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Key Points:

- The dissolved lead along the Kuroshio core shows highly similar concentrations at the same density plane, signifying isopycnal transport
- The lead isotope ratios in the Kuroshio surface water indicate a strong contribution from Chinese aerosols
- The lead isotope ratios in the East China Sea and Kuroshio deep water indicate an isotope mixture between aerosols and upper crust

Supporting Information:

Supporting Information may be found in the online version of this article.

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Dissolved Lead (Pb) Concentrations and Pb Isotope Ratios Along the East China Sea and Kuroshio Transect—Evidence for Isopycnal Transport and Particle Exchange

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Abstract Lead (Pb) isotopes are widely used in tracing processes that transport Pb within the environment due to the globally spread Pb pollution. In today's ocean, Pb is mainly sourced from anthropogenic emissions and is removed by particle scavenging. However, recent efforts involving Pb isotopes have started to indicate that sediments at ocean boundary, either suspended or benthic, are a previously underestimated source and sink of Pb to the seawater dissolved pool. To assess the contributions of Pb from seawater-sediment boundary, we measured the dissolved Pb concentrations and isotopic compositions in seawater from the outer East China Sea (ECS) and along the Kuroshio. Along the Kuroshio, depth profiles exhibit highly similar Pb concentrations across constant density planes, suggesting isopycnal transport. Pb isotope ratios in most of the samples show strong contributions of aerosol Pb, except for seawaters from the ECS and deep Okinawa Trough (>800 m), which show evidences of crustal Pb contribution. The Okinawa Trough deep water has overlapping Pb isotope ratios with ECS water, where the suspended particulate matter is abundant. Our data on Pb isotopes in the ECS and the Okinawa Trough deep water, together with data from previous studies at other continental margins suggest that the seawater-sediment boundary along the continental shelves may be an important source and sink in marine Pb cycling.

Plain Language Summary The distribution of lead in the Western Pacific remains highly limited, despite China has become the world's largest environmental lead contributor. To fill in the gap, we report the dissolved lead concentrations and isotope compositions in seawaters along the Kuroshio and one station in the outer shelf of the East China Sea (ECS). Along the Kuroshio path, we found similar lead concentration in seawater at similar density layer, suggesting lateral transport of lead along the Kuroshio. The lead isotopes in the Kuroshio surface and intermediate water (0–800 m) suggested more than 75% contribution from Chinese lead, while the isotopic composition in the deep waters of the Okinawa Trough (>800 m) and the ECS (0–100 m) show contributions from the natural crust. These observations underscore the exchange of lead between seawater and crustal sediment at ocean boundary, which has been increasingly revealed as an important source and sink in marine lead cycling.

1. Introduction

Exchanges of water, dissolved chemical species, and particulate matter are expected to occur at land-ocean interfaces (Jeandel, 2016; Milliman & Farnsworth, 2011), which is an important process supplying ingredients in marine elemental cycling. Quantifying the trace element and isotope fluxes at ocean boundaries helps to elucidate the processes that impacts sources and sinks of these elements, and helps to predict their response to the on-going ocean changes (Homoky et al., 2016).

Interactions at the seawater-sediment boundary have received increasing attention in recent decades, as systematic investigations of some trace elements and isotopes (e.g., strontium Sr and neodymium Nd) clearly demonstrate exchanges do happen at sediment-water interface (e.g., Jeandel et al., 1998). These exchanges are observed through changed isotopic composition as water masses pass through and along ocean boundaries (e.g., Amakawa et al., 2000; Grasse et al., 2012; Jeandel et al., 1998; Lacan & Jeandel, 2005) or through observations in closed-system experiments (Jones et al., 2012; Pearce et al., 2013). Further budget calculations of marine Nd cycling have concluded that the current observed distribution of Nd isotope in the seawater cannot be explained without a significant particle exchange component (e.g., Lacan & Jeandel, 2005), underscoring the importance of sediment-water exchange in marine element cycling.

Lead (Pb) is a naturally occurring toxic element, and is found in the ocean from both natural and anthropogenic sources (Boyle et al., 2014). Natural sources include dissolution of natural dust (Duce et al., 1991), volcanic aerosols, fluvial (Patterson & Settle, 1987), and hydrothermal sources (Alt, 2003), while anthropogenic sources include usage of leaded gasoline in the recent history (phased out between 1990 and 2020, UNEP, 2020), coal combustion, incineration, metal smelting, and other high temperature industrial activities (Nriagu, 1989). Natural and anthropogenic sources of Pb can be differentiated by Pb isotope ratios in a variety of locations around the world. Pb isotopes in natural continental crust generally have $^{206}Pb/^{207}Pb$ between 1.18 and 1.22 (Bodet & Schärer, 2001; Hamelin et al., 1997; Zhu et al., 2010), which is distinct from the anthropogenic Pb emitted from Europe ($^{206}Pb/^{207}Pb$ as 1.14–1.16, Kelly et al., 2009), Indian subcontinent, South East Asia ($^{206}Pb/^{207}Pb$ as 1.14–1.16, Bollhöfer & Rosman, 2000, 2001; Carrasco et al., 2018; Kayee et al., 2021), and East Asia ($^{206}Pb/^{207}Pb$ near 1.16, Bollhöfer & Rosman, 2001 and references therein, Table S1 in Supporting Information S1). The differences in Pb isotopic composition among various sources make it a useful tool to identify different Pb sources across a reasonably large geographic range.

As indicated by Pb isotopes, the primary source of Pb in today's ocean is of anthropogenic origin (Boyle et al., 2014), transported through aeolian pathways (Flegal, 1986). These isotopic compositions of Pb provide insights on the sources and processes that redistribute the Pb across the ocean; therefore, Pb isotopes are widely used in quantifying the spatial-temporal distributions of Pb in response to anthropogenic emissions (e.g., Alleman et al., 1999; Boyle et al., 2020; Gallon et al., 2011; Weiss et al., 2003), and characterizing processes in oceanography that transport Pb within the oceans (Lee et al., 2015; Noble et al., 2015; Wu et al., 2010). However, as a particle-reactive element, knowledge about the exchange of Pb in seawater with sediments in marine Pb cycling remains relatively understudied.

Regarding sediment-water interaction, numerous early studies using the radionuclide ^{210}Pb showed that a good portion of Pb was attached to particulates in both oceanic (Bacon et al., 1976; Murray et al., 2005; Wei et al., 2011) and estuarine settings (Baskaran & Santschi, 1993; Baskaran et al., 1997; Benninger, 1978). These studies pointed toward efficient scavenging by sediment particles and imply that other isotopes of Pb should behave similarly. However, significant differences exist between pathways of stable Pb isotopes and ^{210}Pb. The ^{210}Pb is produced by the radioactive decay of gaseous radon, and deposited back to the Earth's surface through atmospheric deposition; while at continental margins, much of the stable Pb isotopes are contained within the mineral grains and released to seawater dissolved pool during weathering (Erel et al., 1991). In this case, at continental margins, the results concluded from ^{210}Pb may not be directly applicable to other isotopes of Pb. Early studies on ^{210}Pb did not include data on stable Pb isotopes. Therefore, the exchange of Pb between dissolved and particulate pool is hard to observe by these radionuclide approaches.

With the recent advancements of analytical capability for Pb isotopes in seawater and improved geographical coverage, the two-way exchange of Pb between sediment and seawater are being revealed and is receiving increasing attention. A closed system isotope exchange experiment using waters from Johor River estuary (in equatorial Southeast Asia) showed that fluvial particulates could alter Pb isotope ratios in the dissolved pool without much change in its concentration (Chen et al., 2016), similar to other elements such as Nd and Sr (Jones et al., 2012; Pearce et al., 2013). In this case, in ocean margins where a difference in Pb isotopes between natural and anthropogenic source exists (e.g., Eastern Indian Ocean, North Western Pacific, Equatorial Southeast Asia), sediment-water exchange should potentially be observable as an altered Pb isotopic composition in seawater in continental shelf seas and slopes, similar to other isotopes (Amakawa et al., 2000; Grasse et al., 2012; Jeandel et al., 1998; Lacan & Jeandel, 2005).

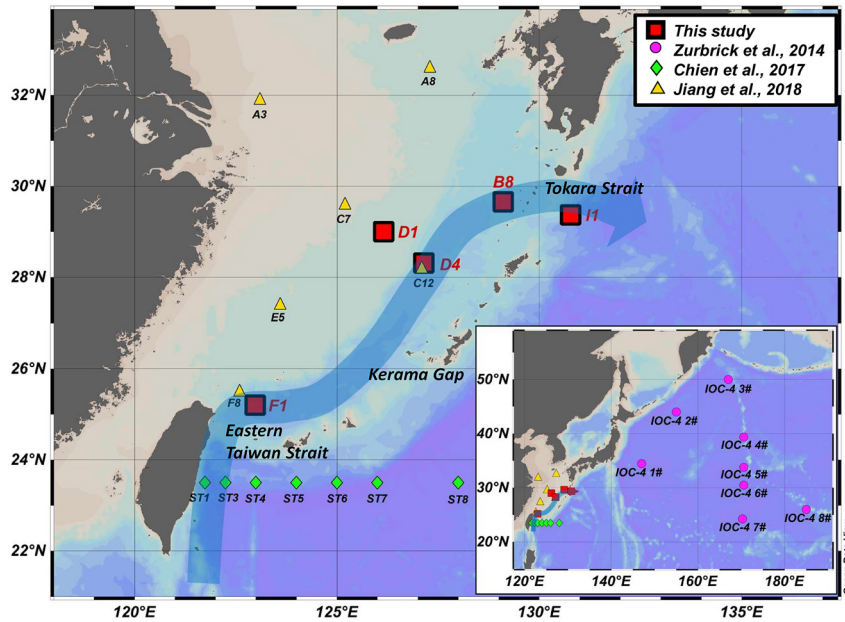

Figure 1. Map of the sampling cruise together with stations of previous studies in comparison. Previous studies including Jiang (2021) in yellow filled triangles, Chien et al. (2017) in green filled diamonds and Zurbrick et al. (2017) in magenta filled circles (inset map). The flow of Kuroshio core is also illustrated in blue arrows.

Some recent field observations of Pb isotope in the Northern Indian Ocean and Western Pacific indeed suggested sediment-water exchange. Profiles of dissolved Pb concentration and isotopic composition were reported in the northern Indian Ocean, the $^{206}Pb/^{207}Pb$ isotope ratio at a station in the Bay of Bengal was 0.05–0.10 higher than stations in the Arabian Sea at the similar latitude, while their concentration profiles were almost identical (Lee et al., 2015). The difference in isotopic composition was observed at all depths, and since there is no deep-water formation in the Bay of Bengal, the difference in Pb isotopes between the Bay of Bengal and the Arabian Sea cannot be explained by different anthropogenic sources. The isotopic difference could neither be explained by different water masses as the deep-waters entering the Bay of Bengal and Arabian Sea have similar isotopic compositions. In this case, the observed Pb isotope difference could be best explained by the exchange with crustal sediments delivered by regional rivers into the Bay of Bengal (Lee et al., 2015).

Exchange of Pb isotopes with sediments have also been observed in the West Philippine Sea. A recent study of Pb isotopes in the West Philippine Sea reported anomalous Pb isotope ratios in two profiles along the continental shelf slope compared to more open ocean sites, suggesting isotope exchange occurred along ocean boundaries by reacting with sediments on the shelf slopes (Chien et al., 2017). Although these recent studies are still limited by geographical coverage (i.e., limited by the number of stations and paucity of sites near end members), they illustrate that boundary exchange is a potentially important process for marine Pb cycling and deserves further investigation. To this end, we report profiles of seawater Pb concentration and Pb isotope ratios along the Kuroshio, a western boundary current that sweeps along the Northwestern Pacific Margin. We also include a profile from the East China Sea (ECS) to illustrate sediment exchange close to potential end members (e.g., continental shelves and shelf slopes).

2. Methodology

2.1. Site, Cruise, and Sampling

The Kuroshio is a western boundary current located in the North Pacific, starting from the equatorial region of the west Philippine Sea, then flowing northward through the Okinawa Trough (sill depth ~775 m, Eastern Taiwan Strait) to the east of the ECS at 24°–30°N, exiting the Okinawa Trough from the Tokara Strait at near 30°N (sill depth ~690 m, Figure 1) and entering the western Pacific. Besides these two straits, some intermediate-to-deep water also enters the Okinawa Trough through the Kerama Gap (Figure 1), located near 26°N, 127°E, with

a sill depth of ~1,100 m (Nakamura et al., 2013). As a western boundary current, Kuroshio is expected to exchange water, sediment and other materials with the adjacent marginal seas, such as the East China Sea (ECS), a marginal sea located near the most populated region of China, receiving large amount of anthropogenic Pb (Jiang et al., 2018, Zurbrick et al., 2017) and lithogenic material from regional sources (Ren et al., 2015).

Sampling cruises were conducted between September and October 2015, by the R/V Hakuho-Maru as the Japanese GEOTRACES cruise GP06 (or KH15-03, https://www.bodc.ac.uk/resources/inventories/ cruise_inventory/report/16015/) along the Okinawa Trough segment of Kuroshio. The sampling sites are F1, D4, B8 and I1, forming a transect from upstream to downstream of the Kuroshio; and D1 is located in the continental shelf of ECS as an endmember of the marginal sea. Profiles of seawater samples were collected using a carousel system (SBE-32, Seabird Scientific) mounted with trace metal clean Niskin-X bottles. The hydrographic data including the temperature, salinity, and depth were measured using a conductivity, temperature, and depth sensor (CTD, SBE-9-plus, Seabird Scientific) mounted on the carousel system (Nakaguchi et al., 2021).

Upon collection, the Niskin-X bottles with seawater were transferred into a plastic bubble room. The seawater samples were then filtered through 0.2 μm pore-size capsule filters (Acropak, Pall Industries, cleaned through GEOTRACES protocols) into 1.0 L acid-cleaned high-density polyethylene (HDPE) bottles and triple bagged before moving out the bubble. Those samples were transferred to our land-based clean lab in Singapore and acidified to pH < 2 with high-purity HNO_3 (Optima grade, Thermofisher) in a class-100 flow bench.

2.2. Determination of Pb Concentrations in Seawater

The Pb concentrations of the seawater samples were determined on an inductive coupled plasma mass spectrometer (ICP-MS, Agilent 8800) using isotope dilution methods. Pre-concentration of Pb from seawater was achieved using single-batch nitrilotriacetate (NTA) resin extraction (Lee et al., 2011). Briefly, an aliquot of ^{204}Pb-enriched spike (Oak Ridge National Laboratories) was added to each 1 mL of seawater sample and then adjusted with an ammonium acetate buffer to pH = 5.3. Then, an aliquot of NTA resin (~2,400 beads) was added directly into to each vial (Eppendorf 1.5 mL micro-centrifuge tubes, cleaned by GEOTRACES protocols) for Pb uptake. The samples with resin beads were kept on a shaker table to maintain in suspension for 4 days to allow the Pb to bind with the resin. The samples and resin were then rinsed for several times with ultrapure water, and then eluted using 0.1 M high purity nitric acid (Optima grade, Thermofisher) for ICP-MS analysis. On the ICP-MS, a fritted cap was added onto the capillary tube to expel the resin beads while running the eluted samples. This in-line fritted capillary tube reduces the blank by removing a conventional elution column step. To manage the precision and accuracy, all samples were run in at least triplicate and the Pb concentration was recorded if at least two out of three replicates agreed (n is given in the concentration data). The external reproducibility was compared with GEOTRACES SAFe D1, for which we report a Pb concentration of 26.4 ± 1.4 pmol/kg (n = 4), comparing well with the consensus value of 27.7 ± 2.6 pmol/kg (GEOTRACES, n. d.). In addition, we compared our Pb concentration profile of station D4 with a nearby station C12 from a previous study (Jiang et al., 2018). We found that the depth profiles of the two stations were generally comparable, except the profile in station D4 in this study was about 10 pmol/kg consistently lower than the station C12 from the previous study at all depths. The consistent offset between the D4 relative to C12 (sampled in August 2013, Figure S1 in Supporting Information S1) could be reasonably explained by the difference in time of sampling and the water masses sampled, as supported by the slight differences in the salinity profiles (Figure S1 in Supporting Information S1).

2.3. Determination of Pb Isotope Ratios in Seawater

Pb isotope ratios in the seawater samples were analyzed in both Boyle's laboratory at Massachusetts Institute of Technology (MIT) and in the Environmental Geochemistry Laboratory at Earth Observatory of Singapore and Asian School of the Environment, Nanyang Technological University (NTU) following an identical preparation method well-calibrated with other participating institutions for GEOTRACES (Boyle et al., 2012). The preparation method involved preconcentrating Pb from aliquots of seawater (100–300 mL) using a minimal addition of redistilled ammonia. The addition of ammonia triggers $Mg(OH)_2$ precipitation which scavenges Pb from the seawater. The $Mg(OH)_2$ precipitates were then redissolved in high purity 1.1 M HBr (Optima grade, Thermofisher) and loaded into AG-1X8 anion exchange resin (chloride form, 200–400 mesh, BioRad) columns to purify the Pb from the matrix through HCl-HBr ion exchange chromatography (Boyle et al., 2012). The column blank was typically less than 7 pg compared with the 1–2 ng of Pb in the seawater samples.

Table 1
The Measured Pb Isotopes in the Standard Reference Materials and Seawater Samples in This Study Compared to the Certified and Consensus Values

Reference materials	Source of measurement	$^{206}Pb/^{207}Pb$	2SE (ppm)	2SD (ppm)	$^{208}Pb/^{206}Pb$	2SE (ppm)	2SD (ppm)	$^{206}Pb/^{204}Pb$	2SE (ppm)	2SD (ppm)
NBS 981	This study	1.09346	55	104	2.16649	77	329	16.9493	333	1500
NBS 981	Certified	1.09333		721	2.16639		2807	N.A.		
NBS 981	Consensus (Yuan et al., 2016)							16.9406		35
NBS981	De Vera et al., 2021	1.0931		500	2.1678		900	N.A.		
Seawaters samples in this study										
D4 100 m	NTU	1.16378	55		2.10240	93				
D4 100 m	MIT	1.16412	181		2.10055	304				
D4 500 m	NTU	1.16611	34		2.10462	94				
D4 500 m	MIT	1.16649	122		2.10284	273				

Note. Five decimal points retained to illustrate the analytical precision.

At the MIT and NTU laboratories, different analytical methods were applied on the samples due to different instrumentations. Both laboratories employed a Multi-collector Inductive Coupled Plasma Spectrometer (MC-ICP-MS) and used a thallium (Tl) spike calibration method to correct mass biases during ICP-MS analysis (beta correction, Reuer et al., 2003). The MIT laboratory used a Micromass/GV IsoProbe with a Daly ion-counting detector measuring ^{204}Pb. In the NTU laboratory, a Thermo Scientific Neptune Plus was used for the Pb isotope analysis. The Pb stable isotopes were detected on Faraday cups equipped with 10^{11} Ω resistors, except ^{204}Pb which was measured on a cup connected to a 10^{12} Ω resistor because of its low signal intensity. Although ^{204}Pb was measured in the both laboratories, we are unable to report isotopic ratios with respect to ^{204}Pb due to the relatively low concentration of Pb (as low as less than 10 pmol/kg for total Pb) in some of these samples, limiting its precision. In this case, the $^{206}Pb/^{204}Pb$ was given as information value without detailed interpretation. Nevertheless, the ratios for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ for both the standard reference material NBS981 and seawater samples compare well with other laboratories (Table 1), and were interpreted in the later sections.

3. Results

3.1. Hydrography

The hydrography resolved from the temperature and salinity suggests several water masses layered from surface to bottom (Figure 2, Figure S2 in Supporting Information S1). In the top 100 m, two main water masses are observed, including a warm and fresh East China Sea (ECS) surface water with temperature higher than 22.5°C and salinity below 34.2, and a warm and salty Kuroshio surface water with temperature higher than 22.5°C and salinity higher than 34.6 (range 34.6–34.9). The lower salinity in the waters from ECS could be a result of regional fluvial freshwater input (Ren et al., 2015). At 100–250 m, the water mass has salinity higher than 34.8, signifying North Pacific Tropical Water, a water mass that is formed in 20–30°N, 160°E−140°W by subduction to a depth where the sigma-theta is ∼24.0 kg/m^3 and subsequently progresses westward (Katsura et al., 2013). Between 400 and 800–900 m depths, the temperature and salinity data show a local minimum that signifies for North Pacific Intermediate Water, a water mass that subducts from the region between the Kuroshio Extension and Oyashio front in the North Western Pacific (Talley, 1993). Only two stations in this study cover depths >1,000 m, and these stations are F1 in the southern Okinawa Trough and I1 in the Western Pacific. The water >1,000 m at station F1 is slightly warmer than station I1 (Figure S2 in Supporting Information S1); however, it is difficult to separate them into different water masses only with these two stations.

3.2. Depth Profiles of Pb Concentration

A section of Pb concentration is shown in Figure 2c, with detailed depth profiles shown in Figure 3. In the Kuroshio stations, dissolved Pb concentrations fluctuate at near 38 pmol/kg at the surface and show a distinct subsurface maximum with Pb concentration close to 57 pmol/kg at 200–400 m. The subsurface Pb maximum is

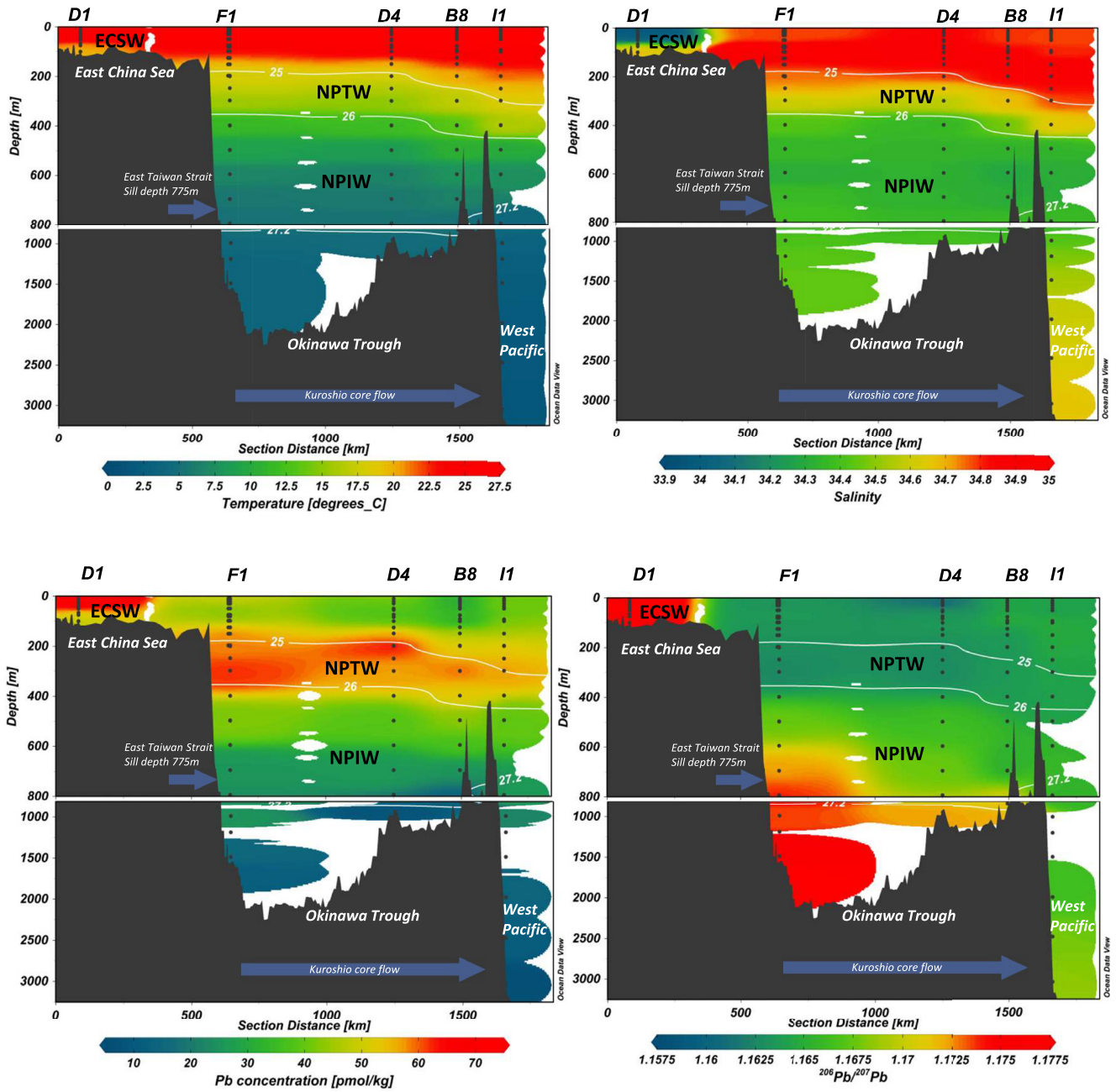

Figure 2. Section maps of (a) temperature; (b) salinity; (c) dissolved Pb concentration; and (d) lead isotope in $^{206}Pb/^{207}Pb$ ratios. The stations, key basins, key water masses, and the flow direction of Kuroshio are also illustrated. All stations except D1 are within the Kuroshio core. The white contours denote for sigma-theta planes (kg/m^3).

consistently observed in many studies across the North Pacific (Chien et al., 2017; Jiang et al., 2018; Nakaguchi et al., 2021; Zurbrick et al., 2017). Below the subsurface maximum, dissolved Pb decreases to depth, with ~10 pmol/kg at bottom. It is worth noticing that all stations along the Kuroshio (F1, D4, B8, I1) overlapped on the plot of dissolved Pb versus sigma-theta (Figure 3), making it a strong case for isopycnal transport of Pb along the Kuroshio.

The depth profile of Pb in the station D1 located at ECS shows higher concentrations compared to the Kuroshio at all overlapping depths. Higher Pb concentrations in the seawater of ECS are expected as the ECS is geographically closer to the most populated areas of China than Kuroshio, where more anthropogenic Pb can be transported through atmospheric/fluvial pathways.

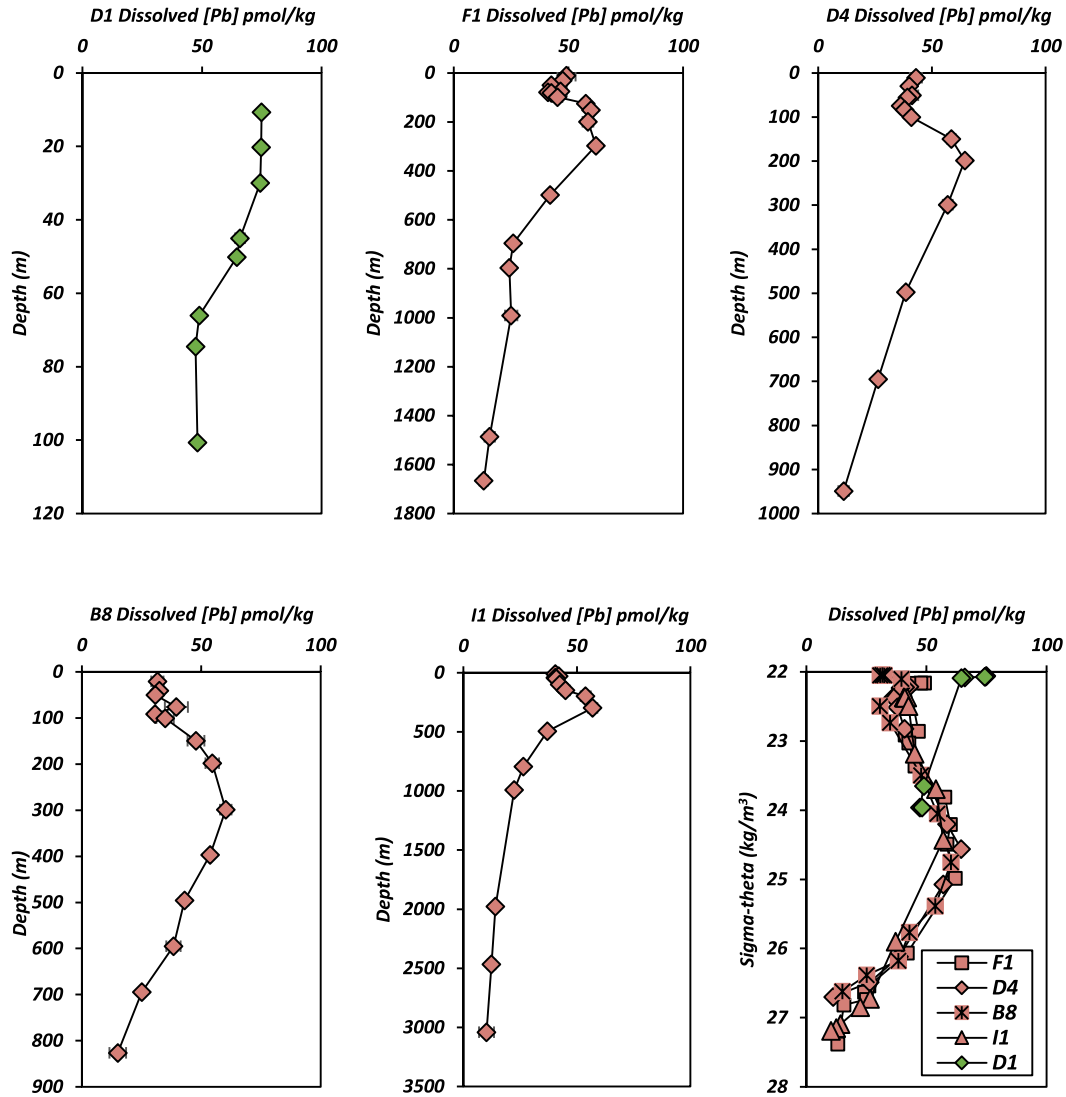

Figure 3. Depth profiles of dissolved Pb concentration in this study. Green symbols denote the station from East China Sea and pink symbols denote stations from the Kuroshio core. The last figure combines all profiles with respect to the potential density anomaly (sigma-theta). Error bars in the plot correspond to one standard deviation over three independently prepared and analyzed replicates. Symbols in the last figure have been modified slightly to differentiate among stations.

3.3. Depth Profiles of Pb Isotope

The most prominent feature in depth profiles and section maps of Pb isotopes (Figure 2d, Figure S3 in Supporting Information S1) was the three patches of water with distinct isotopic compositions: Kuroshio surface and intermediate water (refer to waters in the Kuroshio stations and above the sill depths of East Taiwan Gap and Tokara Gap 0–700 m), ECS water, and Okinawa Trough deep water (refer to waters within the Okinawa Trough and below the sill depth, >800 m). The Kuroshio surface and intermediate water had small variability across stations or depths, with $^{206}Pb/^{207}Pb = 1.165 \pm 0.002$ and $^{208}Pb/^{206}Pb = 2.103 \pm 0.003$ ($n = 43$, 0–800 m). While the ECS and the Okinawa Trough deep water has overlapping Pb isotopic composition, as $^{206}Pb/^{207}Pb = 1.175 \pm 0.002$ and $^{208}Pb/^{206}Pb = 2.099 \pm 0.001$ ($n = 11$), despite these two waters are at vastly different depths (<100 m for ECS water, >800 m for Okinawa Trough deep water, Figure 2). The different isotopic compositions of waters from the ECS and deep Okinawa Trough make them distinct from the Kuroshio surface and intermediate water, resulting in three different patches of Pb isotopic composition in the section map (Figure 2d).

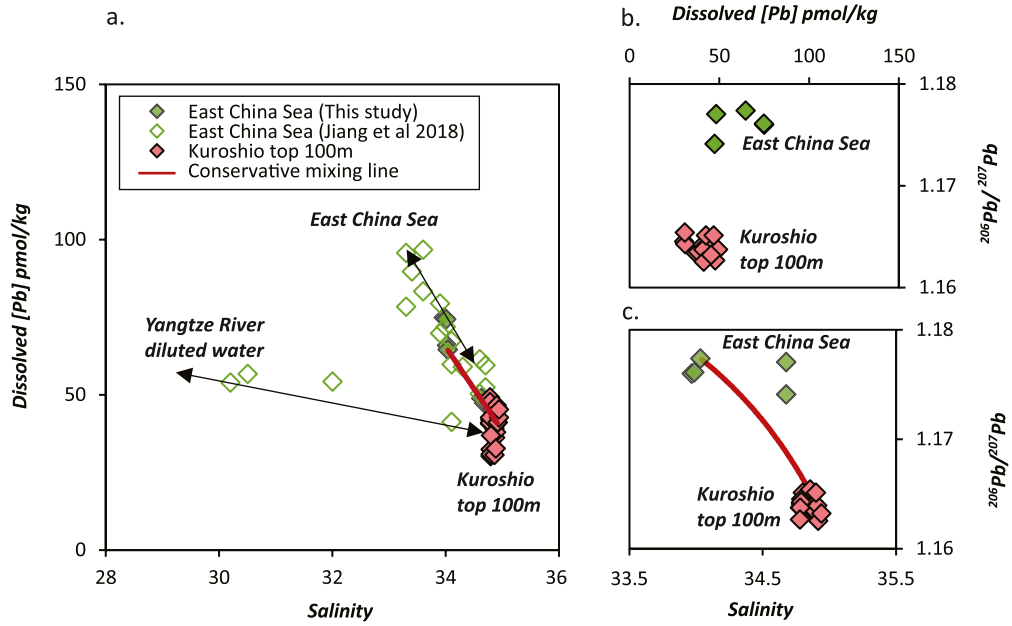

Figure 4. The seawater dissolved lead concentration in the East China Sea and the top 100 m of Kuroshio core. The data set combined both this study (filled diamonds) and a previous study (Jiang et al., 2018a, 2018b, open diamonds). The difference in color denotes East China Sea versus Kuroshio core. The regression statistics between Kuroshio core and East China Sea with respect to salinity is $R^2 = 0.85$, $p < 0.0001$. No regression performed between the Kuroshio core and the Yangtze River diluted water as limited by number of observations. The red thick curve denotes the calculated conservative mixing line between D1 50 m and D4 100 m.

4. Discussion

4.1. Transport of Pb Between the East China Sea and the Kuroshio Core

The hydrographical data shows exchange of water between the ECS and the Kuroshio at depths ~100 m (Figures 2a and 2b, Figure S2 in Supporting Information S1), which is also consistent with the previous findings based on dissolved aluminum concentration (Ren et al., 2015). Therefore, the Pb concentration data at ECS and Kuroshio top 100 m was combined with a previous cruise in 2012 covering similar areas (Jiang et al., 2018). The combined dataset showed at least two lines of mixing between the Kuroshio and two water masses from the ECS (Figure 4). One water mass represents a general ECS that has salinity near 33; and the other represents the Yangtze River diluted water with much lower salinity (salinity <31). The general ECS water contains high Pb, with dissolved Pb concentration above 80 pmol/kg, while the water diluted from Yangtze River plume has lower (<60 pmol/kg) Pb concentration, probably because of effective scavenging by fluvial particulates (Baskaran et al., 1997; Baskaran & Swarzenski, 2007).

The transport of Pb between ECS water and the Kuroshio core happens between salinity 33–35 (Figure 4). The Pb concentration varies linearly with salinity ($r^2 = 0.85$, $p < 0.0001$, $n = 16$), implying conservative transport across the salinity gradient. However, conservative transport is not consistent with the observed Pb isotope ratios (Figures 4b and 4c). A conservative mixing line was calculated based on the highest and lowest observed $^{206}Pb/^{207}Pb$, which corresponded to Station D1 50 m (ECS) and Station D4 100 m (Kuroshio), respectively. Although this mixing line overlaps with the observed Pb concentration across the salinity gradient, the calculated $^{206}Pb/^{207}Pb$ from conservative mixing clearly offsets from the observations (Figure 4c) despite the sparsity of Pb isotope data. The offset between the observed Pb isotope and conservative mixing suggest additional processes are involved in transporting the Pb across ECS and Kuroshio.

One possibility is that the isotopic compositions have been modified by exchange with crustal particulates. A closed-system isotope exchange experiment suggested that Pb can exchange between the dissolved and particulate pools, and as a result alter the Pb isotopic composition in seawater without significant change in its concentration (Chen et al., 2016). The average isotopic composition of waters from the ECS in this study are indeed closer to crustal compositions than the Kuroshio (Figure 5a, Section 4.2); and contain higher concentrations of

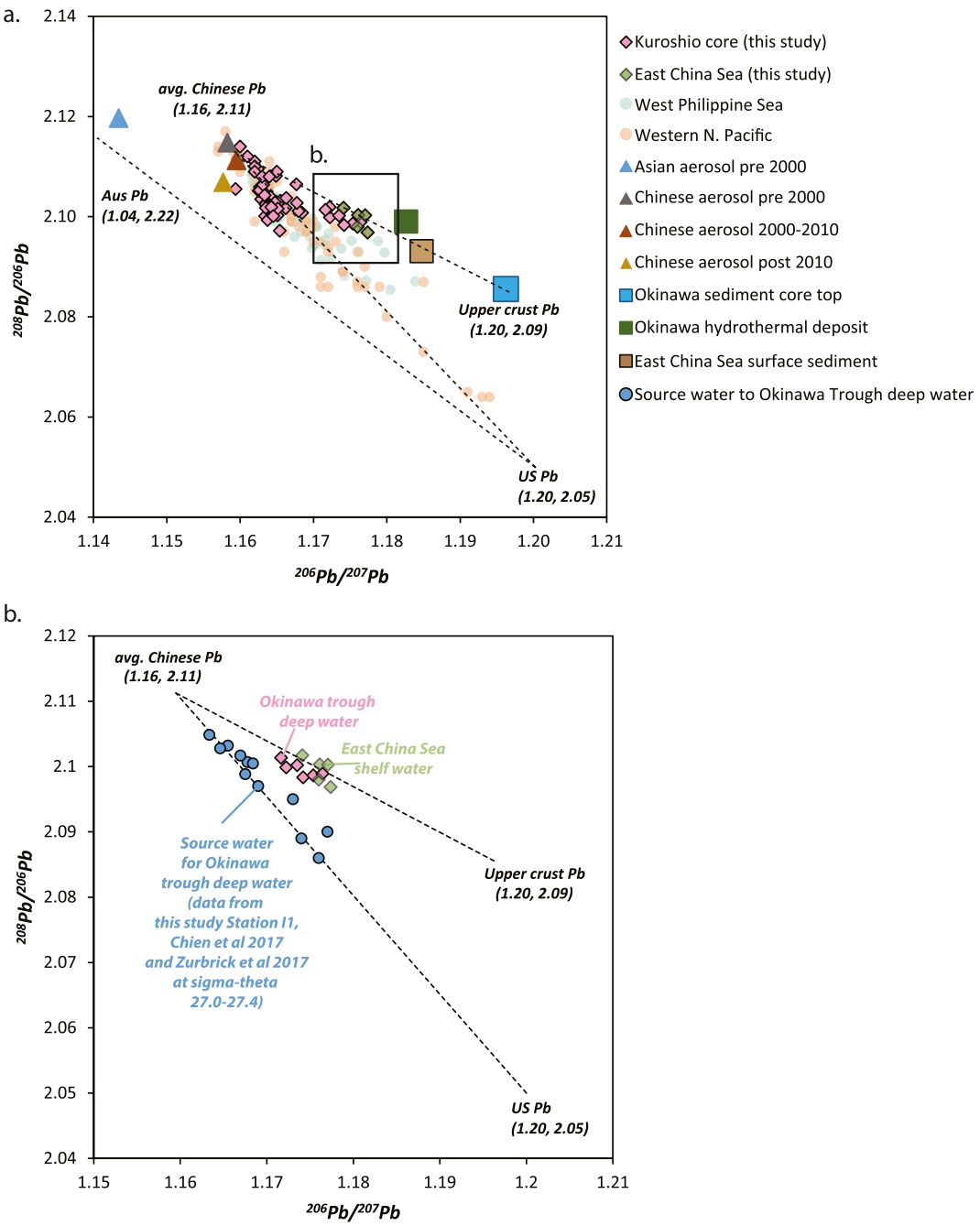

Figure 5. The Pb isotope in observed seawaters and their relation to potential endmembers. (a) The seawater includes this study (pink diamonds), previous study in the Western Philippine Sea (green filled dots, sampled in 2014) (Chien et al., 2017) and North Pacific (orange filled dots, sampled in 2002) (Zurbrick et al., 2017) plotted together with Asian and Chinese aerosols (colored triangles, refer to Table S1 in Supporting Information S1 for data source), surface sediment from East China Sea (Wang et al., 2014), Okinawa Trough (Dou et al., 2016), and hydrothermal deposit from Okinawa Trough (Zhang et al., 2019). Identified endmembers include Chinese Pb, US Pb (Boyle et al., 2020), Australian Pb (Bollhöfer & Rosman, 2000), and Natural Pb (Dou et al., 2016) as discussed in Section 4.2. Difference between Chinese and Asian aerosol is that the latter includes more South and Southeast Asian aerosol data. Error bars are within the size of points. (b) Enlarged figure of "a" with focus on Okinawa Trough deep water and East China Sea water. These waters are compared with the source water to deep Okinawa Trough identified by similar potential density anomaly in Western and North Western Pacific (sigma-theta = 27–27.4 kg/m^3).

suspended particulate matter (SPM) compared to the Kuroshio (Bi et al., 2020; Ren et al., 2015). The high SPM concentration, crustal isotopic composition, and offset from conservative mixing line in isotope space (Figure 4c) collectively indicate exchanges between dissolved and particulates in the ECS. Therefore, the transport of Pb between the ECS and Kuroshio core should be best described as results of quasi-conservative mixing with exchange between dissolved and particulate pools.

4.2. Source Apportionment of Kuroshio Seawater (0–800 m) Using Pb Isotopes

Pb isotopes are helpful for source recognition through comparison of isotopic ratios with potential endmembers. The potential end-members include aerosols and natural crust materials from the Okinawa Trough (Dou et al., 2016; Zhang et al., 2019). Anthropogenic Pb has been identified as the principle Pb sources to the present-day's ocean (Boyle et al., 2014; Flegal, 1986). In the North Western Pacific, based on the emission inventory (Zurbrick et al., 2017) and the Pb ore used associated with these emissions (Bollhöfer & Rosman, 2000, 2001), potential Pb contributors include Australian-type Pb used in Southeast Asian gasoline additives, US-type Pb, and Chinese Pb.

The average Pb isotopic composition of Chinese Pb was investigated through a literature survey on Asian aerosols, with the detailed data included in Table S1 in Supporting Information S1. The Pb isotopic composition of aerosols from 39 Asian cities was included, with the sampling years ranging from 1965 to 2019. These aerosol Pb isotope data pointed that the Pb isotopic composition from Chinese aerosols were different from average Asian aerosols, with the latter including South Asian and Southeast Asian cities that potentially contribute Pb to the Philippine Sea segment of Kuroshio before entering the Okinawa Trough. In specific, the average Asian aerosols have lower $^{206}Pb/^{207}Pb$ (~1.14) than average Chinese aerosols ($^{206}Pb/^{207}Pb$ = ~1.16, $^{208}Pb/^{206}Pb$ = ~2.11), estimated by arithmetic average (Table S1 in Supporting Information S1). The difference between Chinese aerosols and Asian aerosols arises from using leaded gasoline in South/SE Asia with Pb additives mainly from Australian ores (Figure 4). We recognize that uncertainties could arise by taking arithmetic average of aerosols over different studies; however, the available data from the literature prevented us to calculate a weighted average by lacking Pb concentration in some studies and/or inconsistency in sampling strategy (e.g., city center vs. rural area, seasons, etc.). Interestingly, despite the potential uncertainties arithmetic mean, Pb isotopes in Chinese aerosols are remarkably consistent across time. The Pb isotopes in Chinese aerosols remain nearly invariant over the past three decades, with only a few per mil variability (Figure 5a, Table S1 in Supporting Information S1). Therefore, the average Chinese aerosol Pb, together with the well-recognized USA Pb ($^{206}Pb/^{207}Pb$ = ~1.20, $^{208}Pb/^{206}Pb$ = ~2.05, Boyle et al., 2020) and Australian Pb ($^{206}Pb/^{207}Pb$ = ~1.04, $^{208}Pb/^{206}Pb$ = ~2.22, Bollhöfer & Rosman, 2000) were identified as endmembers for the later discussion.

After establishing the endmembers, the observed Pb isotope ratios in seawater were plotted together with these endmembers in an isotope space for source apportionment (Figure 5). As noted in Section 3.3, the Pb isotopes in the Kuroshio water from 0 to 800 m seems to be very similar to each other, with $^{206}Pb/^{207}Pb$ = 1.165 ± 0.002 and $^{208}Pb/^{206}Pb$ = 2.103 ± 0.003 (n = 43, 0–800 m), despite at least three water masses of different origins were involved. In the triple isotope space, the Pb isotopic compositions in these waters suggest a mix between Chinese Pb and US Pb, in agreement with previous studies in waters of the North Pacific (Chien et al., 2017; Flegal, 1986; Gallon et al., 2011; Zurbrick et al., 2017), but offset from average Asian aerosols despite Kuroshio passes through West Philippine Sea before entering the Okinawa Trough. In addition, the Pb isotopes in these waters point strongly toward Chinese Pb, with more than 75% contribution from Chinese Pb for all the waters from Kuroshio 0–800 m and more than 80% for waters from 0 to 200 m if considering Chinese and US aerosol Pb as endmembers (Figure 5). The consistently high contribution of Chinese Pb in Kuroshio water from surface to 800 m depth indicates that Chinese Pb is the principal contributor for three water masses, including Kuroshio surface, North Pacific Tropical Water (NPTW), and North Pacific Intermediate water (NPIW), with the latter two formed in the remote North Central Pacific and North Western Subtropical Pacific, respectively (see Section 3.1 for hydrography).

It is reasonable to expect Chinese Pb has been dominating the Pb contribution in the North Pacific waters. Chinese Pb is the main contributor to Asian Pb emissions based on the emission inventory (Zurbrick et al., 2017). Observations on aerosol Pb isotopes around the North Pacific also point to a strong Chinese Pb contribution. For example, a study on Californian aerosols between 2007 and 2008 found ~29% contribution from Asian Pb, and the isotope data for comparison was predominantly from Chinese cities (Ewing et al., 2010). Since a significant amount of Chinese Pb can be found in California, which is located on the Eastern Pacific margin, an even stronger

contribution of Chinese Pb should then be expected in the western and central North Pacific, which is supported by observations in other locations of remote North Pacific (sampled in year 2002, Gallon et al., 2011) and North Western Pacific (sampled in year 2005–2007, Nagaoka et al., 2010). These studies suggest that Chinese Pb has been dominating the atmospheric deposition of Pb to North Pacific waters for the past two decades, including the site of formation for Kuroshio surface, NPTW and NPIW. And since the isotopic composition of Chinese aerosol Pb was almost stable over the past three decades (discussed earlier in this section), as a result, the waters in Kuroshio surface, NPTW and NPIW could have very similar isotopic compositions. Besides similar sources of Pb during water formation, particle scavenging could also effectively transport Pb to the deeper depth (Murray et al., 2005; Nozaki et al., 1976; Wu et al., 2010), further homogenizing the vertical distribution of Pb isotopic compositions.

4.3. Boundary Exchange of Pb Isotopes in the Western Pacific Margins

One particularly interesting observation is that the deep water from the Okinawa Trough (>800 m) and ECS (0–100 m) have overlapping Pb isotope ratios (Figures 2d, 4a, and 4b, $^{206}Pb/^{207}Pb = 1.175 \pm 0.002$ and $^{208}Pb/^{206}Pb = 2.099 \pm 0.001$, $n = 11$), despite these water masses occurring at very different depths (Figure 2). These waters fall on the mixing line between Chinese Pb and natural crustal Pb in the triple isotopic space, instead of Chinese and US Pb conventionally found in other depths of Kuroshio or elsewhere in the Western Pacific (e.g., Zurbrick et al., 2017).

One possibility is that the water masses at the ECS and deep Okinawa Trough have coincidently similar isotopic compositions. However, the change in isotopic composition of the Okinawa Trough deep water from its source water excludes this possibility. The deep water in the Okinawa Trough with anomalous Pb isotopic composition is constrained within a narrow range of sigma-theta (27.2–27.4 kg/m^3, Figure 2). At this range of sigma-theta, the water is mainly sourced from the West Philippine Sea through the Kerama Gap (sill depth = 1,100 m, Nakamura et al., 2013), and should contain mainly NPIW. The isotopic compositions of the source water have $^{206}Pb/^{207}Pb$ range between 1.166 and 1.177 and $^{208}Pb/^{206}Pb$ range between 2.086 and 2.103 ($n = 11$, see Table S2 in Supporting Information S1 for detailed data included in this calculation), which clearly fall on a different mixing line in the triple isotope plot, that is, between Chinese—US aerosol Pb (Figure 4b). The difference in Pb isotopic composition between Okinawa Trough deep water and its source water indicates that a change in the isotopic composition should have occurred within the Okinawa Trough, which modifies the isotopic composition of the water aerosol toward natural crustal compositions (Figure 4b).

With the isotopic difference between Okinawa Trough deep water from its source water, isotope exchange between seawater and the sediment becomes the most plausible explanation for the isotopic overlap between ECS water and Okinawa Trough deep water. Interactions of Pb between the dissolved and particulate pools have been identified as a key process in marine Pb cycling since early observations using radionuclides (e.g., Bacon et al., 1976; Murray et al., 2005). Recent studies also show such interaction could redistribute the stable Pb isotopes between the dissolved and particulate pool, resulting in modifications of the Pb isotope in the seawater dissolved pool toward crustal compositions over weeks to months (Chen et al., 2016). The deep Okinawa Trough water has an average residence time of 5–10 years (Nakamura et al., 2013), much longer than the timescale for isotope exchange as revealed from the previous close-system experiment. In addition, previous studies in southern Okinawa Trough show high sedimentation rates (over 1,000 m depth, Lee et al., 2004) suggesting abundant particulate matter in the deep of Okinawa Trough. Supported by high dissolved iron (Fe) concentrations in the water near the bottom of Okinawa Trough (Sasayama et al., 2018), these particles interact with the dissolved pool, and modifies the Pb isotopic composition from a mix between Chinese—US sources into Chinese—crustal sources. Similar process could also happen in the ECS. Although no data on the particulate or SPM concentration for this cruise is available, previous studies in ECS show that the marginal sea receives abundant crustal particulates from regional rivers, including field samplings in year 2011 (Bi et al., 2020; Ren et al., 2015) and a remote sensing study on suspended solid concentration using images covering 2003–2016 (Zhou et al., 2020). The isotopic compositions of the ECS surface sediments are in the same mixing line between Chinese—crustal sources (Figures 5a and Wang et al., 2014). The suspended sediments in ECS could modify the Pb isotopic composition from aerosol to crustal sources, resulting in an observed isotopic composition close to crustal values and similar to waters from deep Okinawa Trough. The observed Pb isotope in the ECS water deviated from the conservative mixing line between ESC and Kuroshio waters (Figure 4, Section 4.1), supporting the case of exchange with sediment.

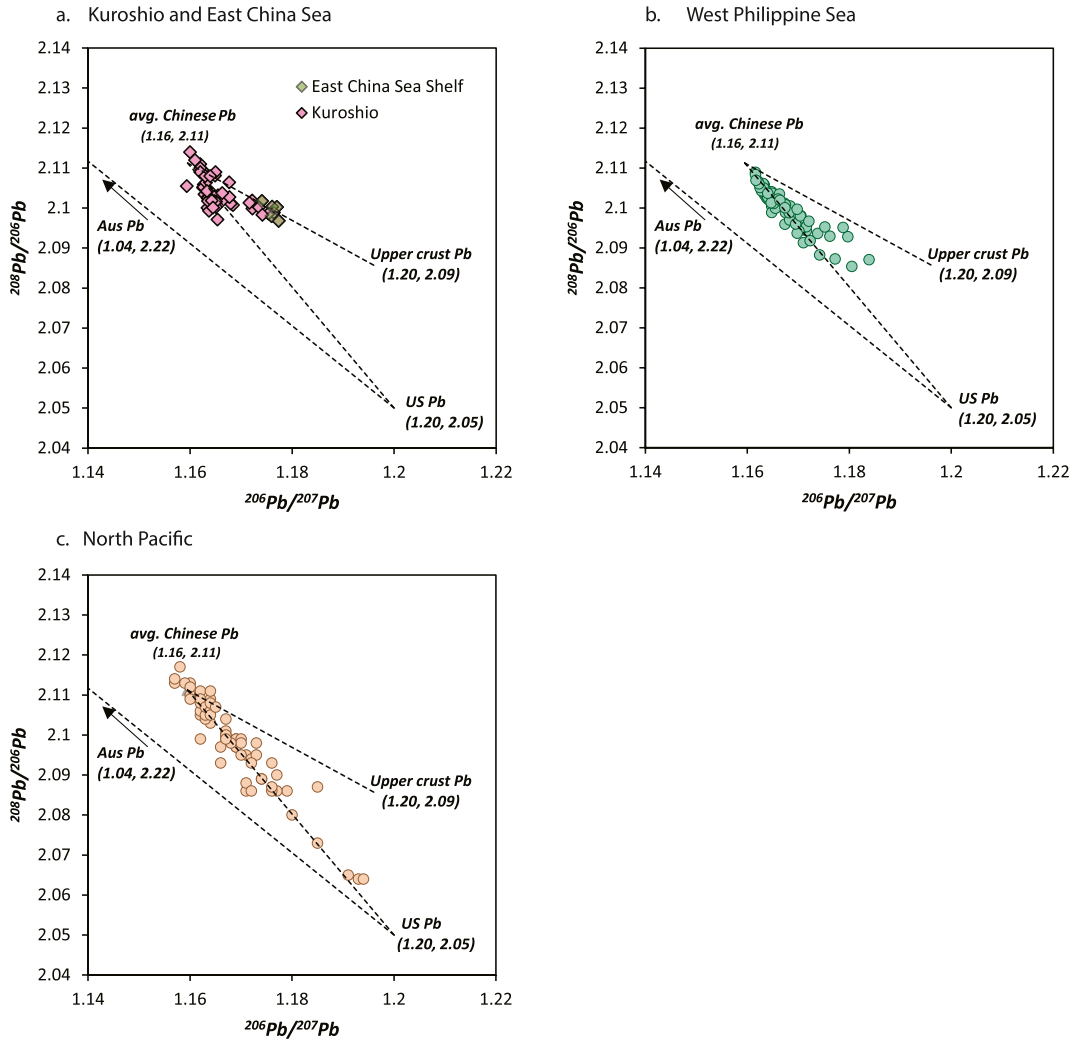

Figure 6. The triple isotope plot of seawaters in Kuroshio and East China Sea from this study (a); West Philippine Sea (Chien et al., 2017) (b); and North Pacific (Zurbrick et al., 2017) (c). Identifications of endmembers are the same as Figure 5.

A literature survey on the Pb isotope in seawaters shows that isotope exchange with sediment occurs in more areas. Besides the East China Sea and Kuroshio (Figure 6a), a study of Pb isotope in the West Philippine Sea shows Pb input from continental slopes at 2,000–5,000 m depths (Chien et al., 2017, Figure 6b). The Pb isotopic compositions in these waters show a deviation from the normally expected Chinese-US Pb mixing line toward the Chinese-natural crust Pb mixing line (Figure 6b), similar to what has been found in this study. Evidence of seawater-sediment interaction can also be found in the Gironde estuary (Elbaz-Poulichet et al., 1984), Celtic Sea (Rusiecka et al., 2018), Bay of Bengal (Lee et al., 2015), Equitorial Southeast Asia (Chen et al., 2023) and East Atlantic Margin (Noble et al., 2015), although the Pb isotope ratios in the seawater was not always available. It is also possible that isotope exchange also happens in shallower depths of Okinawa Trough along the shelf slopes which can be potentially captured by sampling at finer spatial resolution. In contrast, waters from open ocean sites have less chance to interact with sediment (limited by low SPM or limited contact with the continental crust), for which these waters should carry isotopic compositions of mainly aerosol Pb. Examples can be found such as the station I1 in this study, as well as the previous cruise in the North Pacific (Figure 6c) (Zurbrick et al., 2017), which all fall within the mixing line between Chinese and US aerosols.

Lastly, although exchanges of Pb between seawater and sediment are expected to occur in ocean boundaries, the detailed budgets, the timescale of exchange and its potential implications on marine Pb cycling remains under-studied. In the recent decade, boundary exchange has been receiving increasing attention, as the

processes associated with exchanges between seawater and sediment are vital in closing the budget for an increasing number of elements (Homoky et al., 2016). Despite its importance in marine element cycling, systematic investigations on Pb remain highly limited. Investigations with integrative approaches on both dissolved and particulate pool will be essential in elucidating the processes and thus further our understanding in marine Pb cycling.

5. Conclusions

We report the dissolved Pb concentration and the isotopic composition of seawater along the East China Sea (ECS) and Kuroshio, sampled on the GEOTRACES GP06 (or KH15-3) cruise. In the top 100 m, dissolved Pb is high in the ECS, and that Pb decreases with increasing salinity into the Kuroshio core. Within the Kuroshio core, dissolved Pb concentrations exhibit a subsurface maximum between 200 and 400 m, and then decrease with increasing depth. Dissolved Pb in the Kuroshio core over all stations is consistent at similar potential densities, making it a strong case for isopycnal transport. Pb isotope ratios from 0 to 800 m are highly similar (only ±2 per mil in $^{206}Pb/^{207}Pb$ over 43 samples across 800 m depth), and point toward a strong contribution of Chinese aerosol Pb. A deviation from aerosol Pb into natural crustal Pb is observed in the deep water of the Okinawa Trough from its source water, indicating exchange between seawater and sediments. Seawater-sediment exchange is also observed in areas with abundant supply of crustal particulates, such as the ECS and other ocean margins. Overall, this study calls for further investigations involving both dissolved and particulate pools to further elucidate the exchange of Pb between seawater and the sediment boundary.

Data Availability Statement

Data set for this work is available at https://scholarbank.nus.edu.sg/handle/10635/231098.

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