously detailed.²³ Seawater samples were analyzed in counting mode, while sediment samples were analyzed in analog mode. Measurements were made relative to the National Institute of Standards and Technology (NIST) standard reference material 981 (common lead). Precision (2σ) of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ for the seawater samples was 3.8‰ and 5.3‰ ($n = 25$), respectively, and 1.4‰ and 1.4‰ ($n = 8$), respectively, for sediment samples. The NIST 981 reference values used in the study were $^{206}\text{Pb}/^{207}\text{Pb} = 1.0931$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.3696$.

RESULTS AND DISCUSSION

Water Circulation. As previously noted, the ASPIRE expedition focused on the Amundsen Sea because of the accelerated changes occurring along its coastline, largely caused by the melting of the underside of ice shelves by warm CDW.¹² The CDW intrudes onto the Antarctic continental shelf and flows at depth toward the coast by way of deep troughs that bisect the continental shelf region.^{12,14} It is warm ($>0.6\ ^\circ\text{C}$) and salty (>34.5) relative to the overlying Winter Water. The flow of CDW into the ice shelf cavities²⁴ drives basal melting of the ice shelf^{12,25} and the suspension of sediments near the grounding line¹³ or elsewhere within the cavity, resulting in an outflow mixture of CDW, glacial meltwater, and dissolved and particulate trace metals (including Pb). The meltwater-modified CDW is less saline, cooler, and relatively more buoyant, as exemplified by the ice shelf outflow station in θ -S space (Figure 1b in red) and is thus found at shallower depths upon its exit from the ice shelf cavity. The θ -S plot from

Station 57.30 (Figure 1b in yellow) also exhibits some traces of ice shelf meltwater in its profile (where it approaches with the red profile).

Pb Concentrations in the Amundsen Sea and Amundsen Sea Polynya (ASP). The dissolved Pb concentrations range from 4 pmol kg⁻¹ in the ASP to 89 pmol kg⁻¹ in the Amundsen Sea shelf break (Table S2). These concentrations are within the range (3–132 pmol kg⁻¹) of previously published Pb concentration data from the Southern Ocean. These include the Weddell Sea,^{26–28} the Australian sector,²⁹ and more recently the Indian sector.³⁰ From 1987–1991, three expeditions in the Weddell Sea reported an average Pb concentration of 14.6 ± 12.2 pmol kg⁻¹ (mean ± standard deviation, *n* = 201, range 2–72 pmol kg⁻¹).^{26–28} These studies attributed the Pb to a mix of natural and industrial sources from South America based on PbIC measurements. More recently in the Australian sector, Lai et al.²⁹ measured an average of 32 ± 21 pmol kg⁻¹ (*n* = 132, range 8–110 pmol kg⁻¹) from samples collected in 2002. They again attributed their elevated and highly variable Pb concentrations to sporadic aerosol dust deposition events from the Australian subcontinent.²⁹ Lastly, samples collected in 2010–2011 from the Indian sector had the lowest concentrations measured to date in the Southern Ocean (7 ± 2 pmol kg⁻¹, *n* = 18, range 4–13 pmol kg⁻¹).³⁰ Although these concentrations are relatively low, Echegoyen et al.³⁰ stated that the Pb concentration is probably higher than in preindustrial times due to regional anthropogenic emissions. Indeed, McConnell et al.⁸ recently confirmed the validity of both Australia and South America as possible source areas (PSAs) and the sporadic nature of the Pb aerosol deposition in the Antarctic and Southern Ocean. Their study was based on measurements of Pb and PbIC from a composite of 16 ice cores covering a wide area of Antarctica. They showed that aerosol deposition from the aforementioned PSAs has been (and is still) the principal source of Pb to Antarctica for the last 130 years.⁸

Pb Concentration and PbIC Depth Profiles. The Pb concentration and PbIC profiles for the water sampled at the four stations along the Dotson Trough are shown in Figure 2. There is a general decrease in Pb concentration along the Dotson Trough. The average water column (mean ± standard deviation) dissolved Pb concentration decreases by a factor of 3 from 44 ± 24 pmol kg⁻¹ at the shelf break (Station 4) to 9.4 ± 3.1 pmol kg⁻¹ at the coast of the ASP (Station 57.30). The Pb concentration profiles also show a general decrease in Pb concentration with depth (Figure 2a). The much higher Pb concentrations measured at the Amundsen Sea continental shelf break (Station 4) are likely due to a combination of aerosol Pb deposited in the low productivity ACC waters^{26,27} and Pb inputs associated with sediment sources in this bathymetrically and dynamically complex region where the Dotson Trough meets the shelf break. The Pb derived from bottom sediments is likely to incorporate both natural and anthropogenic Pb. Anthropogenic Pb is most likely to consist of Pb accumulated over the last century when global Pb emissions were relatively high from the combustion of leaded gasoline^{5,31} and possibly of emissions from past and contemporary Pb mining activities, e.g., in Australia.^{31,32} Conversely, particle scavenging of dissolved Pb in the highly biologically productive shelf waters of the ASP¹⁷ may tend to keep the Pb concentration low throughout the water column, relative to the less productive Station 4.

The gradual decrease in Pb concentrations from the shelf break to the Antarctica coast is reflected in the similar gradual increase in ²⁰⁶Pb/²⁰⁷Pb ratios (Figure 2b). The average ²⁰⁶Pb/²⁰⁷Pb (mean ± standard deviation for all samples) increases from 1.160 ± 0.012 at the shelf break (Station 4) to 1.195 ± 0.006 in the ASP (Station 57.30). Additionally, the mean Pb concentration and PbIC of the mid transect Station 66 (15 ± 4.0 pmol kg⁻¹ and ²⁰⁶Pb/²⁰⁷Pb = 1.190 ± 0.002) and Station 50 (10.8 ± 5.1 pmol kg⁻¹ and ²⁰⁶Pb/²⁰⁷Pb = 1.188 ± 0.004) reflect the relative contribution of anthropogenic and natural (regional mineral) Pb sources.

Natural and Industrial Pb in the Amundsen Sea. In addition to atmospheric deposition of industrial Pb, other local sources of Pb include (1) the remobilization of lithogenic Pb from sediments on the bottom and sides of the Dotson Trough and (2) release of Pb from basal ice shelf melt or from resuspended sediments in the ice shelf cavity. The relative contributions of the anthropogenic and natural Pb sources are evidenced by a triple isotope plot (²⁰⁶Pb/²⁰⁷Pb vs ²⁰⁸Pb/²⁰⁷Pb) of the water and sediment samples (Figure 3 and Table S2).

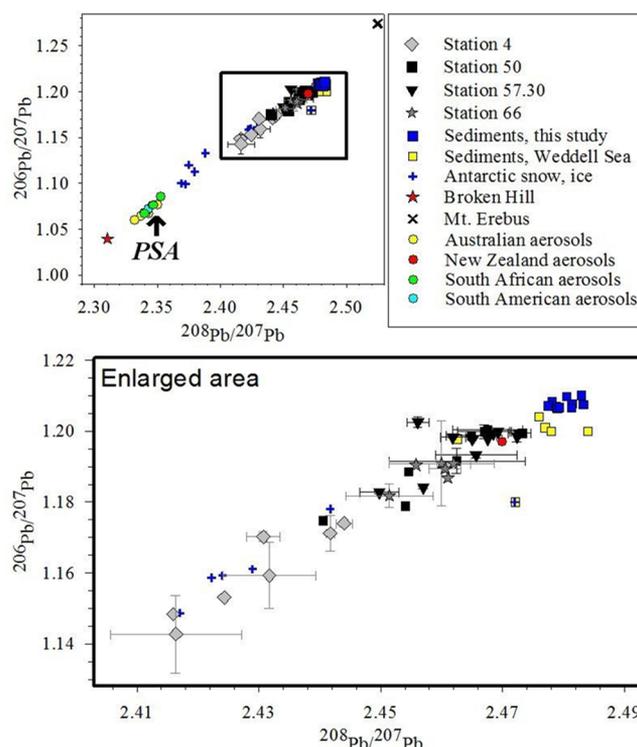


Figure 3. Seawater, sediment, and possible source area Pb isotopes. The PbIC of seawater samples (gray and black symbols) and sediments (blue symbols) closely resemble previously sampled Antarctic sediments,^{33–35} snow, and ice.^{9,36,37} The seawater samples fall along a mixing line between Australian Pb from Broken Hill^{38,39} and that of sediment samples from the ASP (this study). Other possible sources shown include Australian,^{31,32,37,40} South American, South African, and New Zealand aerosols.⁴⁰

The plot shows a clear mixing line along which most of our samples fall. Amundsen Sea bottom sediment PbICs (²⁰⁶Pb/²⁰⁷Pb = 1.208 ± 0.001; ²⁰⁸Pb/²⁰⁷Pb = 2.480 ± 0.002) are characteristic of locally weathered Antarctic crust³³ and are an isotopically supported endmember for these samples (Table S2). Conversely, the PbIC (²⁰⁶Pb/²⁰⁷Pb = 1.160 ± 0.012; ²⁰⁸Pb/²⁰⁷Pb = 2.431 ± 0.014) of the open ACC/Amundsen Sea

continental shelf break (Station 4) is more similar to previous measurements of Antarctic ice and snow from the 1970s–1990s,^{26–28} which were attributed to Pb from Australian industrial aerosol deposition. Unlike the coastal stations (e.g., Stations 50 and 50.73), the continental shelf break waters (Station 4) are more likely to be predominantly influenced by ongoing atmospheric deposition of industrial Pb and/or sediment derived “legacy” pollutant Pb (rather than glacial ice melt), given the relatively large distance between Station 4 and inputs of continental ice or snow.

We used a simple two endmember mixing equation to calculate the relative contribution of Pb in Amundsen Sea waters from the two endmembers: natural Pb from weathered Antarctic crust and industrial Pb from atmospheric deposition. The PbIC of the natural endmember was set as the average of the 10 Amundsen Sea bottom sediments (Figure 1a, $^{206}\text{Pb}/^{207}\text{Pb} = 1.208 \pm 0.001$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.480 \pm 0.002$). The PbIC measurements of the 10 sediments (Table S3) are nearly indistinguishable from the averages of the PbIC measurements reported for sediments from the Weddell Sea ($^{206}\text{Pb}/^{207}\text{Pb} = 1.207 \pm 0.003$)⁴¹ and Bellingshausen Sea.³³

In contrast, these natural PbIC values are markedly different from the industrial Pb deposited in the Southern Ocean^{26,27} and Antarctica.^{8,42,9,37} The estimated PbIC of those industrial fluxes are varied but tend to approach industrial Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.04–1.08$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.310–2.320$)⁴³ from the Broken Hill Pb deposit in Australia,^{32,38,39} which was a principal source of Pb additives for gasoline in the PSAs in the 1990s.^{40,43} The predominance of those industrial Pb fluxes was evidenced by measurements of atmospheric PbIC in aerosols from PSAs between 1994 and 1999 by Bollhofer and Rosman.⁴⁰ The PSAs included the average atmospheric PbIC of aerosols collected from major southernmost Latin American (e.g., Punta Arenas; $^{206}\text{Pb}/^{207}\text{Pb} = 1.072 \pm 0.008$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.343 \pm 0.004$), South African (e.g., Cape Town; $^{206}\text{Pb}/^{207}\text{Pb} = 1.085–1.090$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.353–2.358$), and Australian (e.g., Melbourne $^{206}\text{Pb}/^{207}\text{Pb} = 1.075 \pm 0.015$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.346 \pm 0.013$) cities bordering the Southern Ocean.⁴⁰ There is also a possibility that industrial aerosol Pb from past and contemporary Pb mining activities (e.g., from Mt. Isa in Australia) could also be a minor source of anthropogenic aerosol Pb reaching Antarctica.³² Mackay et al.³² recently (between 2005 and 2008) measured the PbIC of aerosols at the Mt Isa copper and lead mine and determined values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.059 \pm 0.010$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.334 \pm 0.010$) similar to the Broken Hill PbIC.

The PbIC measurements of aerosols from the PSAs⁴⁰ were made several years after most countries had eliminated leaded gasoline for automobiles; however, atmospheric contamination from wind-derived resuspension of historic leaded gasoline emissions was still dominant compared to other industrial sources such as coal burning.⁴⁴ Comparison of PbIC in coals from around the world with aerosol PbIC from the same source regions found that coal combustion was not yet a major Pb source in South Africa and South America, but at the time of the study (2009), coal combustion was the dominant source in China and the eastern U.S.⁴⁴ Diaz-Somoano et al.⁴⁴ concluded that “old Pb pollution” from leaded gasoline, reemitted into the atmosphere, or from long-range transport, was still the main source of contaminant Pb in the PSAs of South Africa and South America.⁴⁴ McConnell et al.⁸ recently demonstrated the persistence of Broken Hill-related industrial Pb in the Antarctic region from the aforementioned PSAs. We therefore selected the average PbIC ($^{206}\text{Pb}/^{207}\text{Pb} = 1.072 \pm 0.008$; $^{208}\text{Pb}/^{207}\text{Pb} =$

2.342 ± 0.012)⁴⁰ for aerosols in Punta Arenas, Chile measured in 1997–1999⁴⁰ to be representative of the PSAs. Those ratios served as the industrial endmember for our calculations of the relative fractions (%) of natural versus industrial Pb in the Amundsen Sea. The relative proportions were calculated as

$$\begin{aligned} & \% \text{ natural Pb in water column} \\ &= \frac{\text{PbIC}_{\text{seawater}} - \text{PbIC}_{\text{aerosols}}}{\text{PbIC}_{\text{sediments}} - \text{PbIC}_{\text{aerosols}}} \times 100\% \end{aligned}$$

These calculations were made twice for each water sample using both the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios. These replicate calculations were in close agreement (2%, $n = 38$). The individual and average values are listed in Table S2 and illustrated in Figure 4. They indicate that most (84–91%) of

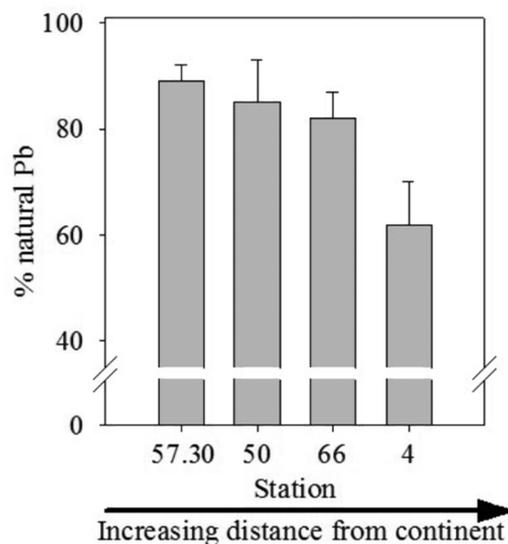


Figure 4. Percentage of natural Pb. Station 57.30 closest to the ice shelf in the ASP has the highest fraction of natural Pb. The fraction of natural Pb decreases northward away from the ASP, approaching a 50/50 mix of natural and anthropogenic Pb at Station 4.

the Pb in waters from the three locations in the ASP (Stations 50, 57.30 and 66) was natural, while 60–64% of the Pb in waters from the ACC/Amundsen Sea shelf break was natural. These estimates are constrained by multiple factors, primarily our assumption of the industrial PbIC endmember. The estimates are, however, consistent with recent reported declines in industrial Pb fluxes to Antarctica^{8,9} that correspond with the global elimination of most Pb additives in gasoline. Planchon et al.⁹ measured Pb concentration and PbIC in accumulated snow from Coats Land, Antarctic over the period ~1840 to 1990.⁹ They reported a 10-fold decrease in Pb concentration in 1990 compared to the mid 1970s, reaching values similar to those observed before the advent of leaded gasoline during the 1930s.⁴⁵ Barbante et al.^{10,46} reported a similar decrease at Styx Glacier Plateau (73°52'S, 163°42'E) in Victoria Land.

Environmental Implications. As climate change continues to drive ocean circulation changes that, in turn, increase the presence of warm CDW circulating under the West Antarctica ice shelves,^{8,9} we expect an increase in the processes that mobilize natural Pb from sediments below those ice shelves. In the coming decades, we hypothesize the overall flux of Pb in the Amundsen Sea will decrease as industrial atmospheric Pb emissions continue to decline. We also hypothesize that a

greater proportion of that Pb flux will be natural Pb from sedimentary sources and basal meltwater, which is thousands of years old, due to changes in ocean circulation. As a result, Pb budgets for this region, and for the greater Southern Ocean, are projected to change over the next few decades as a result of both reductions in atmospheric emissions of industrial Pb and increases in atmospheric emissions of industrial CO₂.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05151.

Blank values, limits of detection, and consensus Pb concentration values for GEOTRACES and SAFE intercalibration seawater samples (Table S1) (PDF) Sample location coordinates, depth profiles of dissolved Pb concentrations, and the Pb isotopic composition (²⁰⁸Pb/²⁰⁷Pb, ²⁰⁶Pb/²⁰⁷Pb) and the percent composition of natural Pb in water samples for the four stations (Table S2); Pb concentration and Pb isotopic composition (²⁰⁸Pb/²⁰⁷Pb, ²⁰⁶Pb/²⁰⁷Pb) of the 10 sediment samples (Table S3) (XLSX)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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