



Lead concentrations and isotopic compositions in the Western Philippine Sea



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ARTICLE INFO

Article history:

Received 17 August 2016

Received in revised form 2 December 2016

Accepted 31 December 2016

Available online 4 January 2017

ABSTRACT

Dissolved lead (Pb) concentrations and isotope ratios in seawater of the Western Philippine Sea (WPS) were determined to investigate sources of Pb in the region. Surface seawater concentrations at seven sampling stations ranged from 36.2 to 68.1 pmol kg⁻¹. Isotopic composition of surface water, with ²⁰⁶Pb/²⁰⁷Pb ranging from 1.162 to 1.170, ²⁰⁸Pb/²⁰⁷Pb ranging from 2.445 to 2.451, and ²⁰⁶Pb/²⁰⁴Pb ranging from 18.14 to 18.27, reflects Asian anthropogenic aerosols input to the WPS. Shallow water Pb concentrations within the Kuroshio Current domain are about 15 pmol kg⁻¹ lower than at other sites and, together with a distinct isotopic signature (²⁰⁶Pb/²⁰⁷Pb = 1.167–1.170, ²⁰⁸Pb/²⁰⁷Pb = 2.447–2.451 and ²⁰⁶Pb/²⁰⁴Pb = 18.22–18.27), reflect water originating from the Equatorial Pacific that is relatively less impacted by contamination from anthropogenic inputs. An isotopically distinct sub-surface Pb maximum at about 100 to 250 m, representing water originating from the Western North Pacific where anthropogenic Pb deposition is high, was seen at all seven sites. Lead concentrations in deep water in the stations further from shore are typically lower than in the surface layer and ranged from 11.2 to 51.6 pmol kg⁻¹. Lead isotopic signatures in deep water at these sites (²⁰⁶Pb/²⁰⁷Pb = 1.162–1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.448–2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.13–18.51) are offset from pre-anthropogenic values and suggest that anthropogenic sources have penetrated the deep water column. Elevated concentrations and isotopic signatures observed in the deep water at stations closer to shore, where sediment transport is prevalent, indicate that sedimentary input is a major source of dissolved Pb at these sites. Differences in Pb concentrations and isotopic signatures between samples collected from the Pacific Deep Water (PDW) water-mass during this study and those collected a decade ago suggest that Pb inputs even in deep water change on decadal scales.

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1. Introduction

Human activities have introduced high amounts of anthropogenic Pb into the environment through the use of leaded gasoline and other activities (Nriagu, 1979). The imprint of anthropogenic Pb in the ocean and its temporal evolution over time however are unevenly distributed in different major oceanic basins (Boyle et al., 2014; Echegoyen et al., 2014; Gallon et al., 2011). For example, the elevated Pb concentrations in the North Atlantic ocean have decreased since the phasing out of leaded gasoline, with Pb concentrations in surface water dropping from ~170 pmol kg⁻¹ in 1970s to ~20 pmol kg⁻¹ in 2010s (Boyle et al., 2014), but, surface water Pb concentrations in the North Pacific Ocean remained relatively high (up to 104 pmol kg⁻¹). The North Indian Ocean also has high Pb concentrations (82 pmol kg⁻¹) (Echegoyen et al., 2014) relative to the North Atlantic. This is likely a result of the late phase-out of leaded gasoline in Southeast Asia and the

rapid growth of coal burning and high temperature industries in Asian countries (Q. Li et al., 2012).

Understanding variations in Pb concentrations and isotope compositions in the ocean can provide information about anthropogenic and lithogenic sources, fluxes, and water mass mixing patterns of Pb (Alleman et al., 1999; von Blanckenburg et al., 1996; Wu et al., 2010). However, there are relatively few studies reporting seawater Pb concentrations and isotopes in the Pacific Ocean (Flegal and Patterson, 1983; Flegal et al., 1984; Gallon et al., 2011; Wu et al., 2010), particularly in the Northwestern Pacific Ocean, a region that might be impacted by the >20 fold increase in coal burning in China over the past three decades (Lee et al., 2014). A vertical advection/diffusion model presented by Wu et al. (2010) demonstrated how Pb concentration and isotopic composition in the central Pacific Ocean may have changed over the past few centuries following changes in the input of anthropogenic Pb. In marginal seas, however, lateral transport from sediments and the contribution of Pb from local sources, together with the unique hydrography of these basins, may lead to Pb concentrations and isotopic signatures that differ from those of the open ocean. In this work, we report Pb

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concentrations and isotopic compositions at 7 vertical profiles in the Western Philippine Sea (WPS), collected during the Taiwan GEOTRACES process study (March 2014). By comparing Pb concentrations and isotopic composition in the WPS to open ocean Pb signatures and to signatures of potential Pb sources, we are able to evaluate the impacts of atmospheric deposition and sedimentary inputs on seawater Pb in this region.

2. Materials and methods

2.1. Study site

The Philippine Sea is a marginal sea located in the Western Pacific Ocean, bordering the Philippines, Taiwan, and Japan from south to north. It is adjacent to the South China Sea on the southwest, the East China Sea to the northwest and the Pacific Ocean to the east. The Kuroshio Current is a strong western boundary surface current that transects the West Philippine Sea (WPS) flowing from south to north transporting water from the tropical Pacific Ocean to the Philippine Sea (Fig. 1). Water samples were collected at 7 vertical profile stations along an off shore transect in March 2014 (Fig. 1). Samples collected represent several oceanic water masses including the Western North Pacific Central Water (WNPCW) between 100 and 250 m, the North Pacific Intermediate Water (NPIW) between 400 and 900 m and the Pacific Deep water (PDW) mass below 2000 m depth.

2.2. Water sampling and analysis

Seawater samples were collected using Teflon-lined GO-FLO bottles (General Oceanics) on a trace metal clean sampling rosette. The GO-FLO bottles were moved into a trace metal clean van after seawater collection and each sample was filtered through an acid cleaned 0.2 μm capsule filter (PolycapTC, Whatman) into an acid washed, sample rinsed, 1 L low density polyethylene (LDPE) bottle and acidified with 4 mL of 6 M ultrapure HCl (final concentration 0.024 M). After collection, samples were shipped to University of California at Santa Cruz (UCSC) and stored at room temperature until they were analyzed. Typically 500 to 1000 g of each seawater sample was extracted by Nobias Chelate-PA1 resin (HITACH, Japan) for seawater matrix removal and Pb pre-concentration (Billler and Bruiland, 2012; Sohrin et al., 2008). The Pb in the seawater was then recovered by eluting the column with 3 mL 1 M HNO₃ and measured using a Thermo Element XR high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at UCSC for concentration determination. To estimate recovery yield, Pb free seawater (pre-treated with the Nobias Chelate-PA1 resin) was spiked with varying

amounts of a Pb standard and processed with every sample batch. The Pb concentrations of these standard spiked seawater samples were compared to standards of similar concentration prepared in 2% HNO₃. The Pb blank for the full procedure was $0.33 \pm 0.16 \text{ pmol kg}^{-1}$. Method accuracy and precision were assessed relative to GEOTRACES SAFe, S and D1 reference seawater samples (see Supplementary material Table S1). After Pb concentration measurements were made, samples were dried on a hot plate in preparation for Pb isotope ratio determination. All work was performed in a class 1000 clean lab inside class 100 laminar flow hoods. Inter-lab comparison of Pb concentration profiles at station 7 between the UCSC Marine Analytical lab and the Marine Biogeochemistry Laboratory in the Research Center for Environmental Changes, Academia Sinica in Taiwan, is shown in Supplementary material Fig. S1. Results show good agreement between data obtained using different methods; our method described above and an automated trace metal extraction system used in Taiwan (Wang et al., 2014a).

Lead isotope ratios in seawater samples were measured using a Thermo Neptune Plus multi-collector ICP-MS the University of California, Davis. Detailed information about measurement conditions and instrument settings are described by (Erhardt, 2013). Sample were dried down and then brought up in 2% HNO₃ to a concentration of at least 3 ppb, NBS SRM 997 Tl solution was added to obtain a Tl/Pb ratio of 0.2 to correct for the mass fractionation using an exponential law correction. The diluted samples were self-aspirated using a 50 $\mu\text{L min}^{-1}$ PFA nebulizer. An ESI APEX-IR desolvating system was used to increase sensitivity with the Neptune Plus configured with a jet sample cone and X-style skimmer cone. Samples (in sets of 5) were bracketed with a 5 ppb solution of the NBS SRM 981 Pb standard. The bracketing standard was used to correct for instrumental mass bias and the mass bias correction was applied to the measured samples. A 2% HNO₃ blank was analyzed after each sample with the analyzed blank subtracted from each sample to ensure no sample crossover contamination. The ²⁰⁴Pb signal in the 2% HNO₃ blank relative to the ²⁰⁴Pb signal of the samples was $< 10^{-4}$ for most samples, hence blank correction was negligible. The instrumental running conditions resulted in 0.5 V for ²⁰⁸Pb and had internal one standard deviations of 0.014 for ²⁰⁶Pb/²⁰⁴Pb, 0.013 for ²⁰⁷Pb/²⁰⁴Pb and 0.036 for ²⁰⁸Pb/²⁰⁴Pb.

To evaluate the influence of the pre-concentration procedure on Pb isotope ratios, NIST SRM 981 was added to Pb free seawater (processed using the Nobias Chelate-PA1 resin twice) and analyzed. The Pb concentrations used covered almost the whole range of seawater concentration observed in this study (15 to 150 pmol kg^{-1}). The samples with the NIST SRM 981 Pb addition were treated exactly as all other samples. Fig. S2A–C in the supplementary materials show that our sample processing did not result in fractionation of the ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb ratios.

3. Results

Lead concentrations in the upper 400 m of the water column in the WPS range from 36.2 to 68.1 pmol kg^{-1} and show a distinct sub-surface maximum at about 100 to 250 m associated with the Western North Pacific Central Water (WNPCW) water mass. Surface water concentrations are lower at stations 1 and 3 within the Kuroshio Current than in off-shore stations and are also lower at station 8 the furthest station from shore. Lead in deep water (2000 m and deeper, corresponding to Pacific Deep Water (PDW) water mass) are typically lower than in the upper 400 m and range from 11.2 to 19.1 pmol kg^{-1} with higher values close to the bottom at sites where sediments are re-suspended. Specifically Pb concentrations decrease with depth below the sub-surface maxima at sampling sites 4–8 which were farther from shore while at stations closer to shore (Stn. 1 and 3) Pb concentrations increase below 2000 m following the mid depth decrease (Fig. 2A–D).

Isotopic ratios show strong correspondence to the concentrations. In the upper layer (0–400 m) where concentrations are relatively high the isotope ratios are: ²⁰⁶Pb/²⁰⁷Pb = 1.162–1.170; ²⁰⁸Pb/²⁰⁷Pb = 2.445–

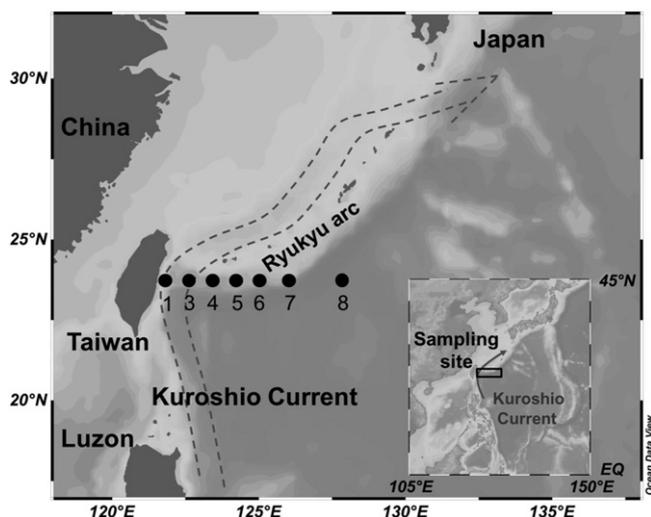


Fig. 1. Location of sampling stations in Western Philippine Sea.

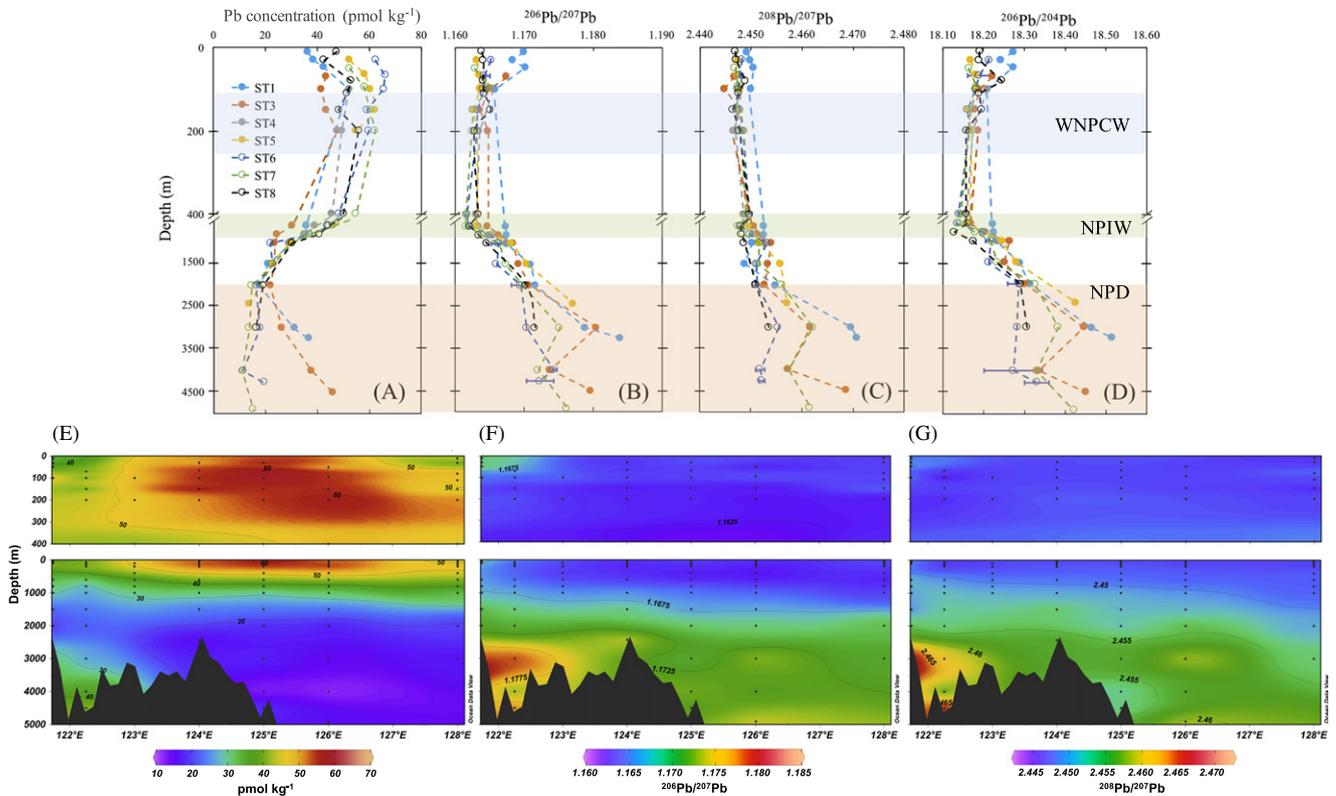


Fig. 2. Pb concentration and isotopic composition. (A) Pb concentration profile, (B) ²⁰⁶Pb/²⁰⁷Pb ratio, (C) ²⁰⁸Pb/²⁰⁷Pb ratio and (D) ²⁰⁶Pb/²⁰⁴Pb ratio. The error bar at station 6 represented analyses error (2 S.E.). (E–G) Full water column and zoomed in 0–400 m Pb concentration, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb profile in ocean data view, respectively.

2.451; ²⁰⁶Pb/²⁰⁴Pb = 18.14–18.27 and the ratios increase with depth as Pb concentrations decrease (²⁰⁶Pb/²⁰⁷Pb = 1.162–1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.448–2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.13–18.51). Similar to the concentration profiles, isotopic signatures at stations 1 and 3 are distinct. In the surface

layer ²⁰⁶Pb/²⁰⁷Pb ratios are higher compared to the other sites and below 2000 m the ratios at some depths at these sites are higher reaching ²⁰⁶Pb/²⁰⁷Pb = 1.184; ²⁰⁸Pb/²⁰⁷Pb = 2.471; ²⁰⁶Pb/²⁰⁴Pb = 18.51) (Fig. 2A–D). Two dimensional section profile plots for the

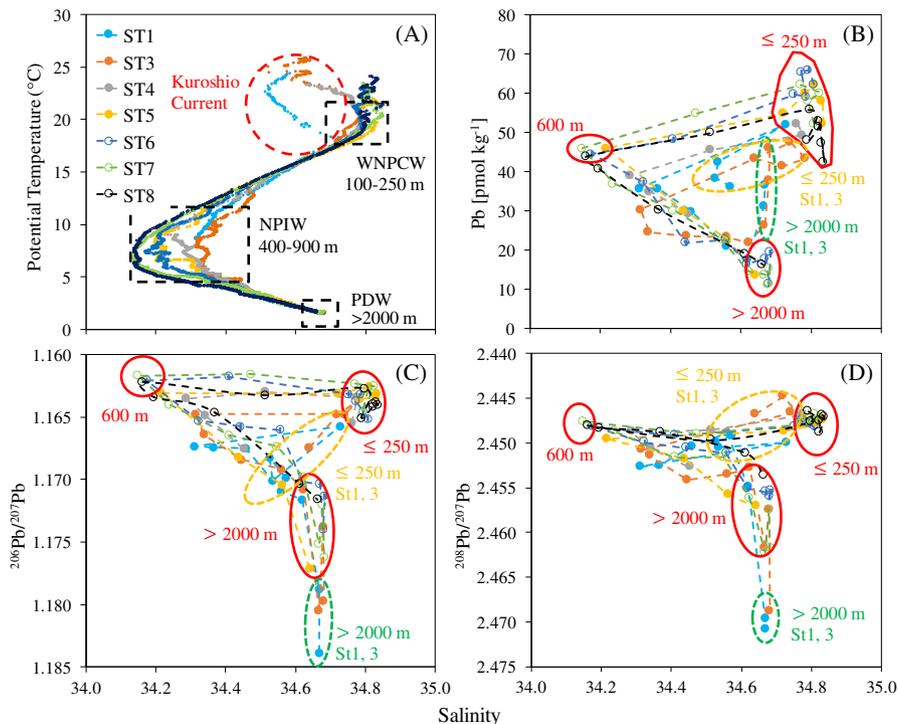


Fig. 3. Salinity vs (A) Potential temperature, (B) Pb concentration, (C) ²⁰⁶Pb/²⁰⁷Pb and (D) ²⁰⁸Pb/²⁰⁷Pb in the Western Philippine Sea. Note that yellow and green circles represent Pb concentrations and isotopic ratios at stations 1 and 3 in water shallower than 250 m and deeper than 2000 m, respectively.

whole water column depth and for the upper 400 m are shown in Fig. 2E–G), and all data are listed in Table S2.

4. Discussion

4.1. Pb concentrations and isotope ratios in the WPS

In the WPS Pb concentrations and isotope ratios as well as their trends with depth (Fig. 2) are related to water masses distribution in the area. A distinct surface water mass and three deeper water masses can be identified in the region based on their Temperature–Salinity (S–T) characteristics (Fig. 3A). The Kuroshio Current, a strong western boundary current, is a branch of the North Equatorial Current (NEC) that moves northward after the NEC encounters the Philippine coast. The Kuroshio Current occupies the surface water at the near shore stations in the study area. Stations 1 and 3 are within the Kuroshio Current and Pb concentrations in the surface water at these sites are lower compared to the other stations. The sub-surface layer throughout the sampling stations represents the WNPCW. The WNPCW is formed near the centre of the Western North Pacific (Emery and Meincke, 1986) and is then transported through subduction and advection to the Philippine Sea (PS) as a sub-surface salinity maximum typically between 100 m and 250 m depth. At intermediate depth the North Pacific Intermediate Water (NPIW) is present. This water mass originates at the west Pacific subtropical gyre and moves towards the south while sinking to water depths between 400 and 900 m in the Western Pacific including the WPS (You et al., 2000). The deep water mass in the region is the Pacific Deep Water (PDW) which is derived from the shallower Circumpolar Water in the Southern Ocean and can be found below 2000 m at our sites (Mantyla and Reid, 1983).

4.1.1. Near surface water Pb in the WPS

The Pb concentrations and isotope ratios in the WPS near surface water at the 7 stations sampled show some small differences. Specifically, the two sites closest to shore (stations 1 and 3) have lower Pb concentrations and Pb isotope ratios that are distinct from the offshore sites (stations 5 to 8), which are more similar to each other (Fig. 2). Near surface water at stations 1 and 3 are expected to have a higher influence of atmospheric Pb deposition as they are closest to land (Taiwan) a potential source of high Pb atmospheric aerosols. However, they have lower Pb concentrations than the offshore samples (15 pmol kg^{-1} lower than at station 8). Near surface water isotopic signatures of the Pb at these stations are also distinct ($^{206}\text{Pb}/^{207}\text{Pb} = 1.167\text{--}1.170$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.447\text{--}2.451$ and $^{206}\text{Pb}/^{204}\text{Pb} = 18.22\text{--}18.27$). This suggests that sites 1 and 3 are within a different water mass influenced by different Pb sources than the open ocean surface water. This grouping is likely because the

offshore stations are less impacted by the influence of the Kuroshio Current (see Fig. 3A T–S diagram). Specifically, the Kuroshio Current dominates near surface water at station 1 and is also present at station 3 and to some degree at station 4, as can be seen in the salinity of these waters (Kuroshio Current ranged from 34.49 to 34.70 while offshore sites salinity ranges from 34.76 to 34.85; Fig. 3A). The Kuroshio Current is coming from the Equatorial Pacific Ocean (southeast of the WPS), an area with less anthropogenic impact and lower atmospheric deposition. The lower concentrations close to shore also suggest that Taiwan is not the main source of aerosols to the region. The high speed of the Kuroshio Current also leads to a short residence time of the near surface water in the region allowing for less aerosol deposition to accumulate. Consequently, the overall Pb concentrations are lower and isotopes are slightly different from offshore sites although the Pb isotopic composition still carries the dominant signature of anthropogenic Pb.

A recent study reports that in a coral from around Vietnam the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has decreased from 1.191 to 1.195 before the mid-1950s to ~ 1.165 in 2004 (Chen et al., 2016a). This change indicates that Pb from Asian emissions may be impacting the whole region. In order to better understand Pb sources to the WPS, we applied a triple-isotope plot ($^{208}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$, Fig. 4) to distinguish between aerosol particles collected from Taipei, Taiwan and regional Asian aerosol signatures. Based on the plot, the Pb signature in seawater <400 m in the WPS is likely due to the input of aerosols from Asian countries throughout the region and not specifically from Taiwan. This Pb signature is similar to that reported for the anthropogenic sources to the North Pacific by Gallon et al. (2011) and consistent with the observation of lower Pb concentrations in near surface water at stations 1 and 3 despite the proximity to Taiwan.

Among the offshore stations, near surface Pb concentration at station 8, the station furthest from shore and the most representative of open ocean conditions are somewhat lower than at stations 5–7 (Fig. 2). This is likely due to a combination of lower input from atmospheric Pb due to distance from land and less influence of water from the South China Sea, which has higher surface Pb concentration and could be a source of Pb in this area. Indeed seawater Pb concentrations in South China Sea (Ho et al., 2010) are higher than those of the WPS (up to 126 pM) and any mixing with this water mass will increase Pb concentrations in the WPS. The Pb isotope ratios at station 8, however, didn't show distinguishable difference from stations 5 to 7 (Fig. 2B, C and D). It is possible that the Pb in the near surface waters throughout this region (East and South China Seas and the WPS offshore stations) is dominated by similar sources; hence the isotope signatures are indistinguishable, despite differences in concentrations.

Collectively, the near surface water Pb data indicate that near surface waters at the WPS are all receiving anthropogenic Pb (with a

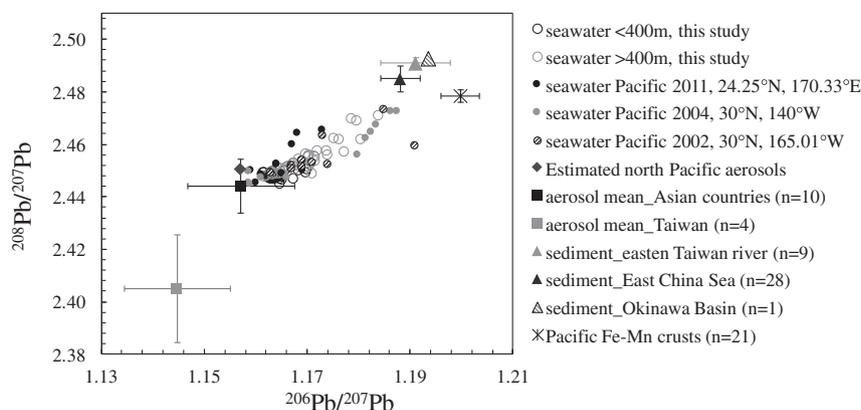


Fig. 4. Triple-isotope plot of Pb in WPS seawater in this study and Pacific Ocean seawater (Zurbrick, 2014; Wu et al., 2010), estimated north Pacific aerosols (Gallon et al., 2011), average Asian countries aerosols from Korea, Japan, China and Vietnam (Bollhöfer and Rosman, 2001), average Taiwan aerosols (Hsu et al., 2006), sediments (Dou et al., 2016; Wang et al., 2014a, 2014b; Bentahila et al., 2008) and Pacific Fe–Mn crusts (von Blanckenburg et al., 1996). The error bars represent 1 S.D.

$^{206}\text{Pb}/^{207}\text{Pb} = 1.157$; Gallon et al., 2011) which is mixed to varying degrees by different water masses, the Kuroshio Current with low Pb concentrations (with weaker anthropogenic signature) close to shore and waters from the East and South China sea (with higher Pb concentration and a strong anthropogenic signature) offshore. The near surface water Pb concentrations in this region are lower than those seen in the East China Sea and the Indian Ocean suggesting that this area does not get as much atmospheric deposition as surface waters in the East China Sea (Mahowald et al., 2005) and the Indian Ocean (Echegoyen et al., 2014) because it is located outside the main path of the Asian monsoon.

4.1.2. Sub-surface and deep water Pb in the WPS

In all profiles from the WPS, a clear sub-surface maximum (between ~100–250 m depth) in Pb concentration is observed, as also seen in all North Pacific profiles measured thus far (Flegal and Patterson, 1983; Schaule and Patterson, 1981; Wu et al., 2010; Zurbrick, 2014). The sub-surface concentration maximum has been attributed to a water mass carrying anthropogenic Pb that originates from subduction and advection of North Pacific surface water (Wu et al., 2010). From the T-S diagram and a plot of Pb concentration vs. salinity (Fig. 3A and B), we can identify that this concentration maximum is associated with the WNPCW which originates near the centre of the Western North Pacific (Emery and Meincke, 1986); indeed atmospheric deposition of Pb is currently, and has been for decades, high in the zone where the WNPCW originates at the Western North Pacific Ocean around 40°N resulting in the distinct sub-surface signatures (higher Pb concentration and slightly lower $^{206}\text{Pb}/^{207}\text{Pb}$).

Despite the clear concentration maximum in the sub-surface (and change in salinity), at the offshore stations the Pb isotope ratios associated with the sub-surface maximum show only a small difference from the surface waters above (Pb ratios between 100 and 250 m $^{206}\text{Pb}/^{207}\text{Pb} = 1.1623\text{--}1.1651$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4465\text{--}2.4487$) or the water below (400–900 m). From the T-S diagram (Fig. 3A) the NPIW occupies the depth around 400–900 m. The west part of NPIW is dominated by Okhotsk Intermediate Water (OIW) which originates at the west Pacific subpolar gyre (You et al., 2000). Indeed, these isotope ratios are consistent with those reported for the western Pacific subpolar surface water (Zurbrick, 2014). Overall, while a small difference is observed particularly in station 1 the differences in Pb isotope ratios of surface water, the WNPCW and the NPIW are relatively small and may suggest similarity in Pb sources (e.g. anthropogenic emissions possibly from China) or different sources with similar isotopic signatures.

Deep water Pb concentrations in our samples are higher than those reported for the north eastern and south Pacific Ocean (Wu et al., 2010). Specifically, at station 8 at 3000 m, the Pb concentration is 16.3 pM while in the south Pacific, the source of this deep water, it is only about 1.5 pM. This suggests that >85% of Pb observed in the WPS deep water was contributed by atmospheric Pb input via vertical transportation during water mass propagation from the south Pacific to the WPS. Alternatively, there could be a local lateral source of Pb contributing to the deep water Pb inventory in this region. Isotope ratios in the deep water below 2000 m at stations 5 to 8 ranged from 1.1695 to 1.1772 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.4512–2.4623 for $^{208}\text{Pb}/^{207}\text{Pb}$, these values are different from the isotopic signatures of surface sediments in the WPS with $^{206}\text{Pb}/^{207}\text{Pb} = 1.1805$ and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4782$ (Bentahila et al., 2008) or those from the southern Okinawa Trough ($^{206}\text{Pb}/^{207}\text{Pb} = 1.1958$; $^{208}\text{Pb}/^{207}\text{Pb} = 2.4954$; (Dou et al., 2016)), and are closer to surface water signatures of the eastern Pacific Ocean (Wu et al., 2010; Zurbrick, 2014) and western/central Pacific Ocean sampled in 2002 (Zurbrick, 2014). This deep water Pb isotopic signature in the WPS agrees with deep water values reported in Zurbrick (2014) for the western/central Pacific Ocean sampled in 2011. Zurbrick (2014) proposed that higher Asian anthropogenic Pb input to the west Pacific Ocean resulted in a change in the Pb isotope ratios in the deep water of the Pacific Ocean between 2002 and 2011. It is likely that the deep water in the WPS also shows this shift in Pb isotope ratios towards

increased anthropogenic influence and may indicate similar anthropogenic Pb sources impacting deep water throughout most of the western Pacific Ocean. A recent laboratory study indicates a rapid (days–months) Pb isotope exchange between seawater and suspended particulate materials (Chen et al., 2016b), which is consistent with fast changes in deep water Pb signature in the western Pacific Ocean resulting from high anthropogenic Pb inputs and rapid Pb isotope exchange between seawater and particles.

It is possible that since the WPS is geologically closer to the continent, it receives higher anthropogenic Pb from atmospheric deposition. Indeed, two years of marine aerosol collection in the East China Sea show that overall Pb solubility is over 30% (Hsu et al., 2010) and Mackey et al. (2015) emphasize the rapid dissolution of atmospheric Pb in seawater. However, if that were the case one would expect that the surface Pb concentration in WPS would also be elevated. In this study, surface Pb concentrations are not higher than at other locations in the centre and eastern Pacific (Fig. 5), hence local atmospheric deposition is likely not higher in the WPS when compared to other Pacific sites. Regardless we do see high Pb concentration in the deep water specifically at stations 1 and 3 therefore there must be other sources of lead to the deep water at this location.

One potential source of Pb to the deep waters in the WPS, which are distinct from the open Pacific Ocean deep water, can be gleaned from the Pb concentration trend below 2000 m at stations 1 and 3. From 2000 m to the bottom, Pb concentration increases from 17.7 to 36.7 pmol kg⁻¹ at station 1 and from 21.9 to 46.1 pmol kg⁻¹ at station 3 (Figs. 2A and 6A). Although terrestrial inputs seem unlikely at this depth, a previous study reveals the possibility that sediments could be transported to the deep ocean basin during tropical cyclone events around Taiwan (Kao et al., 2010). Furthermore, another study showed that sediment transport to depth can result from flood runoff from Taiwan rivers, as well as following large earthquakes (Hsu et al., 2004). The deep water mass at stations 1 and 3 is not distinguishable from deep water at other stations sampled based on the T-S diagram (Fig. 3A). However, Pb concentrations are much higher below 2000 m at these two stations (Fig. 3B). Further more, beam transmittance data show that below depths of 2000 m, suspended particle levels are higher at stations 1 and 3 than at stations 5, 6, 7 and 8 (Fig. 6B). In order to quantify the contributions of sediment inputs to the WPS deep water at stations 1 and 3, we use the average concentration from stations 6, 7 and 8 at the depth of 3000 m as representative of regional deep water signatures, the contributions of sediment input of Pb at stations 1 and 3 at 3000 m can then be calculated by mass balance to contribute as much as 49% and 40%, respectively.

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios associated with the high concentrations in the deep water at stations 1 and 3 are higher than those seen at similar depths in off shore stations (Figs. 3C–D and 6C), and are closer to Pb signatures of sediment seen in the East China Sea (Wang et al., 2014b), the WPS (Bentahila et al., 2008), eastern Taiwan rivers and the Okinawa Trough (Dou et al., 2016). This similarity in isotope signatures of these potential sources and deep water in stations 1 and 3 indicates that sediments could be an important source of Pb to the deep water at stations close to shore in the WPS. This is seen also in Fig. 4 where the seawater Pb isotopes in the WPS (particularly for samples below 400 m depth) lay on the trend between anthropogenic aerosols and sediments of the Okinawa Basin, East China Sea and rivers in Taiwan (Fig. 4), further supporting sediment transport as a local source of Pb to deep water in the WPS. Notably none of the isotope ratios we measured seem to be similar to pre anthropogenic Pb signatures as recorded in Pacific Fe–Mn crusts that represent pre-anthropogenic Pb.

4.2. Comparison between the WPS and other North Pacific Ocean Pb profiles

While surface Pb concentrations in the North Atlantic Ocean have decreased >8-folds over the last four decades as a result from phasing out of leaded gasoline, the Pb concentrations in the upper water in the

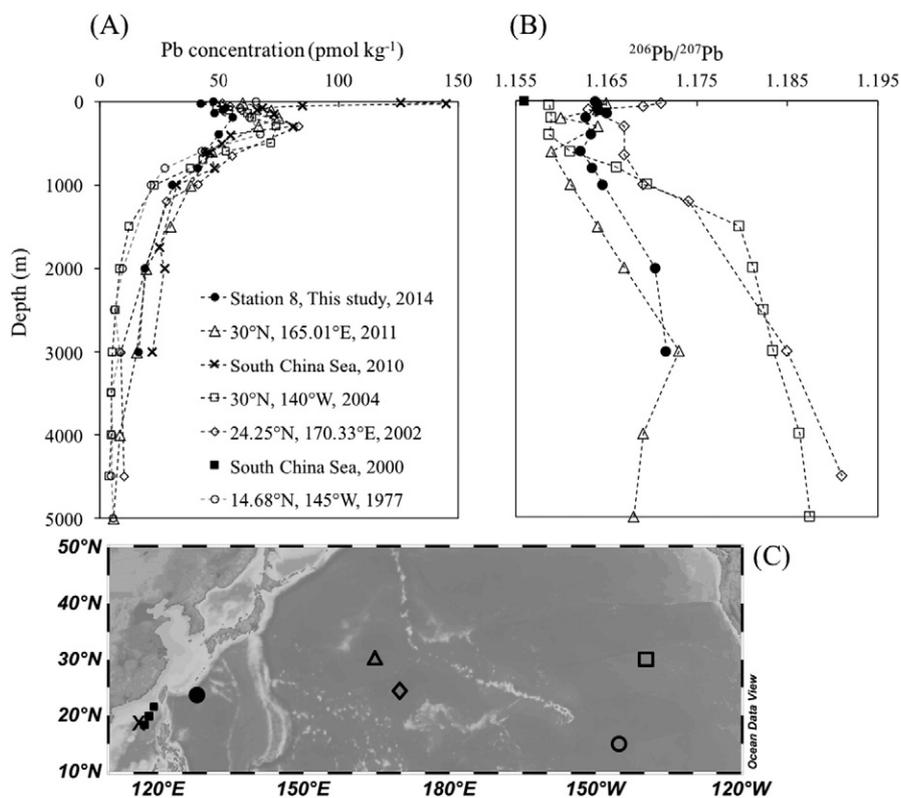


Fig. 5. Comparison of Pb concentration and ²⁰⁶Pb/²⁰⁷Pb of North Pacific seawater. Include seawater collected in 1977 (concentration only) (Schaule and Patterson, 1981), 2000 (²⁰⁶Pb/²⁰⁷Pb only, mean value from three surface water samples at South China Sea) (Lee et al., 2014), 2004 (Wu et al., 2010), 2002 and 2011 (Zurbrick, 2014), 2010 (concentration only, South China Sea) (Ho et al., 2010) and station 8 in this study.

North Pacific Ocean remain relatively high due to the rapid growth of coal burning in China and other Asian countries in the last decades. The typical Pb concentration trends with depth observed in the off shore stations of the WPS are similar to those seen in previous studies from the North Pacific open ocean, with low concentrations in the surface, a sub-surface maximum and a decrease with depth below the maximum (Flegal and Patterson, 1983; Schaule and Patterson, 1981; Wu et al., 2010; Zurbrick, 2014; Zurbrick et al., 2012). The similarity is indicative of the basin-wide anthropogenic impact on Pb in the Pacific Ocean. Comparing these data to the model prediction of natural Pb distribution in the ocean reported by Henderson and Maier-Reimer (2002), the anthropogenic contribution of Pb in this region is >8-folds larger than Pb from natural sources.

Isotope signatures of Pb in surface and sub-surface water are also comparable to those seen in previous studies (Gallon et al., 2011; Wu et al., 2010; Zurbrick, 2014). ²⁰⁶Pb/²⁰⁷Pb = 1.162–1.170 and ²⁰⁸Pb/²⁰⁷Pb = 2.445–2.451 are close to the values which Gallon et al. (2011) estimated for anthropogenically sourced Pb in the North Pacific Ocean (²⁰⁶Pb/²⁰⁷Pb = 1.157 and ²⁰⁸Pb/²⁰⁷Pb = 2.451). A comparison of

Pb concentrations and isotope ratio in the water column at station 8 in the WPS (the station furthest away from shore) to two sites from the North Pacific Subtropical Gyre (NPSG) collected in 2002 and 2011 (Zurbrick, 2014), two sites from eastern Pacific Ocean collected in 1977 and 2004 (Schaule and Patterson, 1981; Wu et al., 2010) and results from the South China Sea (SCS) collected in 2000 (Lee et al., 2014) and 2010 (Ho et al., 2010) reflects the similarity in trends as well as the differences (Fig. 5). Lead concentrations and isotope ratios in the near surface and sub-surface water at station 8 are comparable to those at the other locations. In deep water, station 8 concentrations are close to those in the NPSG and SCS collected after 2010 but are higher than those in the NPSG and eastern Pacific Ocean collected in 2002 and 2004, respectively. Specifically the isotopic signatures of Pb in the deep water below 2000 m at station 8 in the WPS are comparable to those seen in the western Pacific Ocean at 30°N in 2011 (Zurbrick, 2014) (²⁰⁶Pb/²⁰⁷Pb = 1.167–1.173 and ²⁰⁸Pb/²⁰⁷Pb = 2.450–2.466), the concentration in the WPS deep water is also comparable to this western Pacific Ocean deep water (16.3 and 15.3 pmol kg⁻¹ at 3000 m, respectively). These concentrations are higher than those in

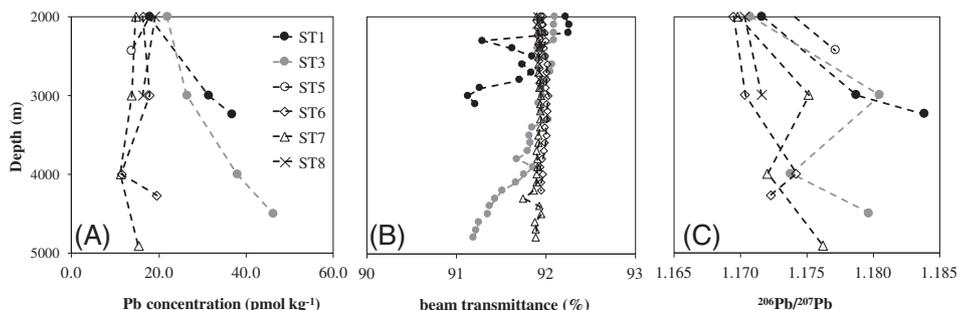


Fig. 6. Deep water profiles at stations 1, 3, 5, 6, 7 and 8 (A) Pb concentration (B) beam transmittance and (C) ²⁰⁶Pb/²⁰⁷Pb.

water sampled in western Pacific Ocean in 2002 (8.9 pmol kg^{-1} at 3000 m) (Zurbrick, 2014) and eastern Pacific Ocean in 2004 (5.1 pmol kg^{-1} at 3000 m) (Wu et al., 2010) (Figs. 2A and Fig. 5A). The concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ differences in deep water among sites seem to be related to the years of collection, with samples collected in 2002 and 2004 (Wu et al., 2010; Zurbrick, 2014) being similar to each other, while samples collected in 2011 (Zurbrick, 2014) and 2014 (this study) both show considerably lower values and are similar to each other. We note that while these stations are far from each other the deep water at all sites represent a single water mass the PDW. Lead concentration and isotope signatures are influenced by regional water mass, as well as terrestrial and anthropogenic inputs. The observed variability among sites within the PDW mass collectively suggest that Pb in seawater is very dynamic spatially and temporally showing distinct differences for profiles collected at NPSG from the same water mass (PDW) less than a decade apart (Fig. 5), while profiles collected at the same time only 180 km apart (e.g., stations 1 and 3 relative to the other stations in the WPS) also differing from each other. This is consistent with the short residence time of Pb in surface seawater. The trend towards lower $^{206}\text{Pb}/^{207}\text{Pb}$ in the deep water over time is likely due to the larger contribution of anthropogenic Pb which penetrates into deeper water masses since the increase in coal use in Asia.

5. Conclusion

Several depth profiles of seawater Pb concentrations and isotopic composition in the WPS have been studied. Possible sources of Pb to this region have also been identified. Overall Pb concentration profiles are comparable to those reported for other locations in the North Pacific Ocean. The upper layer seawater Pb in the WPS has an anthropogenic signature related to a mixture of Pb from aerosol emissions from Asian countries rather than local aerosol from Taiwan. This anthropogenic input is also seen in deep water. Deep water isotopic signatures also suggest sediment transport from the continental arc and other land sources as an important source of Pb to deep water in the WPS. Overall, this study indicates that the Pb system in the Pacific Ocean is very dynamic, concentrations and isotopes change even in deep water on decadal scales. This rapid change should be considered in future Pb studies when sediment and coral materials are used to reconstruct past Pb signatures.

Acknowledgement

We thank the technical support of the personnel of R/V Ocean Research V, and TORI (Taiwan Ocean Research Institute). We thank Bo-Shian Wang, Hsu-Han Yang, Chih-Ping Lee, Shun-Chung Yang and Wen-Hsuan Liao for their technical support on sampling and analysis. This work was supported by NSF-OCE grant 0850467 to Adina Paytan.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2016.12.007>.

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