Dynamics and Mass Balance of Polycyclic Aromatic Hydrocarbons in and around the Seto Inland Sea, Japan

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Research Article

Keywords: polycyclic aromatic hydrocarbons, Seto Inland Sea, mass balance, transport flux, risk assessment

Posted Date: September 20th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-890473/v1>

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were analyzed to elucidate the distribution, ecological risk, pathways, and fluxes of these pollutants in and around the Seto Inland Sea, Japan. High molecular weight PAHs (5–6 rings) were primarily found in regions close to the bay estuaries, and their proportions decreased at distances further from the estuaries (offshore areas), where low molecular weight PAHs (2–4 rings) were more ubiquitous. Ecological risk assessments revealed that the PAHs found in the sediments should have no adverse effects on benthic communities, with the exception of fluorene, which was detected in high levels in the sediment from Beppu Bay. A mass balance for PAHs in the Seto Inland Sea, calculated based on data collected in the field and published literature findings, showed the PAH flux into the Seto Inland Sea from atmospheric deposition were ca. 5 times higher than that from riverine inflows. Comparison of the amount of the PAH flux between the Seto Inland Sea and other seas suggested that the Seto Inland Sea is less polluted than the Gulf of Lion and the Bohai Sea, and more polluted than the Yellow Sea.

1. Introduction

Marine coastal areas tend to accumulate various harmful substances as a result of human activity around the coast, including operations of the automobile and agriculture industries, landfill development efforts, and shipbuilding, which release chemical substances, gaseous emissions, and excess industrial wastewater and sewage that exceed the available treatment capacities. Therefore, marine coastal areas represent important regions that are vulnerable to the impacts of proximal human activity (Hu et al., 2017). Japan's Seto Inland Sea is a typical coastal sea influenced by mildly- to heavily-polluted environments. This body of water is the largest semi-enclosed coastal sea in Japan, with an average depth of 38 m and a surface area of 23,203 km². About 30% of Japan's population (35 million) live in the area around the Seto Inland Sea, and the population is highly concentrated in the coastal area of the Seto Inland Sea (Ministry of the Environment, Government of Japan, 2018). It is surrounded by three larger islands (Honshu, Kyushu, and Shikoku) and contains more than 700 small islands within its area (EMECS, 2008). The Seto Inland Sea likely receives and accumulates various chemicals, including harmful substances, because of the slow water exchange rate with the open ocean (ca. 82% of the Seto Inland Sea water exchanges with Pacific Ocean water during 1 year (Fujiwara, 1983)).

Polycyclic aromatic hydrocarbons (PAHs) are a class of chemical compounds composed of two or more fused aromatic rings, and they are widely distributed in the environment. Certain PAHs have caused global concern owing to their biochemical characteristics (e.g., carcinogenicity, teratogenicity, and mutagenicity), which make them a threat to the health of living organisms, including humans (Abdel-Shafy and Mansour, 2016; Bartkowski et al., 2016). The International Agency for Research on Cancer (IARC) has classified chemical agents according to their carcinogenic risk, and many PAHs are on that list, including benzo[a]pyrene (in group 1, meaning it is carcinogenic to humans), as shown in Table 1. In general, PAHs may be released into the environment from petrogenic (accidental oil spills, oil exploration and/or crude oil loading/unloading), pyrogenic (combustion of fossil fuels and other organic matter),

biogenic (biological generation and/or degradation processes), or diagenetic (chemical/biological transformations of natural organic matter) sources (Cabrerizo et al., 2014; Iqbal et al., 2008). PAHs tend to transfer to and accumulate in underwater sediments because of their geochemical properties, such as their high hydrophobicity, persistence, and affinity for organic substances (Seker et al., 2005).

Table 1
List of the 17 PAHs analyzed in this study.

Compound	Abbreviation	Rings	Molecular weight	log K_{ow} ^{a)}	Surrogate ^{b)}	IARC classification for carcinogenicity ^{c)}
Naphthalene	Nap	2	128	3.30	Nap- d_8	2B
Acenaphthylene	Acy	3	152	3.93	Ace- d_{10}	–
Acenaphthene	Ace	3	154	3.92	Ace- d_{10}	3
Fluorene	Flu	3	166	4.18	Ace- d_{10}	3
Phenanthrene *	Phe	3	178	4.46	Ace- d_{10}	3
Anthracene *	Ant	3	178	4.45	Ace- d_{10}	3
Fluoranthene *	Flt	4	202	5.16	Phe- d_{10}	3
Pyrene *	Pyr	4	202	4.88	Phe- d_{10}	3
Benz[a]anthracene *	BaA	4	228	5.76	Phe- d_{10}	2B
Chrysene *	Chr	4	228	5.73	Phe- d_{10}	2B
Benzo[b]fluoranthene *	BbF	5	252	5.78	Chr- d_{12}	2B
Benzo[k]fluoranthene *	BkF	5	252	6.11	Chr- d_{12}	2B
Benzo[e]pyrene	BeP	5	252	6.44	Chr- d_{12}	3
Benzo[a]pyrene *	BaP	5	252	6.13	Chr- d_{12}	1
Dibenz[a,h]anthracene *	DahA	5	278	6.50	Per- d_{12}	2A

*the 12 PAHs analyzed from the atmosphere in Osaka city.

^a K_{ow} = octanol-water partitioning coefficient (NCBI, 2020).

^b Surrogate compound used for quantification.

^c IARC classified groups and definitions for carcinogenicity (1 = carcinogenic to humans; 2A = probably carcinogenic to humans; 2B = possibly carcinogenic to humans; 3 = not classifiable as carcinogenic to humans; – = no IARC classification) (IARC, 2020).

Compound	Abbreviation	Rings	Molecular weight	log K_{ow} ^{a)}	Surrogate ^{b)}	IARC classification for carcinogenicity ^{c)}
Indeno[1,2,3-cd]pyrene *	Inc dP	6	276	6.70	Per- d_{12}	2B
Benzo[g,h,i]perylene *	BghiP	6	276	6.63	Per- d_{12}	3
*the 12 PAHs analyzed from the atmosphere in Osaka city.						
^a K_{ow} = octanol-water partitioning coefficient (NCBI, 2020).						
^b Surrogate compound used for quantification.						
^c IARC classified groups and definitions for carcinogenicity (1 = carcinogenic to humans; 2A = probably carcinogenic to humans; 2B = possibly carcinogenic to humans; 3 = not classifiable as carcinogenic to humans; – = no IARC classification) (IARC, 2020).						

PAHs deposited onto such sediments can negatively impact the surrounding marine life, especially benthic organisms, so there is a growing demand for ecological risk assessments of sedimentary PAHs to protect benthic ecosystems. An ecological risk assessment is a practical method for assessing the risks that PAHs pose to an ecosystem (Keshavarzifard et al., 2018; Lan et al., 2020). Long et al. (1995) and Macdonald et al. (1996) established sediment quality guidelines (SQG), which are used to screen sediments from a chemical perspective and identify potential biological effects, particularly in benthic communities (e.g., flatfish, sea urchins, amphipods, and oysters). Their SQG studies dealt with a dataset of biological effects compiled from numerical modeling, laboratory, and field studies, which investigated the individual and mixed PAH levels in sediments from different areas with varied pollution influencing benthic organisms. The endpoints were evaluated in terms of species abundance, species diversity, and toxic and lethal concentrations in the tested organisms. The PAH toxic thresholds and the possible impacts on benthic communities exposed to PAHs above these thresholds were summarized in the SQG studies. However, there is limited information on the ecological risk assessment of PAHs in sediments from the Seto Inland Sea.

Determining the sedimentary PAH concentrations alone may not be sufficient to understand the behavior, sources, and sinks of PAHs in coastal seas. For example, determining organic carbon (OC) contents and grain size distribution of sediments would provide details to elucidate the behavior of PAHs in marine sediments. The relationships between PAH concentrations, OC contents, and sediment grain sizes in the Seto Inland Sea are not yet clearly understood. Additionally, there is limited information available regarding the environmental transport and mass flux of PAHs around the Seto Inland Sea.

In our previous work (Tsuji et al., 2020), we have reported the concentration, horizontal and vertical distribution, and sources of PAHs in the sediments from the Seto Inland Sea. This study aimed to provide

comprehensive understanding of the transport pathways and environmental fate and risk of PAHs around the Seto Inland Sea. The specific objectives of this study were to (i) determine the spatial variations and chemical compositions of PAHs in sediments, (ii) explore the relationships between PAH concentration, OC content, and grain size of sediments, (iii) assess the ecological risks of PAHs in sediments, and (iv) estimate the input pathways, accumulation fluxes, and mass balance of PAHs, all in the Seto Inland Sea. As far as our knowledge, this is the first report on mass balance of PAHs in Japan. The results presented herein provide valuable information in terms of the environmental behavior, ecological risk, and fate of PAHs in the coastal sea in Japan.

2. Materials And Methods

2.1. Sample collection

The sediment sampling sites for this work are described in Fig. 1 (map) and Table S1 (geographical information). In this study, 19 surface sediment samples were collected from each sea area in the Seto Inland Sea: Suo-Nada (St. 1–3), Beppu Bay (St. 4), Bungo Channel (St. 5 and 6), Hiroshima Bay (St. 7–12), Iyo-Nada (St. 13–15), Osaka Bay (St. 17 and 19), Kii Channel (St. 22 and 23). In addition, 36 core sediment samples were collected at four sites: Hiuchi-Nada (St. 16), Osaka Bay (St. 18 and 20), and Kii Channel (St. 21).

River water samples were collected from a mid-stream site in the Kurose River (1 L × 2 samples), which runs from the city of Higashi-Hiroshima to the city of Kure in Hiroshima Prefecture (length = 51 km, catchment area = 239 km²), and from four sites in the Yodo River (1 L × 4 samples, from upstream to downstream), which runs through Shiga, Kyoto, and Osaka prefectures (length = 75 km, catchment area = 8,240 km²) in November 2019.

The air sampling sites investigated in this study are also shown in Fig. 1. Rainwater samples were collected on the rooftop of the School of Integrated Arts and Sciences building at Hiroshima University, Higashi-Hiroshima.

Details of the sampling of sediment, river water, air and rainwater were described in Supplementary Materials.

2.2. Chemical analysis

The PAHs were extracted from the collected sediments according to procedures described in the literature (Nunome et al., 2018; Tsuji et al., 2020). Surrogate standard recoveries (mean ± standard deviation) (n = 53) were 32 ± 8 %, 50 ± 9 %, 64 ± 10 %, 84 ± 21 % and 92 ± 19 % for naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂, respectively.

Overall, 17 PAHs from sediments, river waters, and rain waters were analyzed, including 16 US EPA (United States Environmental Protection Agency) priority PAHs and benzo[*e*]pyrene (Table 1). The

samples were analyzed using gas chromatography-mass spectrometry (GC-MS; Agilent 7890A/5975C) equipped with an Agilent J&W HP–5MS capillary column (30 m length × 0.25 mm inner diameter × 0.25 µm film thickness) to determine the individual PAH concentrations.

Analysis of the PAHs in air samples from Osaka city was performed according to the “Manual for Measuring Harmful Air Pollutants” published by the Japan’s Ministry of the Environment (http://www.env.go.jp/air/osen/manual2/pdf_rev201903/01_chpt1-3-1.pdf).

The OC content, organic nitrogen (ON) content, and hydrogen (H) content in freeze-dried sediment samples were analyzed with a CHNS/O elemental analyzer (PerkinElmer 2400 series $\square$) at the Natural Science Center for Basic Research and Development at Hiroshima University. The grain size distribution of sediments was analyzed using a laser diffraction particle size analyzer (Shimadzu SALD–2000J) at the Graduate School of Advanced Science and Engineering at Hiroshima University.

Details of the analytical method for the PAHs in sediment, river water, rainwater and air were described in Supplementary Materials.

2.3. Ecological risk assessment

To assess the ecological risk of individual PAHs in sediment samples from the Seto Inland Sea, two thresholds (i.e., effects range low (ERL) and effects range median (ERM)) were applied using the SQG. The ERL represents the lower 10th percentile of the effects, and the ERM represents the lower 50th percentile of the effects; PAH concentrations at these levels have less than a 10% or 50% change of affecting organisms, respectively. The individual PAH concentrations in the Seto Inland Sea sediments were compared with these guideline values to evaluate the ecological risk of the selected PAHs.

2.4. PAH mass balance

To estimate the annual PAH influx from rivers, the concentration of PAHs in suspended particles from the Yodo River and Kurose River were measured. Yodo River is one of the largest rivers, and the Kurose River is one of the smallest rivers in the Seto Inland Sea. Since the PAH data were obtained from different size rivers, flow rate adjusted PAH values were used to calculate the annual PAH influx from rivers. The concentration of atmospheric PAHs measured at several coast sites surrounding the Seto Inland Sea were employed to estimate the average concentration of atmospheric PAHs in the Seto Inland Sea. The PAH data in atmospheric samples from Osaka city (urban sites), Wakayama prefecture (rural sites), and Higashi-Hiroshima city (rural site) were obtained (Jadoon and Sakugawa, 2016). Only a few data are available for the PAH concentration in rainwater in Japan. The average PAH concentration in rainwater from Higashi-Hiroshima (in this study) and Niigata (Oura et al., 2007) were used to estimate the annual deposition flux from the atmosphere into the Seto Inland Sea.

The seawater PAHs concentrations in the Seto Inland Sea seldom determined. In this study, *ave.* 8.2 ± 3.1 ng L^{−1} of the PAHs concentration measured in Hiroshima Bay (Tanaka and Kono, 2014) was employed to estimate the total mass of PAHs in seawater of the Seto Inland Sea. The average PAH concentration in

sediments, the surface area of the Seto Inland Sea, and the accumulation rate and moisture content of sediments were employed to estimate the annual PAH accumulation in sediments throughout the Seto Inland Sea. The accumulation rate of sediments (cm yr^{-1}) was calculated using the sedimentation rate ($\text{g cm}^{-2} \text{ yr}^{-1}$), sediment density, and sediment porosity (determined from analysis of sediment samples from the Seto Inland Sea). The sediment density was calculated using Eq. (1),

$$\rho_{\text{wet}} = M_{\text{wet}} / V, (1)$$

where ρ_{wet} is the wet sediment density, M_{wet} is the mass of wet sediment, and V is the volume of the sediment container used for the analysis. The sediment porosity (γ) was calculated using Eq. (2),

$$\gamma = ((M_{\text{wet}} - M_{\text{dry}}) / \rho_{\text{wet}}) / V, (2)$$

where M_{dry} is the mass of dry sediment.

3. Results And Discussion

3.1. Spatial distribution of PAHs in sediments from the Seto Inland Sea

The spatial distribution of the total PAH concentration ($\Sigma 17\text{PAH}$) in the surface sediments from the Seto Inland Sea is shown in Fig. 2. The $\Sigma 17\text{PAH}$ ranged from 14.6 to 1,160 ng g^{-1} dry weight (dw) with a mean concentration of 198 ng g^{-1} dw (Fig. 2a). Considering the OC content, the normalized $\Sigma 17\text{PAH}$ values ranged from 0.776 to 71.1 g gC^{-1} , with a mean concentration of 10.8 g gC^{-1} (Fig. 2b). The highest $\Sigma 17\text{PAH}$ was found at St. 4 (1,160 ng g^{-1} dw), which was located in the center and deepest area (53 m) of Beppu Bay. Because Beppu Bay has a basin-like submarine topography (Itoh et al, 1998), PAHs and other organic matter are likely to accumulate on the sea basin, and it is difficult for them to diffuse or be transported out of the bay. Oita Prefecture is the third most influential industrial zone in Japan, and its industrial shipment value is about one quarter that of Osaka Prefecture (Fig. S1). Therefore, Beppu Bay is considered a typical semi-closed sea, and PAHs from industrial activities in the surrounding area accumulate in this bay's sediment. In contrast, the lowest $\Sigma 17\text{PAH}$ was found at St. 6 (14.6 ng g^{-1} dw) in the Bungo Channel, likely because this channel is connected to the open ocean, so the PAHs were diluted and diffused into the ocean water.

Sedimentary PAH concentrations may be correlated with the OC content, so the $\Sigma 17\text{PAH}$ concentrations were normalized relative to the OC content. This normalization revealed a similar distribution pattern as that exhibited by the PAH concentrations (Fig. 2b), indicating that the PAH distribution was independent from the organic matter content in the sediments. The OC-dependent distribution of PAHs in sediment was investigated previously (Notar et al., 2001), but a dependence of PAHs on OC was not observed.

In this study, the $\Sigma 17\text{PAH}$ in Osaka Bay ($69.0\text{--}441\text{ ng g}^{-1}\text{ dw}$) was similar to or slightly lower than that measured in our previous study ($70.6\text{--}1,590\text{ ng g}^{-1}\text{ dw}$) (Tsuji et al., 2020). In addition, the $\Sigma 17\text{PAH}$ found in the Kii Channel in this study ($56.1\text{--}104\text{ ng g}^{-1}\text{ dw}$) was around the same level as that found in our previous study ($65.8\text{--}82.3\text{ ng g}^{-1}\text{ dw}$) (Tsuji et al., 2020).

3.2. PAH levels in river waters

The suspended $\Sigma 17\text{PAH}$ from the Kurose River water was $176 \pm 9.1\text{ ng L}^{-1}$ ($n = 2$) and that from the Yodo River water was $42.1 \pm 6.0\text{ ng L}^{-1}$ ($n = 2$). The PAH concentration in the Kurose River was higher than that in the Yodo River because the Kurose River is much smaller, so pollutants, such as PAHs, are more likely accumulate there. These considerations are supported by the fact that the dissolved organic carbon (DOC) and suspended solids (SS) were also higher in the Kurose River ($\text{DOC} = 2.2\text{ mg C L}^{-1}$; $\text{SS} = 4.8\text{ mg L}^{-1}$) than in the Yodo River ($\text{DOC} = 1.4\text{--}1.5\text{ mg C L}^{-1}$; $\text{SS} = 3.1\text{--}4.2\text{ mg L}^{-1}$). The concentration of suspended PAHs in the Kurose River in this study was close to those reported previously in water samples from the Yamato River (length = 68 km, catchment area = $1,070\text{ km}^2$) in Osaka Prefecture ($\Sigma 16\text{PAH} = 7.1\text{--}210\text{ ng L}^{-1}$) (Ito et al., 2007).

3.3. Atmospheric PAH levels in areas surrounding the Seto Inland Sea

The monthly average atmospheric PAH concentrations ($\Sigma 12\text{PAH}$) and total suspended particle (TSP) concentrations at 4–5 sites (depending on the year) are shown in Fig. 3. The $\Sigma 12\text{PAH}$ values were $0.38\text{--}7.4$ (2.3 ± 1.8) ng m^{-3} ($n = 228$) during the years from 2011 to 2014 and 2017 to 2018. Seasonal variations could be observed; $\Sigma 12\text{PAH}$ tended to be high in winter and low in summer. This seasonal trend was consistent with a study by Jadoon and Sakugawa (2016), who found high PAH concentrations in the winter and low PAH concentrations in the summer in Higashi-Hiroshima and Kamihaya. These PAH variations are believed to reflect the effects of meteorological conditions, such as solar radiation, temperature, and wind direction (Jadoon et al., 2015; Jadoon and Sakugawa, 2016). In the present study, the PAH level in Osaka city was almost the same as that in Wakayama (mean $\Sigma 17\text{PAH}$ from Kamihaya = 1.63 ng m^{-3} ; Hiki = 1.18 ng m^{-3}), Higashi-Hiroshima (mean $\Sigma 17\text{PAH} = 2.43\text{ ng m}^{-3}$) (Jadoon and Sakugawa, 2016), and Tokyo (mean $\Sigma 12\text{PAH} = 3.95\text{ ng m}^{-3}$) (Saha et al., 2017). The TSP concentrations were generally high in cold seasons, possibly as a result of flying particles and Yellow Sand (Asian dust originating from Chinese desert regions) due to the prevailing westerlies in the east Asia. PAHs tend to be carried along with fine particles (Zhang et al., 2020); therefore, the distribution of TSP (i.e., particles collected without size discrimination) was not related to the distribution of PAHs.

3.4. Relationships between $\Sigma 17\text{PAH}$, OC, and grain size

Sediment properties, including the OC and grain size distribution, may be related to the sedimentary PAH concentrations (Ameur et al., 2010; Raza et al., 2013; Sciarrillo et al., 2020). Indeed, a relationship between PAH concentration and OC or sediment grain size was observed in some previous studies (Notar et al., 2001), although no significant correlation among these parameters was observed in other studies (Gu et

al., 2013; Ünlü and Alpar, 2006; Wang et al., 2014). Notar et al. (2001) observed a significant correlation between PAH concentration and clay and/or OC content in sediments from the Gulf of Trieste (northern Adriatic Sea), which indicated that PAHs were related to the organic matter in sediment. However, Gu et al. (2013) found a poor correlation between OC and organic pollutants in sediments from Baisha Bay (Nan'ao Island in southern China). They proposed that OC and PAHs were not reaching an equilibrium because there was a continuous influx of fresh contaminants from specific sources. Ünlü and Alpar (2006) also observed a poor correlation between PAHs and OC in sediment from Gemlik Bay (Marmara Sea, Turkey). They suggested that diverse benthic biota and their high OC productivities contributed to the OC level in bottom sediments, thereby obscuring the possible relationship between PAHs and OC.

Figure S2 describes an example of sediment particle size distribution (St. 17, Osaka Bay). Table S2 presents the OC, ON, $\Sigma 17\text{PAH}$, and grain size distribution of the sediment samples. The correlations between PAH concentration, OC content, ON content, H content, sediment grain size, and moisture content were investigated to explore their mutual relationships. However, there were no significant correlations detected among the measured 17PAH concentrations and the other sediment properties considered in this study.

The plots in Fig. 4a–e show the correlations between $\Sigma 17\text{PAH}$ (ng g^{-1} wet weight (ww)) and the OC content (% ww), median diameter, and [gravel + sand], silt, and clay contents. The PAHs existed on sediment particles with a mean OC content of 4.65% ww (ranged from 2–5% ww), mean median diameter of 51.6 μm (9.72–630 μm), silt content of 80–85%, clay content of 10–15%, and gravel and sand contents $\sim 5\%$. There were no statistically significant correlations between the $\Sigma 17\text{PAH}$ concentration and OC or grain size. The PAH concentration was relatively high in the sediment from Hiroshima Bay, Hiuchi-Nada, and Osaka Bay, wherein the sediment had significant amounts of silt-sized particles (85–90 %), small amounts of clay-sized particles (10–15 %), and very small amounts of gravel- and sand-sized particles ($< 5\%$). The PAH concentration was low in several specific stations in Iyo-Nada, Bungo Channel, and Kii Channel, wherein the sediment had a very large quantities of gravel- and sand-sized particles ($> 95\%$) and very small amounts of silt- and clay-sized particles ($< 5\%$). It was clear that the OC could not fully explain the distribution pattern of PAHs in the Seto Inland Sea. The particle size distribution partially explained the PAH distributions, but did not fully explain the variation in PAH distribution from region to region within the Seto Inland Sea.

The plot in Fig. 4f illustrates the correlations between $\Sigma 17\text{PAH}$ (ng g^{-1} ww) and the distance from the sampling site estuary. Based on the distribution of $\Sigma 17\text{PAH}$ in sediments from Osaka Bay, $\Sigma 17\text{PAH}$ was the highest in the inner area of the bay and decreased towards the offshore areas (as the distance from the estuary increased). Similarly, in Hiroshima Bay, the $\Sigma 17\text{PAH}$ in sediments was high in the inner part of the bay and decreased towards the offshore regions further away from the estuary. The results presented in Fig. 4 suggested that a major factor governing the distribution of sedimentary PAHs in the Seto Inland Sea is the distance from the estuary. Osaka Prefecture, which is the second metropolitan region in Japan after Tokyo, contains numerous PAH emission and discharging sources (see Fig. S1), so Osaka Bay is

often considered a “receiver tank” of anthropogenic PAHs. Hiroshima Prefecture is a mid-sized industrial region in Japan, and thus, Hiroshima Bay also receives significant amounts of anthropogenic PAHs.

3.5. Composition of PAHs in the Seto Inland Sea

The chemical composition breakdowns of PAHs (in terms of the number of aromatic rings) in the sediments from the Ohta River estuary of Hiroshima Bay (through Iyo-Nada and the Bungo Channel) and from the Yodo River estuary of Osaka Bay (through the Kii Channel) are presented in Fig. 5a and 5b, respectively. The percentage of high molecular weight PAHs (5–6 rings) relative to the total PAHs was highest in the estuaries of the Hiroshima and Osaka Bays, and it gradually decreased as the distance from the estuary increased, reaching the lowest fractions in the offshore areas (i.e., Bungo Channel and Kii Channel). In contrast, the percentage of low molecular weight PAHs (2–4 rings) was lowest in the estuaries and increased with increasing distance from the estuary, reaching the highest values in the offshore areas. It is believed that high molecular weight PAHs may be rapidly deposited into sediments from the estuary (i.e., close to the anthropogenic sources on land) owing to their low volatility, high octanol-water partition coefficient (K_{ow}), and high particle adsorption capacity. In contrast, low molecular weight PAHs tend to be transported and deposited in sea areas, away from the estuary because of their high volatility, low K_{ow} , and low adsorption capacity. Reports on PAH distributions in soil confirmed that low molecular weight PAHs can be transported far from the original sources thanks to their higher volatility and weaker adsorption to particulates, relative to high molecular weight PAHs (Hong et al., 2020; Wang et al., 2020). The behavior of PAHs in soil observed in this study similarly indicated that high molecular weight PAHs could be deposited on marine sediments relatively close to the source, while low molecular weight PAHs were more likely to be transported far away from the source.

3.6. Ecological risk assessment of PAHs in sediments

The PAH levels at almost all of the sampling sites in this study were below the ERL (meaning they have a 10% or less chance of affecting organisms) based on the SQG (Long et al., 1995; Macdonald et al., 1996). Thus, it was determined that the PAHs (with the exception of Flu) should have no appreciable adverse effects on benthic communities. Flu is a three-ring PAH that was detected at St. 4 (in Beppu Bay) at a level between the ERL and the ERM (meaning it has up to a 50 % chance of affecting organisms), as shown in Table 2. This indicates that adverse biological effects from Flu are likely to occur in Beppu Bay, and special attention should be paid in terms of the potential ecological risk of PAHs in Beppu Bay. In previous studies in China, Flu was also detected between the ERL and the ERM levels at two sites in the Luan River estuary (Zhang et al., 2016) and one site on Caofeidian Long Island (Han et al., 2019). Another three-ring PAH (Acy) was also detected between the ERL and ERM at a site on Caofeidian Long Island (Han et al., 2019), but all other PAHs were below the ERL in all sites. A study probing the effect of Flu on living organisms revealed that Flu caused early growth and metamorphosis of the Ascidian, *Ciona intestinalis* Type A (Sekiguchi et al., 2020).

Table 2

PAH concentrations and risk assessment guideline values ($\text{ng g}^{-1} \text{ dw}$) for the surface sediments of the Seto Inland Sea.

Compound	Concentration range			Mean	SQG		Sites		
	Min	~	Max		ERL	ERM	<ERL	ERL ~ ERM	>ERM
Nap	0.63	~	89.1	6.14	160	2100	all sites	–	–
Acy	0.63	~	12.4	1.84	44	640	all sites	–	–
Ace	0.48	~	6.16	1.25	16	500	all sites	–	–
Flu	0.69	~	22.0	2.59	19	540	except St. 4	St. 4	–
Phe	1.41	~	160	17.9	240	1500	all sites	–	–
Ant	0.98	~	31.5	4.21	85.3	1100	all sites	–	–
Flt	2.77	~	164	23.6	600	5100	all sites	–	–
Pyr	0.96	~	124	19.2	665	2600	all sites	–	–
BaA	1.06	~	136	18.1	261	1600	all sites	–	–
Chr	1.02	~	78.3	15.4	384	2800	all sites	–	–
BbF	0.82	~	87.6	21.5	–	–	–	–	–
BkF	0.65	~	42.3	9.09	–	–	–	–	–
BeP	0.34	~	24.9	8.35	–	–	–	–	–
BaP	0.49	~	56.9	12.6	430	1600	all sites	–	–
DahA	0.23	~	12.9	3.22	63.4	260	all sites	–	–
IncdP	0.17	~	68.0	19.7	–	–	–	–	–
BghiP	0.84	~	46.8	13.4	–	–	–	–	–
$\Sigma 17\text{PAH}$	14.6	~	1162	198	4022	44792	all sites	–	–
ERL = effects range low; ERM = effects range median; SQG = sediment quality guidelines.									

3.7. Mass balance of PAHs

Table 3 presents the parameters used in mass balance calculations involving $\Sigma 17\text{PAH}$ in the Seto Inland Sea. The flux of $\Sigma 17\text{PAH}$ from rivers into the Seto Inland Sea was estimated to be $2.3 \pm 0.3 \text{ tons yr}^{-1}$ (Fig. 6). Multiplying the sum of the PAH fluxes from wet and dry depositions by the surface area of the Seto Inland Sea, led to an estimation of the atmospheric deposition flux of PAHs ($13 \pm 1 \text{ tons yr}^{-1}$). These PAH mass balance calculations revealed that the atmospheric deposition flux of PAHs was higher than

the river influx of PAHs. After adding the river inflows and atmospheric depositions of $\Sigma 17\text{PAH}$, it was determined that 15 ± 1 tons of $\Sigma 17\text{PAH}$ are input into the Seto Inland Sea annually.

Table 3
Parameters used for mass balance calculations regarding PAHs in the Seto Inland Sea.

Item	Value	References
Riverine inflow of PAHs		
PAHs concentration in Kurose River water	$176 \pm 9.1 \text{ ng L}^{-1}$	This study
PAHs concentration in Yodo River water	$42.1 \pm 6.0 \text{ ng L}^{-1}$	This study
Flow rate of Kurose River	$5.00 \text{ m}^3 \text{ s}^{-1}$	Hiroshima Prefectural Government, 2020
Flow rate of Yodo River	$163 \text{ m}^3 \text{ s}^{-1}$	Ministry of Land, Infrastructure, Transport and Tourism, 2003
Total inflow of river water to the Seto Inland Sea	$50 \text{ km}^3 \text{ yr}^{-1}$	Imai et al., 2006
Atmospheric PAHs deposition		
PAHs concentration in rain water at Higashi-Hiroshima	137 ng L^{-1}	This study
PAHs concentration in rain water at Niigata	$499 \pm 84.1 \text{ ng L}^{-1}$	Oura et al., 2007
Annual total precipitation at Kure city for 2015 ~ 2019	$1577 \pm 129.2 \text{ mm yr}^{-1}$	Japan Meteorological Agency, 2020
Atmospheric PAHs concentration in Osaka city	2.28 ng m^{-3}	This study
Atmospheric PAHs concentration at Kamihaya in Wakayama	1.63 ng m^{-3}	Jadoon and Sakugawa, 2016
Atmospheric PAHs concentration at Hiki in Wakayama	1.18 ng m^{-3}	Jadoon and Sakugawa, 2016
Atmospheric PAHs concentration at Higashi-Hiroshima	2.43 ng m^{-3}	Jadoon and Sakugawa, 2016
Dry deposition rate (particles < 2.5 μm)	0.1 cm s^{-1}	Duce et al., 1991

¹ The cutting intervals (2 cm, 5 cm) of the collected sediment cores were averaged.

Item	Value	References
The Seto Inland Sea surface area	23,203 km ²	EMECS, 2008
PAHs accumulation in sediments		
PAHs concentration in sediments from the Seto Inland Sea	198 ng g ⁻¹ dw	This study
Surface area of sediment sampler	95 cm ²	This study
Volume of surface sediments (3.5 cm thick ¹⁾)	332.5 cm ³	This study
Sedimentation rate	0.2 g cm ⁻² yr ⁻¹	Hoshika and Shiozawa, 1984a; Hoshika and Shiozawa, 1984b; Hoshika and Shiozawa, 1985; Matsumoto and Yokota, 1978
Sediment porosity	0.591	This study
Sediment density	1.451 g cm ⁻³	This study
Moisture content of sediment	47.1 ± 20.2 %	This study
PAHs mass in seawater		
PAHs concentration in seawater of the Seto Inland Sea	8.2 ± 3.1 ng L ⁻¹	Tanaka and Kono, 2014
The Seto Inland Sea water volume	881.5 ± 5.24 km ³	EMECS, 2008
Biodegradation of PAHs		
BaP biodegradation rate constant	0.0026 day ⁻¹	Kot-Wasik et al., 2004
PAHs uptake in bivalves		
PAHs concentration in bivalves including <i>Mytilus galloprovincialis</i> and <i>Septifer virgatus</i> in the Seto Inland Sea	18 ng g ⁻¹ wet weight	Tanaka and Onduka, 2010
Biomass of the bivalve population in Kurushima Strait of the Seto Inland Sea	11.5 kg wet flesh weight m ⁻²	Itô and Yamamoto, 1984
¹ The cutting intervals (2 cm, 5 cm) of the collected sediment cores were averaged.		

Following PAH mass balance calculations, the magnitudes of the PAH influx and PAH sedimentation flux matched well. The difference between the $\Sigma 17$ PAH influx and the sedimentation flux of $\Sigma 17$ PAH in the Seto Inland Sea (i.e., $15.3 \text{ ton yr}^{-1} - 5.5 \text{ ton yr}^{-1} = 9.8 \text{ ton yr}^{-1}$) was considered the outflow flux, which included discharge to the open ocean, uptake into marine organisms, photodegradation, and biodegradation.

A mass balance study of PAHs in Lake Suwa in Japan (Miyahara and Ikenaka, 2007) indicated that the annual PAH sedimentation (4.0 kg) was lower than the annual PAH load flowing into the lake (8.6 kg). This is consistent with our finding that the PAH sedimentation (5.5 ton yr^{-1}) was smaller than the PAH input (15 ton yr^{-1}) in the Seto Inland Sea. Additionally, it was reported that the atmospheric deposition of PAHs was higher than the riverine inflows in the Mediterranean Sea (Lipiatou et al., 1997); this is also consistent with our results. However, atmospheric deposition and river input were almost equivalent in the case of the East China Sea (Wang et al., 2017). In areas where riverine inflow of PAHs is greater than or equal to atmospheric deposition of PAHs, the PAH sources (industries) are likely located in inland areas, so pyrogenic PAHs are mostly deposited on land and eventually flow into rivers. However, in the Seto Inland Sea, heavy industries and large cities are located along the coastal areas, so PAHs from burning fossil fuels and biomass could be directly deposited into the seawater.

The annual PAH input (per km^2 of water surface area) into the Seto Inland Sea was compared with the PAH input into other bodies of water, as reported in the literature (Fig. S3). The annual PAH influx per km^2 of the Seto Inland Sea ($0.66 \text{ kg km}^{-2} \text{ yr}^{-1}$) was lower than into the Bohai Sea (in China; $1.5 \text{ kg km}^{-2} \text{ yr}^{-1}$) (Wang et al., 2017), and into the Gulf of Lions (northwestern basin of the Mediterranean Sea; $0.84 \text{ kg km}^{-2} \text{ yr}^{-1}$) (Bouloubassi et al., 2012). However, it was similar to the influx into Lake Suwa (central Japan; $0.65 \text{ kg km}^{-2} \text{ yr}^{-1}$) (Miyahara and Ikenaka, 2007), and higher than that into the Yellow Sea ($0.42 \text{ kg km}^{-2} \text{ yr}^{-1}$) (Wang et al., 2017). Based on these comparisons, the Seto Inland Sea is less polluted with PAHs than the Bohai Sea and the Gulf of Lion, as polluted as Lake Suwa, and more polluted than the Yellow Sea.

4. Conclusions

The results of this study indicated that the concentration of PAHs in Seto Inland Sea sediments decreased as the distance from the estuary increased. There was no significant correlation between the PAH concentration and the OC content or the sediment particle size, although high PAH concentrations were observed in sediment containing high proportions of silt particles. Therefore, the OC content and sediment particle size were not the primary factors for determining the horizontal distribution of PAHs. Instead, the distance from the estuary of major rivers flowing into the Seto Inland Sea was likely the major factor controlling PAH distribution.

High molecular weight compounds comprised the majority of the PAHs near the Osaka and Hiroshima Bay estuaries, but these concentrations decreased in areas further from the estuary in offshore areas,

where low molecular weight PAHs were the dominant species. It was proposed that high molecular weight PAHs may be rapidly deposited onto sediment from the estuary owing to their low volatility, high K_{ow} , and high particle adsorption capacity. In contrast, low molecular weight PAHs tended to be transported and deposited in areas far from the estuary, depending on their volatility, K_{ow} , and adsorption capacity.

Risk assessments of sedimentary PAHs were performed using the sediment quality guidelines, which revealed that the fluorene level in sediments from Beppu Bay was above the ERL, thus having potential adverse effects on benthic communities. However, all other PAHs were predicted to have no adverse effects on benthic communities in Beppu Bay or other regions of the Seto Inland Sea.

This report first provided on the mass balance of PAHs in coastal sea in Japan. The transport and accumulation fluxes of PAHs were determined that PAHs originated mostly from atmospheric deposition (13 ton yr^{-1}), rather than river inflows (2.3 ton yr^{-1}), and sinking flux to marine sediment accounted for 36 % of the total outflow. The outflow fluxes of PAHs were considered as discharge to the open ocean, uptake by marine organisms, or photochemical or biological degradation. It was estimated that the uptake by bivalves and microbial degradation were 0.17 and 4.4 ton yr^{-1} , respectively, but other outflow fluxes were not evaluated in this study. Comparison of the amount of the PAH mass flux between the Seto Inland Sea and other seas indicated that the Seto Inland Sea is less polluted than the Gulf of Lion and the Bohai Sea, and more polluted than the Yellow Sea.

Declarations

Funding: This work was financed by the Japan Society for the Promotion of Science (JSPS) (KAKENHI grant number 16KT0149).

Conflicts of interest/Competing interests: The authors declare that they have no conflict of interest.

Availability of data and material: Not applicable.

Code availability (software application or custom code): Not applicable.

Authors' contribution: All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Hiroaki Tsuji, Yuta Akiyoshi, Daichi Asakawa, Shinya Nakashita, Yoko Iwamoto, Hiroshi Sakugawa, and Kazuhiko Takeda. The first draft of the manuscript was written by Hiroaki Tsuji and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Additional declarations for articles in life science journals that report the results of studies involving humans and/or animals: Not applicable.

Ethics approval: Not applicable.

Consent to participate: All the authors mentioned in the manuscript have agreed for authorship, read, and approved the manuscript, and given consent for submission and subsequent publication of the manuscript.

Consent for publication: Not applicable.

Acknowledgments

Authors acknowledge Professor Satoshi Chiba (Faculty of Environmental and Information Sciences, Yokkaichi University) for providing valuable information on the mass balance of PAHs. The authors appreciate Associate Professor Satoshi Asaoka (Graduate School of Integrated Sciences for Life, Hiroshima University) for allowing us to use the HR-type core sampler to collect sediment core samples. The authors thank Ms. Momoko Kubota (Natural Science Center for Basic Research and Development, Hiroshima University) for support with the analysis of the OC content in sediment samples. The authors thank all the crew members of the R/V Toyoshio-maru, Hiroshima University. The authors thank the Japan Society for the Promotion of Science (JSPS) for their funding for this work (KAKENHI grant number 16KT0149). We also thank Suzanne Adam, PhD, from Edanz Group (<https://en-author-services.edanz.com/ac>) for editing a draft of this manuscript.

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Figures

Figure 1

Locations of 23 sediment sampling stations (filled circles) and 8 air sampling stations (open circles) in and around the Seto Inland Sea, Japan.

Figure 2

(a) Concentrations of the 17 PAHs in surface sediments ($\text{ng g}^{-1} \text{ dw}$), and (b) PAH concentrations normalized based on the OC content in the surface sediments (g gC^{-1}). The numbers below the graphs show the sampling sites.

Figure 3

Monthly variations in the average atmospheric $\Sigma 12\text{PAH}$ (ng m^{-3}) and TSP ($\mu\text{g m}^{-3}$) in Osaka city during the years 2011–2014 and 2017–2018. The dotted red line represents the average value of $\Sigma 12\text{PAH}$ during the sampling period.

Figure 4

Correlations between $\Sigma 17\text{PAH}$ (ng g⁻¹ ww) and (a) OC (% ww) in sediments; (b) median diameter of sediment particles; (c) content of gravel and sand in sediments; (d) silt content in sediments; (e) clay content in sediments; (f) distance from estuary to the sampling site.

Figure 5

Composition of PAHs (classified based on the number of benzenoid rings) at each site from (a) the Ohta River estuary of Hiroshima Bay to the offshore areas (Iyo-Nada and Bungo Channel), and from (b) the Yodo River estuary of Osaka Bay to the offshore area (Kii Channel).

Figure 6

Mass balance of $\Sigma 17\text{PAH}$ in the Seto Inland Sea. The seawater value is reported as a mass (tons), while the other values are reported as transport fluxes (ton yr^{-1}) of $\Sigma 17\text{PAH}$.

Supplementary Files

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