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Increase in anthropogenic mercury in marginal sea sediments of the Northwest Pacific Ocean



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- The flux of Hg^{ANTH} into sediments increased from the western Arctic Ocean to the East China Sea.
- The highest rate of Hg^{ANTH} flux into sediments was found in the East China Sea.
- Hg^{ANTH} has reached open ocean sediments over extended areas of the northwestern Pacific Ocean.

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ABSTRACT

Over the past century, the addition of anthropogenic mercury (Hg^{ANTH}) to vast areas of North Pacific marginal seas adjacent to the northeast Asian continent has tripled. Analysis of sediment cores showed that the rate of Hg^{ANTH} addition $(Hg^{ANTH}$ flux) was greatest in the East China and Yellow Seas $(9.1 \ \mu g \ m^{-2} \ yr^{-1})$ in the vicinity of China (the source continent), but was small in the Bering and western Arctic Ocean (Chukchi Sea) $(0.9 \ \mu g \ m^{-2} \ yr^{-1})$; the regions furthest from China). Our results show that Hg^{ANTH} has reached open ocean sedimentary environments over extended areas of the northwestern Pacific Ocean, via the formation of organic-mercury complexes and deposition. The implication of these findings is that the addition of Hg^{ANTH} (via atmospheric deposition and riverine input) to the ocean environment is responsible for elevated Hg flux into sedimentary environments in the northwest Pacific Ocean.

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1. Introduction

Gaseous elemental mercury (Hg⁰) emitted from natural and anthropogenic sources is photochemically oxidized to reactive mercury (Hg²⁺) in the atmosphere. If deposited onto the ocean surface (primarily via wet and dry deposition), some of the Hg²⁺ can be reduced to Hg⁰ in the surface waters and re-emitted to the atmosphere, and some is absorbed onto suspended particulate matter to produce particulate Hg (Hg^P), and then deposited into sediments. Other established pathways for Hg²⁺ include conversions to insoluble mercury sulfide, which settles out of the water column and is incorporated into sediments or converted to the more toxic methylmercury (CH₃Hg⁺) by methanogenic (methane producing) and sulfate-reducing bacteria in restricted anaerobic conditions. These toxic CH₃Hg⁺ are released by anaerobic bacteria as a dissolved form, consumed by phytoplankton and zooplankton at higher tropic levels, and accumulated in the food chain, from where it can eventually be incorporated into sediments in the form of organo-mercury complexes (Engstrom, 2007; Percival et al., 2015).

Mercury isotope compositions (e.g., Δ^{199} Hg, Δ^{200} Hg, δ^{202} Hg) of various Hg sources are widely used as a basis for discriminating anthropogenic Hg (Hg^{ANTH}) from Hg derived from other natural emissions (Blum et al., 2014; Lepak et al., 2015). However, the isotope composition of sediment Hg can be complicated by either isotope fractionation (depending on the mass of the Hg isotopes, MDF) or isotope separation (in no proportion to the difference in the mass of the isotopes, MIF) in the atmosphere and the ocean, prior to its deposition into sediments (Blum et al., 2014; Sun et al., 2014; Enrico et al., 2017). Moreover, microbial-mediated reactions (e.g. methylation and demethylation), chemical reactions (e.g. photo-reduction or chemical reduction) and purely physical processes (e.g. volatilization, evaporation, adsorption, and dissolution) all yield additional MDF and MIF in aquatic environments, and thereby alter the isotope composition of sediment Hg. Moreover, the isotope values of anthropogenic sources of Hg overlap, which makes estimation of the contributions of various anthropogenic sources to sediment Hg ambiguous. As a result, studies using methods based on isotope composition data have been mostly performed in restricted basins having a few dominant sources (Sherman et al., 2012; Lepak et al., 2015; Wiederhold et al., 2015), and not in open ocean ecosystems having numerous sources (Yin et al., 2015).

Measurement of the Hg content in ice cores is a newly introduced method of estimating the Hg^{ANTH} input to terrestrial or ocean ecosystems (Schuster et al., 2002). However, this method is only applicable to high latitudes including the Arctic region or temperate glaciers where ice cores record the input history of Hg. Therefore, another method is needed for the northwestern Pacific Ocean where Hg^{ANTH} input was reported to be largest. The Hg accumulation rate (i.e. the Hg flux) in sediment is an alternative method of identifying Hg^{ANTH} inputs if the physical and chemical effects (i.e. grain size, organic matter content, sedimentation rate and Fe/Mn reduction) on the Hg accumulation rate are properly taken into account, because these rates can reflect the historical trend of Hg accumulation and are consistent with atmospheric Hg deposition rate data.

The atmospheric deposition of Hg^{ANTH} to the open ocean is estimated to be 5200–6600 Mg yr⁻¹ (Holmes et al., 2010; Corbitt et al., 2011) that is twice that of riverine input (Sunderland and Mason, 2007; Amos et al., 2014). Therefore, Hg^{ANTH} could be discernable in off-shore sedimentary environments. The majority of studies performed to date have focused on the total (anthropogenic plus natural) content of Hg in estuarine or coastal shelf sediments that are primarily influenced by riverine Hg^{ANTH} (Covelli et al., 2001; Johannessen et al., 2005; Morris et al., 2014). Studies have not considered the influence of Hg^{ANTH} on the open ocean sedimentary environments because data on sediment Hg content from widespread open ocean areas are limited, and more importantly, a reliable method to account for regional variations in the sediment Hg content is not yet available. Consequently, some studies on the influence of Hg^{ANTH} on offshore sedimentary environments

have taken an indirect approach, relying on modeled results derived from Hg emission data rather than field measurements (Sunderland and Mason, 2007; Amos et al., 2014).

A key hurdle in determining the content of Hg^{ANTH} in a sedimentary environment is to estimate the natural level of Hg, and then to subtract this from the total Hg content. However, the accurate estimation of the natural level of Hg in sediment is not straightforward because the adsorption of Hg onto particles (which directly influences the Hg flux) in the water column immediately above the sediment being sampled is sensitive to the physical and chemical properties of those particles. Due to this inherent difficulty, the majority of studies have focused on limited areas having similar natural levels of Hg and similar water column particles associated with Hg (Covelli et al., 2001; Johannessen et al., 2005; Morris et al., 2014; Zhou et al., 2014; Zohar et al., 2014). These studies involved a simple comparison of the sedimentary Hg concentrations or total sedimentary Hg flux between pre-industrial and industrial periods, or in contaminated and less contaminated regions (Covelli et al., 2001; Johannessen et al., 2005; Morris et al., 2014; Zhou et al., 2014). Therefore, to better understand the occurrence of Hg^{ANTH} in open ocean sedimentary environments, studies investigating extensive ocean regions from contaminated to less contaminated regions should be performed, and importantly the natural levels of Hg need to be accurately estimated.

In this context, we assessed the influence of Hg^{ANTH} on the ocean sedimentary environments by analyzing the sedimentary Hg flux for 319 surface sediments and in several sediment cores obtained from all basins in our study area, including the East China and Yellow Seas, East Sea, Okhotsk Sea, Bering Sea, and the western Arctic Ocean (Chukchi Sea). We also assessed the % fraction of Hg^{ANTH} accumulated in each sedimentary environment relative to the total Hg^{ANTH} input (via atmospheric deposition and riverine inputs) into each basin.

2. Materials and methods

2.1. Study sites

The study sites were located over an area extending from the East China and Yellow Seas in the south to as far north as the western Arctic Ocean. The East China and Yellow Seas are close to the Chinese coast (the major Hg^{ANTH} source), whereas the Bering Sea and the western Arctic Ocean are far from China and regarded as being more pristine. All of the basins examined here are located downwind of the major Hg^{ANTH} source country (China) and thus, westerly winds carry gaseous elemental Hg⁰ progressively less from the East China and Yellow Seas to the western Arctic Ocean, resulting in a northeastward decrease in Hg^{ANTH} deposition. Each basin receives additional Hg via riverine flux: the Changjiang and Huang He rivers flow into the East China and Yellow Seas, respectively; and the Amur and Yukon rivers flow into the Okhotsk Sea and the western Arctic Ocean, respectively (Table 1). The basins examined here receive varying amounts of Hg^{ANTH} via atmospheric deposition and riverine flux based on models. The East China and Yellow Seas have the highest Hg^{ANTH} flux (approximately 133 $\mu g m^{-2} yr^{-1}$ and 86 $\mu g m^{-2} yr^{-1}$, respectively) (Sunderland and Mason, 2007; Corbitt et al., 2011; Percival et al., 2015), followed by the East Sea (approximately 33 μ g m⁻² yr⁻¹) (Amos et al., 2014), the Okhotsk Sea (approximately 10 μ g m⁻² yr⁻¹), the Bering Sea (approximately 8 $\mu g \ m^{-2} \ yr^{-1}),$ and the western Arctic Ocean (lowest and approximately 5 μ g Hg^{ANTH} m⁻² yr⁻¹) (Zhang et al., 2016).

2.2. Sediment sampling methods

Single surface sediment was sampled from each of 268 sites in the Huang He (n = 22) and Changjiang (n = 24) estuaries, and from the East China (n = 27) and Yellow (n = 195) Seas using a grab sampler or a box corer over various Korea Institute of Ocean Science and Technology expeditions conducted since 2000. One sediment core from the

Table 1

Characteristics of the basins from which sediment samples were taken, and the rivers flowing into each basin.

Basin	Water depth (m)	Area (km ²)	River
East China Sea	<50	1,249,000	Changjiang
Yellow Sea	<50	380,000	Huang He
East Sea	977	978,000	
Okhotsk Sea	1213	1,583,000	Amur
Bering Sea	1766	2,000,000	
Western Arctic Ocean	1062	620,000	Yukon

East China Sea and two sediment cores from the Yellow Sea were also collected using box and piston cores. Note that data on the Huang He and Changjiang estuaries and the East China and Yellow sea sediments were obtained from the literature (Lim et al., 2017; Kim et al., 2018).

The sediment cores collected using a multi/gravity corer were also taken from the East Sea (n = 3), the Okhotsk Sea (n = 2), and the western Arctic Ocean (n = 2); the latter were collected along with the western Arctic Ocean surface sediments (n = 5) during Korea Polar Research Institute expeditions conducted using RV Araon between 2010 and 2013. All sediment samples were stored onboard at -20 °C, samples were freeze-dried for 4 days, and then ground to a powder using a mortar and pestle.

We additionally included data on the concentrations of Hg, total organic carbon (TOC), and Al, and mass accumulation rates (MAR) for 39 sites in the East (n = 3), Okhotsk (n = 25), and Bering (n = 11) Seas; these data were obtained from literatures. Detail information on the sampling methods and sites is summarized in Table 2, and Tables S1, S2 and S3 in the Supplementary Information.

2.3. Concentrations of total Hg, Al, Fe and TOC in sediments

Total Hg (THg) concentrations were measured using an automatic Hg analyzer, and involved thermal decomposition followed by catalytic reduction, amalgamation, desorption, and the use of an atomic absorption module (model Hydra II Direct Hg analyzer; Teledyne Leeman Labs, Hudson, NH, USA), and were calibrated against marine sediment reference materials (MESS-3; Hg = 91 \pm 9 ng g⁻¹ certified by the National Research Council of Canada) for trace metals and other constituents. The analytical accuracies were determined to be <5%, based on replicate analysis of the certified reference materials (MESS-3), and the analytical precision in measurements of the THg concentration was determined to be <10%, based on replicate measurements of standard materials and

sediment samples. For determining the concentrations of Al and Fe, the powered samples including a standard reference material (MAG-1; Al₂O₃ = $16.4 \pm 0.3\%$ and Fe₂O₃ = $6.8 \pm 0.6\%$; certified by U.S. Geological Survey) were dissolved in a mixture of hydrofluoric and perchloric acids, and the elemental concentrations were measured using inductively coupled plasma atomic emission spectroscopy (Spectro Flame Modula EOP; SPECTRO Analytical Instruments Inc., Kleve, Germany). The analytical accuracy and precision ranged from 5% to 10%, and the concentrations were then calibrated against Marine Sediment-1 reference material (certified by the U.S. Geological Survey) (Lim et al., 2012). The concentrations of total carbon (TC), and total inorganic carbon (TIC) in the dried and ground sediment samples were measured using a Thermo Electron Corporation Flash EA 1112 Series NC Soil Analyzer for TC, and a CO₂ coulometer (model CM5014; UIC Inc.) for TIC (Waltham, MA, USA). The accuracy and precision in analysis of these elements were <5%, based on analysis of standard reference materials (1cysteine in the TC analysis, and calcium carbonate having 12% C in the TIC analysis). TOC concentrations were calculated by subtracting TIC from TC (Nelson, 1996). Note all data that we used in our analysis are presented in Table S3 in the Supplementary Information.

2.4. Sedimentation rate for sediment cores

The sedimentation rates for 7 sediment cores (Yellow Sea I, II; East Sea I, II, III; Okhotsk Basin; western Arctic Ocean) were measured using excess 210 Pb (210 Pb_{ex}) activity, which is equivalent to the total ²¹⁰Pb activity (²¹⁰Pb_{tot}) minus the ²¹⁰Pb activity supported by an indigenous parent radionuclide (Lim et al., 2007; Lim et al., 2012). All sediment cores were sectioned at intervals of 2-5 cm, and were then freeze-dried and powdered. For age analysis, 5 g of the powdered sediment was added to acidic solution and spiked with ²⁰⁹Po for leaching. After drying the ²⁰⁹Po was dissolved in 1 M HCl and separated from the acidic solution using a centrifuge. The ²⁰⁹Po in particles was then plated onto a silver planchet, and ²¹⁰Pb activities were determined by counting the alpha decay of its grand-daughter isotope ²¹⁰Po (Lim et al., 2007). The sedimentation rate for the East China Sea core was calculated on the basis of the accelerator mass spectrometry (AMS) ¹⁴C age (1030 \pm 40 year before present) of foraminifera at a core depth of 150 cm (Dou et al., 2015). The ages of cores from the Okhotsk Basin were obtained from published scientific reports (Table 2) (Astakhov et al., 2005; Chen et al., 2016). Mass accumulation rates (= sedimentation rate \times dry bulk density) for all basins were obtained from the literatures and summarized in Table 2.

 Table 2

 Information on the surface sediments used in this study.

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Basins	No.	Hg	MAR	Hg ^{ANTH} flux	Age	Texture	Al	TOC	Reference	
		$(\mathrm{ng}\mathrm{g}^{-1})$	$(g cm^{-2} yr^{-1})$	$(\mu g \ m^{-2} \ yr^{-1})$	(y)		(%)	$(\mathrm{mg}\mathrm{g}^{-1})$		
Huang He River	22	20 ± 3	0.5	38 ± 14	-	_	6 ± 0.1	3 ± 0.4	Kim et al., 2017; Lim et al., 2017; Kim et al., 2018; Hu et al., 2016	
Changjiang River	24	105 ± 11	0.87	776 ± 56	-	-	7.4 ± 0.1	7 ± 0.5	Lim et al., 2017; Kim et al., 2018; Deng et al., 2006; Fang et al., 2009	
East China Sea	27	18 ± 1	0.2	9 ± 2	8 ± 10	calcareous ooze, sand	6.4 ± 0.2	5 ± 0.4	Lim et al., 2017; Kim et al., 2018; Dou et al., 2015	
Yellow Sea	195	19 ± 1	0.15	8 ± 1	8 ± 2	siliceous mud	6.5 ± 0.1	5 ± 0.2	Lim et al., 2017; Kim et al., 2018	
East Sea	8	89 ± 22	0.02	11 ± 4	18 ± 10	clay, siliceous mud	5.3 ± 0.8	18 ± 5	Song et al., 2015; Hong et al., 1997	
Okhotsk Sea	27	91 ± 30	0.02	5 ± 1	42 ± 15	clay, siliceous mud, diatom ooze	4.6 ± 0.2	15 ± 1.2	Astakhov et al., 2005	
Bering Sea	11	45 ± 9	0.07	0.4 ± 0.3	20	clay, diatom ooze, sandy silt, siliceous mud	3.9 ± 0	9 ± 0.9	Iricanin and Trefry, 1990; Oguri et al., 2012	
Western Arctic Ocean	7	78 ± 8	0.04	0.9 ± 0.7	8 ± 4	siliceous mud, silt, slay, sand	7.0 ± 0.2	12 ± 1.5	Chen et al., 2016	

2.5. Calculation of Hg^{ANTH} flux

The absolute concentration of Hg in sediment is primarily determined by the rate of sedimentation, and to a lesser but significant extent by the physical properties of the sediment, including sediment texture (grain size), organic matter content, porosity and compaction (Daskalakis and O'Connor, 1995). Our measurements showed that the Hg concentrations in sediment samples from the western Arctic Ocean are generally higher than in those from the East China and Yellow Seas (Table 2 and Table S3, Fig. S1 in the Supplementary Information). Therefore, if the absolute concentration of Hg were to be used to estimate Hg^{ANTH} input into sedimentary environments, the Arctic sedimentary environment would be determined to receive more Hg than the East China and Yellow Seas. However, to compare Hg^{ANTH} inputs into the various sedimentary environments of our study area, we must first account for basin-to-basin differences in sediment Hg content associated with differences in sedimentation rate and the physical properties of the sediments. Therefore, instead of using the absolute Hg concentration (ng g⁻¹) in sediment samples, we use the total Hg flux (μ g m⁻² yr⁻¹) into the sediments (Fig. S2 in Supplementary Information) calculated using the equation:

Total Hg flux (
$$\mu$$
g m⁻² yr⁻¹) = (sedimentation rate x ρ_{SED}) x [Hg]_{SED} (1)

where MAR (g cm⁻² yr⁻¹) is the mass accumulation rate that is the product of the sedimentation rate (cm yr⁻¹) and dry bulk density (ρ_{SED} g cm⁻³); and [Hg]_{SED} (Fig. S1 in the Supplementary Information) is the total sediment concentration of Hg (ng g⁻¹). Here, MAR was calculated using the dry bulk density in order to remove the difference in total Hg content arising from differences in the physical properties of sediments (e.g. sediment texture and porosity).

Next, we must separate the Hg^{ANTH} flux (Fig. 3B) from the total Hg flux (Fig. S2 in the Supplementary Information; anthropogenic and natural components combined). To achieve this, we used the sediment Hg to Al concentration ratio measured in the sediment core samples. This method of normalization, which has been found to be robust, commonly uses the sediment Al content because Al is the most abundant component of aluminosilicate minerals and clavs. and derives only from natural sources (no anthropogenic source exists) (Loring and Rantala, 1992). Moreover, compared to sands and silts, clay minerals tend to have the larger surface areas, and thereby facilitating direct contact with greater numbers of Hg atoms. The strong link between Hg and clays is supported by the observation of positive correlations between Al, clay, and Hg contents (Loring and Rantala, 1992). Thus, given that Al comes almost exclusively from natural sources (predominantly from the weathering of bedrocks in watersheds), the natural Hg fraction can be determined by normalization of the sediment Hg content by sediment Al content.

Normalization of the Hg content by the Al content in sediment samples is therefore a useful method for accounting for temporal and regional variations in Hg content associated with variations in sediment texture (grain size) and bedrock weathering. The Hg content in sediment samples is expressed as the enrichment factor of Hg ($\rm EF_{Hg}$) that was calculated by dividing the Hg/Al ratio for surface or core samples ([Hg/Al]_{SAMP}) by the same ratio for Hg^{ANTH}-free samples ([Hg/Al]_{BACKGROUND}) collected during the pre-industrial era:

$$EF_{Hg} = [Hg/Al]_{SAMP} / [Hg/Al]_{BACKGROUND}$$
(2)

The accuracy of this normalization depends on the consistency in $Hg/Al_{BACKGROUND}$ within each basin. For all basins examined, we found no significant differences in the background Hg/Al ratios obtained from Hg^{ANTH} -free sediment core samples within each basin. This indicates that a unique $Hg/Al_{BACKGROUND}$ ratio was identified for each basin that could then be used to normalize the total (Hg/Al)_{SAMP} ratios

measured throughout sediment cores and for all surface sediment samples in such a way to calculate EF_{Hg} and hence the flux of Hg^{ANTH} (Fig. 1). Finally, the Hg^{ANTH} flux to sediments is calculated using Eq. (3) by

Finally, the Hg^{ANTH} flux to sediments is calculated using Eq. (3) by subtracting the background flux for Hg: {([Hg] × MAR)_{SAMP}/EF_{Hg}} (Fig. S3 in the Supplementary Information) from the total flux for Hg: ([Hg] × MAR)_{SAMP} (Fig. S2 in the Supplementary Information) (Hermanns and Biester, 2013):

$$\begin{array}{l} \mathsf{Hg}^{\mathsf{ANTH}}\mathsf{flux} \left(\mu g \ m^{-2} \ yr^{-1} \right) \\ = \left([\mathsf{Hg}] \times \mathsf{MAR} \right)_{\mathsf{SAMP}} - \left\{ \left([\mathsf{Hg}] \times \mathsf{MAR} \right)_{\mathsf{TOTAL}} / \mathsf{EF}_{\mathsf{Hg}} \right\} \end{array} \tag{3}$$

Variations in the organic matter content of sediments also influence the concentration of Hg, because Hg has a strong affinity for organic matter (Chakraborty et al., 2015). The strong positive correlations we observed between the sediment Hg/Al and Hg/TOC ratios for all basins examined (Fig. 2) indicate that the Al-based normalization can satisfactorily account for variations in sediment Hg associated with sediment grain size and organic matter content. Therefore, additional correction for variations in the concentration of organic matter was not needed.

2.6. Statistical methods

The distribution of Hg^{ANTH} flux in Fig. 3A was created using Ocean data view (Version 5.1) and the other plots (Figs. 1, 2, 3B, 4 and 5) were created using a sigma plot (Version 13.0). The statistical analysis between chemical parameters and Hg contents were performed using a R soft program.

3. Results

3.1. Geochemical properties of surface sediments

The concentration of Hg in sediment was found to be the highest in the Changjiang River estuary, followed by the Okhotsk Sea, the East Sea, the western Arctic Ocean, the Bering Sea, and the Yellow and East China Seas (Table 2). As the absolute concentration of sediment Hg is closely associated with MAR, the Changjiang River basin had the highest MAR (0.87 g cm⁻² yr⁻¹) and then MAR progressively decreased in accordance with the order of sediment Hg content. With the exception of sediments obtained from the Okhotsk Sea and deep western Arctic Ocean, surface sediments from all basins were deposited within the last 17 y, indicating that most surface sediments used in our analysis would likely to have contained discernable amounts of Hg^{ANTH} (Table 2).

In terms of sediment texture, sediments from the East China and Yellow Seas consist largely of sand and mud, respectively, whereas the East Sea and the western Arctic Ocean sediments consist of clays and are rich in organic carbon. The Okhotsk and Bering sea sediments consist largely of a mixture of clay, silt and sand (Müller et al., 2016).

Sediment Al content is higher in the western Arctic Ocean than in other basins, whereas TOC content is higher in the East, Okhotsk Seas and western Arctic Ocean. The East China and Yellow Seas are shallow basins (100 m depth), whereas the East, Okhotsk, and Bering Seas are more like deep basins (977 m for the East Sea to 1766 m for the Bering Sea). The physical properties of samples from the various seas are more summarized in Table 2 and in Supplementary Information Tables S1 and S2.

3.2. The background ratio of Al concentration to Hg concentration in sediment

For each basin in our study area, the background ratio of the Hg concentration to the Al concentration (the ratio representing sediment accumulated during the pre-industrial era before 1900) was derived from two or three sediment cores. The differences in the resulting background Hg/Al ratio were not statistically significant within individual



Fig. 1. The ratios of Hg to Al for the background sediment samples. The samples were obtained from cores of sediment that accumulated during the pre-industrial times in the Yellow (*n* = 2; red) and East China (*n* = 1; red) seas, the East Sea (*n* = 3; green), the Okhotsk Sea (*n* = 2; yellow) and the western Arctic Ocean (*n* = 2; purple).

basins, and this background ratio increased in a northeastward direction from the Yellow and East China Seas to the western Arctic Ocean (Fig. 1).

3.3. Spatial distribution of ${\rm Hg}^{\rm ANTH}$ flux in sediments of the Northwest Pacific Ocean

The highest rate of Hg^{ANTH} addition was found in sediments in close proximity to the Changjiang (776 \pm 56 µg m⁻² yr⁻¹; n = 24) and Huang He (38 \pm 14 µg m⁻² yr⁻¹; n = 22) river estuaries. For remote open ocean sedimentary environments (except for the East China and Yellow Seas where riverine input of Hg is equally important), which mainly receive Hg^{ANTH} by atmospheric deposition, higher rates of Hg^{ANTH} were found in the East China (9 \pm 2 µg m⁻² yr⁻¹; n = 27), Yellow

 $(8 \pm 0.8 \ \mu\text{g m}^{-2} \ \text{yr}^{-1}; n = 195)$ and East $(11 \pm 4 \ \mu\text{g m}^{-2} \ \text{yr}^{-1}; n = 6)$ Seas than were found in the Okhotsk $(5 \pm 1 \ \mu\text{g m}^{-2} \ \text{yr}^{-2}; n = 27)$ and Bering $(0.4 \pm 0.3 \ \mu\text{g m}^{-2} \ \text{yr}^{-1}; n = 11)$ Seas, and the western Arctic Ocean $(0.9 \pm 0.7 \ \mu\text{g m}^{-2} \ \text{yr}^{-1}, n = 7)$ (Table 2). These locations are increasingly distant from the major source continent for Hg^{ANTH} (Fig. 3A).

3.4. Down-core variations in sedimentary Hg^{ANTH} flux in the Northwest Pacific Ocean

The historical trends of Hg^{ANTH} input to the northwestern Pacific Ocean marginal sea sediments were obtained from analysis of core sediments sampled from all basins. During the industrial era (~1900s onwards for Asian countries), the Hg^{ANTH} flux increased in all basins except the western Arctic Ocean (Fig. 3B). Hg^{ANTH} flux was generally



Fig. 2. The relationships between Hg/TOC ratios and Hg/AI ratios in the sediment depth profiles from the Yellow, East China, East, and Okhotsk Seas, and the western Arctic Ocean. As the effect of Hg^{ANTH} input on sediment Hg/AI or Hg/TOC ratios differed among the basins, we sought to minimize the effect of such basin-to-basin difference by normalizing each sediment sample value ([Hg/AI]_{SAMP}) to the corresponding basin-mean background values ([Hg/AI]_{MEAN}^{EASIN} or [Hg/TOC]_{MEAN}^{BASIN}). Samples from the western Arctic Ocean II did not show the positive relationship because all data except one were clustered in terms of the Hg/AI ratio.



Fig. 3. Spatial and historical distributions of Hg^{ANTH} flux in the northwestern Pacific Ocean sediments. (A) Hg^{ANTH} flux deposited to surface sediments (Circles) in the Huang He (n = 22) and Changjiang (n = 24) estuaries, and the East China Sea (n = 27), the Yellow Sea (n = 195), the East Sea (n = 6), the Okhotsk Sea (n = 27), the Bering Sea (n = 11), and the western Arctic Ocean (n = 7). The dash line indicates the atmospheric Hg deposition and the pie graph is the input of riverine and atmospheric Hg^{ANTH} to the East China and Yellow Seas and the input of atmospheric Hg^{ANTH} to the East, Okhotsk, and Bering Seas and the western Arctic Ocean (Amos et al., 2014; Liu et al., 2016; Zhang et al., 2015, 2016). (B) The Hg^{ANTH} flux in the cores from the East China Sea, the Yellow Sea, the East Sea, Okhotsk Bay and Basin, and the western Arctic Ocean (Horizontal bar chart; black: Natural Hg flux; red: Hg^{ANTH} flux).

higher in the sediments of the East China and Yellow Seas, and sharply decreased in a northeastward direction toward the Okhotsk Sea and western Arctic Ocean. It is notable that the Hg flux (largely natural plus minor anthropogenic) to the western Arctic Ocean sediments remained unchanged during the pre-industrial and industrial eras (Fig. 3B).

3.5. Hg contents relative to other elements (TOC, Al, and Fe) in core sediments

To investigate the effects of all possible processes (i.e. grain size, organic matter content, redox cycling and change of sedimentation rates) on the historical trend in Hg contents in the sediment core samples, the sediment Hg content was plotted against the Hg/Al and Hg/TOC ratios for all sediment cores collected from the same basin. For each basin, the sediment Hg content was strongly related to the Hg/Al or Hg/TOC ratios (Fig. 4), and not related to the sediment Fe contents (Fig. 5 and Fig. S4 in Supplementary Information). Note that we did not find discernable change in sedimentation rate for all sediment cores (Fig. S5 in Supplementary Information).

4. Discussion

4.1. Properties of surface sediments in the Northwest Pacific Ocean

The basin-to-basin variations in natural Hg concentration were mainly attributed to the bedrock type in the watershed of the basins, where weathering leaches out the Hg, Al, and other minerals and subsequently delivers them to the basins. For example, the background Hg concentration was reported to be 22 ng g^{-1} (Chen et al., 2013; Huang et al., 2005) for Lake Tai in the vicinity of the Changjiang River (China), and 100 ng g^{-1} (Fitzgerald et al., 2005) for the northern Alaska. These background Hg concentrations are consistent with the pre-industrial (since 1900) values for several sediment cores obtained from the East China and Yellow Seas and the western Arctic Ocean, respectively (Fig. S1 in the Supplementary Information). Moreover, the higher Al content in the western Arctic Ocean sediment indicates that the sediments in that ocean probably receive higher levels of natural

Hg by weathering of bedrocks (Table 2). Consequently, the higher natural Hg content in the western Arctic Ocean relative to the East China Sea was probably because of differences in indigenous Hg levels rather than anthropogenic influences.

A key requirement in our calculation of the flux of Hg^{ANTH} into surface sediments is that the ages of the top-core sediments sampled across the study area are similar, because surface sediments with extremely low sedimentation rates may contain natural Hg deposited prior to the industrial period. According to this criterion, we excluded from our analysis some open western Arctic basin samples (close to 1000 years old) but included the western Arctic shelf samples. Most surface sediment samples used in this study are similar in age (17 \pm 12 y), indicating that they contained an anthropogenic Hg component that accumulated during the industrial period (Table 2).

4.2. Distribution of surface sediment Hg^{ANTH} flux in the Northwest Pacific Ocean

The flux of Hg^{ANTH} in all basins of our study area is generally consistent with the northeast decrease in the input of Hg^{ANTH} from the Yellow and East China Seas (<133 µg m⁻² yr⁻¹) (Liu et al., 2016) to the western Arctic Ocean (5 µg m⁻² yr⁻¹) (Amos et al., 2014) (Fig. 3A). This indicates that the addition of Hg^{ANTH} leads to an increase in the burial of Hg^{ANTH} in open ocean sediments. Based on the rates of input of Hg^{ANTH} and its subsequent accumulation in sediments, it was estimated that approximately 8% of the deposited Hg^{ANTH} accumulates in sediments of the Yellow and East China Seas, which is broadly consistent with the global average value of 5%. This finding implies that the open ocean sediments act as a sink for Hg^{ANTH}.

The recent increase in Hg^{ANTH} addition to the East China Sea and Okhotsk Bay indicates that the Hg^{ANTH} from the Changjiang (581 \pm 541 Mg yr⁻¹) (Zhang et al., 2015) and Amur (68 \pm 52 Mg yr⁻¹) (Zhang et al., 2015) rivers has spread by ocean currents into extensive areas of the East China Sea and Okhotsk Bay, respectively (Liu et al., 2016) (Fig. 3). However, the absence of a discernable change in the sedimentary input of Hg to the western Arctic Ocean during the past 200 years indicates that little Hg^{ANTH} has reached the western Arctic Ocean by atmospheric transport and deposition. This is consistent



Fig. 4. The relationships between total Hg contents with Hg to Al or TOC ratios. The Hg contents ($ng g^{-1}$; red dot) and Hg to Al (blue triangle) or TOC (gray square) ratios in the core profiles from the Yellow (n = 43), East (n = 23) and Okhotsk (n = 49) Seas and western Arctic Ocean (n = 9). Circles in the Yellow Sea I were outliers.

with the recent finding that the Arctic Hg is mainly derived from river discharge rather than atmospheric Hg deposition (Emmerton et al., 2013; Zhang et al., 2015). For example, the Hg input from the Yukon River was estimated to be 4.4 Mg yr⁻¹ (Schuster et al., 2011) that is insignificant compared to the input (581 Mg yr⁻¹) to the East China and

Yellow Seas. Thus, the recent increase in the Hg content of Arctic sediments was largely confined to coastal areas that have received Hg derived from adjacent rivers, and is probably not from the atmospheric transport and deposition (Schuster et al., 2011; Emmerton et al., 2013; Zhang et al., 2015). In addition, the wet deposition of Hg over the Arctic



Fig. 5. The relationship between Fe (%) and Hg_{SAMP}/Hg_{MEAN}^{BASIN} concentrations in the cores. These cores came from the Yellow, East and Okhotsk Seas and western Arctic Ocean. In order to minimize the effect of basin-to-basin difference, Hg contents (Hg_{SAMP}) were normalized to the corresponding basin-mean background Hg (Hg_{MEAN}^{BASIN}).

Ocean was reported to be considerably lower $(0.5-2.0 \ \mu g \ m^{-2} \ yr^{-1})$ (Kirk et al., 2012) than over the East China and Yellow Seas (24.8 $\ \mu g \ m^{-2} \ yr^{-1})$ (Fu et al., 2016), confirming that the western Arctic Ocean has been far less affected by atmospheric Hg^{ANTH}. It is noteworthy that Hg^{ANTH} fluxes (5–14 $\ \mu g \ m^{-2} \ yr^{-1})$ to selected

locations (5 samples) in the Okhotsk Sea were abnormally high, suggesting that submarine hydrothermal activity may be a source of sediment Hg in these locations. In the vicinity of hydrothermal vents seawater Hg²⁺ forms HgS (cinnabar) or is scavenged by metal hydroxides (oxidized Fe and Mn), and becomes incorporated into sediments. Therefore, the sediments enriched in Fe, Mn, and S^o are generally found in the vicinity of the hydrothermal vents or submarine volcanoes (Boström and Fisher, 1969; Cox and McMurtry, 1981; Salinas-de-León et al., 2018). In the Okhotsk Sea the hydrothermal vents or submarine volcanoes near our sampling sites probably biased the surface Hg^{ANTH} flux estimation, because the ferromanganese crust and brown color of sediments in these locations are signs of materials resulting from volcanic or hydrothermal activity (oxidized Fe and Mn enrichment) (lin et al., 2011; Mikhailik et al., 2012; Salinas-de-León et al., 2018). However, this natural addition of Hg did not occur in the East China and Yellow Seas, which had the highest Hg^{ANTH} flux.

A recent study reported that enhanced primary productivity could increase the sequestration of Hg by diatoms, eventually adding more Hg to the Southern Ocean sediments (Zaferani et al., 2018). However, our method using Eq. (3) (i.e. Hg content normalized by Al content) should reasonably account for differences in Hg content arising from differences in biological production among our study areas.

Finally, it is important to note that the recent increase in anthropogenic nitrate in the East China and Yellow Seas (Kim et al., 2011; Kim et al., 2014b) may result in a comparable increase in biological production, although a direct association between anthropogenic nitrate input and phytoplankton biomass is yet to be confirmed (Kim et al., 2014c). If such an association were to exist, the resulting increase in biological production would be expected also to increase the input of Hg into the sedimentary environment of the East China and Yellow Seas.

4.3. Down-core Hg^{ANTH} flux in the Northwest Pacific Ocean

Historically, Hg^{ANTH} emissions from the North America and Europe derived from silver mining, which reached peak activity in the 1880s. In recent times, Hg emissions have decreased in these countries because of the strict enforcement of legal regulations. However, Hg^{ANTH} emissions in northeast Asian countries have continuously increased since 1900, with coal combustion and artisanal gold mining being two main sources (Street et al., 2011). Consistent with this, an increasing trend of Hg^{ANTH} flux was observed in down-core sediments accumulated since 1900s in the East China, Yellow and East Seas, which largely reflects historical Hg^{ANTH} emissions from China, Korea and Japan.

One interesting deviation from this general trend in Hg^{ANTH} flux was observed in the Okhotsk basin, where a sharp increase was observed before 1960, followed by a plateau in the mid-1990s. This deviation appeared to be associated with Hg emissions from countries in the former Soviet Union. High levels of industrial activity in the former Soviet Union between 1920 and 1960 resulted in greater fossil fuel consumption, which in turn led to greater Hg emissions, whereas the economic crisis in that region after 1980 resulted in a dramatic decrease in fossil fuel consumption and hence to lower Hg^{ANTH} emissions (Street et al., 2011; Maddison, 2006).

To confirm the recent increase in the accumulation of Hg^{ANTH} in sediments in the East China, Yellow and East Seas, natural factors that could bias estimates of the sediment Hg^{ANTH} content need to be properly accounted for. These include post-depositional digenesis, grain size (sediment texture), organic matter content, sedimentation rate, and methylation, all of which could affect the sediment Hg concentration by mobilizing and redistributing Hg within the sediment cores (Fitzgerald et al., 2007).

Conflict of interest

The authors declare that they have no conflict of interest.

Author contributions

H.K. and K.L. designed the study and wrote the manuscript. The analysis of data was performed by H.K., D.I.L., J.K. and S.I. N, collected samples and S.H., E.L., I.H., Y.J. and Y.Z. contributed to the manuscript with discussions and comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2018.11.076.

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Variations in grain size and organic matter content could also cause depth-core variations in Hg content, because these two factors strongly affect the Hg adsorption to sediments. This possibility was investigated by normalizing the Hg concentration to the concentrations of Al or TOC, because this normalization method can account for the effects of grain size and organic matter on Hg concentrations (Windom et al., 1989). The results showed that the depth profiles for Hg normalized to Al (Hg/Al) or TOC (Hg/TOC) were almost identical to the depth profile for Hg concentration. This congruence indicates that the effects of grain size and organic matter on the Hg^{ANTH} flux profile were not significant, so did not affect our conclusions (Fig. 4). Note that for the Yellow Sea sediment core I, the deviations in the Hg/TOC ratio found in nearsurface sediments and in the sediment dated to 1920 were probably caused by sampling error or bioturbation. Despite these deviations, the increasing trend of the Hg/TOC for the two sediment cores collected from the Yellow Sea was largely consistent.

The diagenesis of Fe and Mn redox cycling followed by the desorption of Hg onto oxides and hydroxides (Fe/Mn) can redistribute Hg vertically in sediment cores (Gobeil et al., 1999). However, we found no positive relationship between the concentrations of Hg and Fe in any sediment cores sampled from the Yellow and Okhotsk Seas or the western Arctic Ocean, indicating that sediment digenesis had little effect on the Hg profiles in cores taken from our study area (Fig. 5). A slight positive relationship in sediment cores sampled from the East Sea may be a sign of Fe reduction. However, the good agreement between the profiles of Hg content and those of Hg/Fe ratio confirmed little impact of Fe reduction on sediment Hg content (Fig. S4 in the Supplementary Information).

In addition, no change in sedimentation rate for the past 100 years (covering the upper 9–19 cm in sediment cores) (Fig. S5 in the Supplementary Information) indicates that sedimentation rate change as an explanation for any increase in the Hg^{ANTH} flux is excluded. The high Hg^{ANTH} flux observed in the East China, Yellow, and East Seas could also be because of sedimentary methylation in those basins. However, the concentration of MeHg accounts for <1% of the total Hg contents and demethylation is also simultaneously occurring (Gworek et al., 2016). Therefore, methylation was not a major factor dictating the Hg^{ANTH} flux in the marine sediments of the basins investigated.

5. Conclusion

This study revealed a consistent signal of Hg^{ANTH} deposition to sedimentary environments in the northwestern Pacific Ocean downwind of the Asian continent, through the formation of organo-mercury complexes. The recent increase in Hg^{ANTH} flux determined from several sediment core profiles provides compelling evidence of historical Hg^{ANTH} input into open ocean sedimentary environments downwind of this industrialized continent.

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