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Persistent organic pollutants are still present in surface marine sediments from the Seto Inland Sea, Japan

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Abstract

Although persistent organic pollutants (POPs) are currently banned or strictly controlled under the Stockholm Convention on Persistent Organic Pollutants, POPs are still distributed worldwide due to their environmental persistence, atmospheric transport, and bioaccumulation. Herein we investigated the current concentrations of POPs in the sediments from Seto Inland Sea, Japan and sought to clarify the factors currently controlling the POPs concentration of the surface sediments from Seto Inland Sea. The concentrations of hexachlorocyclohexane isomers (HCHs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), and chlordane isomers (CHLs) in sediments from Seto Inland Sea were <0.002–1.20 ng g^{-1}, 0.01–2.51 ng g^{-1}, and 0.01–0.48 ng g^{-1}, respectively. Resuspension increased the concentrations of HCHs, HCB, and DDTs in the surface sediment with the release of historically contaminated pollutants accumulated in a lower layer. We speculate that CHLs in air that were removed by atmospheric deposition affects the concentration of CHLs in surface sediments.

Keywords: atmospheric deposition, chlordane, dichlorodiphenyltrichloroethane, hexachlorobenzene, hexachlorocyclohexane, resuspension

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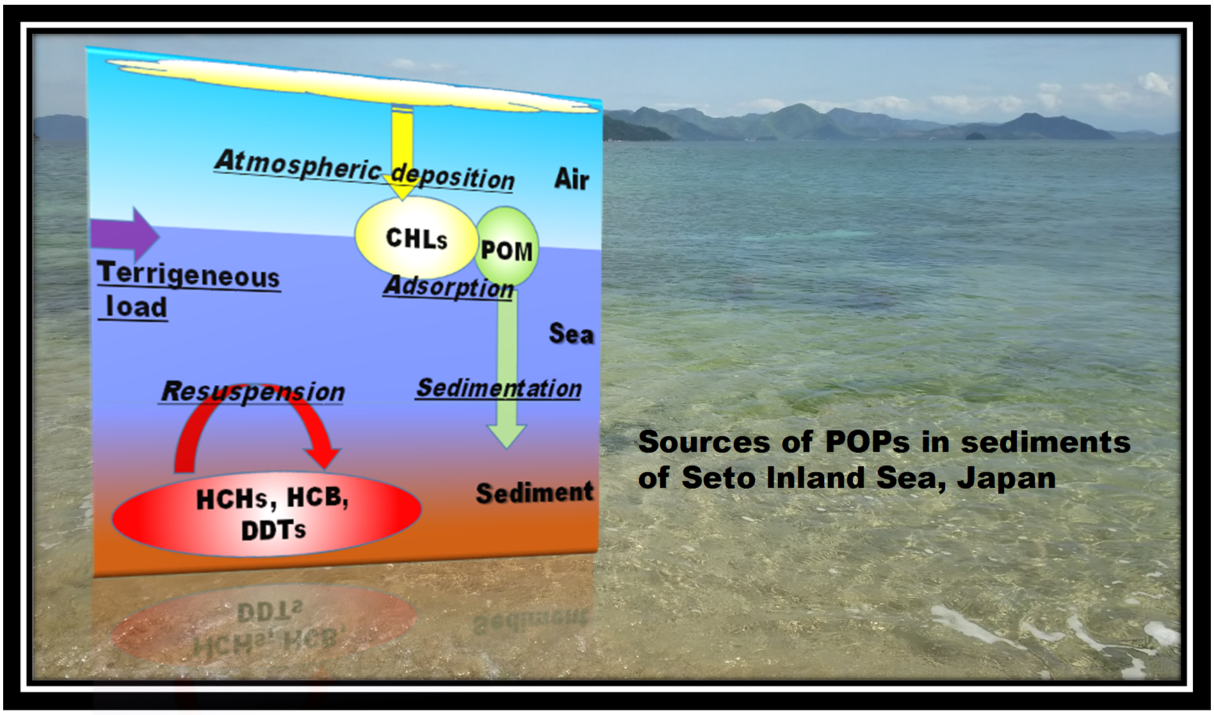

Highlights

- The current POPs concentrations in sediments from Seto Inland Sea were examined.
- The factor controlling the Sea's sediment POPs concentrations was revealed.
- Resuspension increased the concentrations of HCHs, HCB, and DDTs in surface sediments.
- Atmospheric deposition affects the concentration of CHLs in the surface sediments.
- Both mechanisms decelerate the decrease of the POPs concentration in sediments.

1. Introduction

The sediments that have settled in enclosed water bodies are affected by significant terrigenous organic matter loads. Chemical pollution is thus closely associated with domestic and industrial activities in coastal areas. Organic matter in marine sediment is categorized mainly into two fractions depending on its degradability: i.e., labile or refractory organic matter. The labile organic matter is easily decomposed by aerobic and anaerobic microbial activities. In contrast, the components of the refractory organic matter fraction include humic substances and persistent organic pollutants (POPs), which are ubiquitous contaminants that have adverse biological effects such as toxicity, endocrine disruption, genetic mutations, and cancer (Harada et al. 2016; Chen et al. 2019). Due to their bioaccumulation through the food chain, POPs have a negative impact on top predator species (Kelly and Gobas 2001; Voutsas et al. 2002; Fisk et al. 2001). POPs such as hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroetha (DDT), and chlordane used to be applied as a pesticide for vegetable crops and home lawns and gardens, and as a soil insecticide (Bidleman et al. 2002). The use of these pesticides are currently banned or strictly controlled under the Stockholm Convention on Persistent Organic Pollutants (POPs Convention).

However, POPs are still distributed worldwide due to their environmental persistence, atmospheric transport, and bioaccumulation through the food chain (Berrojalbiz et al. 2011;

Sharma et al. 2014; Ma et al. 2015a, b; Jin et al. 2017). In aquatic systems, POPs are removed from the water column and adsorbed on particulate matters and accumulated in sediments. Therefore, sediments and their resuspension are considered a secondary contamination source of POPs. The continuous monitoring and assessment of POPs in the sediments thus remains necessary. In the present study, we identified POPs derived from contamination with pesticides such as HCHs, DDTs and CHLs in coastal marine sediments even though these pesticides are no longer allowed to be used in Japan. It is very important to elucidate reasons why these pesticides are still detected in coastal surface marine sediments.

The Seto Inland Sea is the largest semi-enclosed sea in Japan, with both a eutrophic area (facing one of the most industrialized and populated areas affected by terrigeneous loads) and an oligotrophic and less populated area. The intensive monitoring of POPs has been conducted throughout the Seto Inland Sea (including the POPs' bioaccumulation) since the 1970s (Fujii et al. 2007; Isobe et al. 2011; Takabe et al. 2012). However, few recent investigations of POPs such as HCHs, DDTs and CHLs in sediments from Seto Inland Sea have been reported, and although the concentrations of POPs in the sediments were reported to be positively related with that of organic carbon (Iwata et al. 1995; Sweetman et al. 2005), the relationship between the degradability of organic carbon in sediment (i.e., the labile, semi-labile, and refractory fractions) and POP concentrations in the sediment has not been established. In this study, we addressed the issue of why HCHs, DDTs, and CHLs are still detected on the surface of the sediments which accumulated in recent years and are distributed heterogeneously in the Seto Inland Sea. The purposes of the study were to (1) determine the current concentrations of POPs in the sediments from the Seto Inland Sea, and (2) identify the factor(s) that affect the POP concentrations of those surface sediments.

2. Experimental

2.1. Sediment and marine particulate matter sampling sites

Sediment and marine particulate matter samples were collected from 15 stations in the Seto Inland Sea, Japan in 2016 and 2017 by a Hiroshima University training and research vessel, the Toyoshio Maru (**Fig. 1)**. The coordinates of the sampling sites are shown in **Table 1**. The Seto Inland Sea is a semi-enclosed sea approx. 450 km from east to west and 15–55 km from north to south, with an average depth of 38 m. The sea is surrounded by Japan's Honshu Island, Shikoku Island, and Kyushu Island and contains more than 700 islands. The total area of the sea is 23,203 km^2, and the catchment is one of the most industrialized and populated areas in Japan, with a watershed population of approx. 30 million.

2.2. Sampling procedures

Sediment core samples were collected using an undisturbed core sampler (11 cm dia., 50 cm long: HR type; Rigo, Osaka, Japan). The collected cores were cut at every 5 cm on board the vessel. Each collected sediment sample was immediately transferred into a methanol-rinsed stainless steel container and stored in a refrigerator at 4°C before being transferred to a laboratory. The particulate matter in 1.5–2.0 L of surface seawater (0–2 m depth) was collected with pre-combusted (600°C, 2 hr) glass-fiber filters (GF/F; Whatman, Maidstone, UK).

2.3. Sample extraction for the analysis of persistent organic pollutants in sediments

Extraction of POPs from marine sediments was conducted based on Haga et al., 2017, with minor modifications. Weighed wet sediment samples (approx. 10 g), 10 g of hydromatrix (198003: Agilent, Santa Clara, CA, USA), and 3 g of reduced copper particles (60–80 mesh: Kishida Chemical Osaka, Japan) were mixed together, and the mixture was then transferred to a 99-mL volume cell for accelerated solvent extraction (ASE). Thereafter, 50 ng mL^{-1} of POPs clean-up spike (100 μL^{-1}) prepared from #ES-5261-1.2 POPs Clean-up Spike (Cambridge Isotope Laboratories, Tewksbury, MA) as a surrogate was added to the mixture. The POPs in the sediment samples were extracted by three cycles of acetone (for Dioxins Analysis Grade; Kanto Chemical Co., Tokyo) using an ASE system (ASE 350: Thermo Scientific, Waltham, MA) under 100°C and 1500 psi.

The extracts were concentrated to 50 mL using a rotatory evaporator (RE500: Yamato Scientific Co., Tokyo) coupled with a solvent recovery unit (NVC-1100, Eyela, Tokyo). The concentrated extract was transferred to a separating funnel. Each concentrated extract was shaken at 300 rpm for 10 min and left standing for 10 min at room temperature in the separating funnel. After the extracts were dehydrated with anhydrous sodium sulfate, the extracts were transferred to a pear-shaped flask and concentrated to 2–3 mL with the rotary evaporator.

Next, 1 g of sodium sulfate anhydrous（for pesticide residue and PCB Analysis Grade; Kanto Chemical Co.) was stuffed into a pretreatment cartridge (a 12-mL SPE tube: Si/44% H_2SO_4/Si SPE Tube 54040-U; Merck, Darmstadt, Germany), and the cartridge was lined by introducing 10 mL hexane. The extract was loaded to the cartridge, and the POPs in the extract were successively eluted by the introduction of 50 mL of hexane. Purified POPs in the extracts were concentrated to 3–4 mL by the rotary evaporator. Activated copper powder (Wako Chemicals, Osaka, Japan) was then added to the extract, and the extract was transferred to a spits glass and concentrated under a nitrogen gas flow. The volume of the extract was then filled up to 0.5 mL with hexane, and it was added to 20 μL of MBP-15 (50 ng mL^{-1}; Wellington Laboratories, Ontario, Canada) and MBP-70 (50 ng mL^{-1}; Wellington). The POP concentrations in the extract sample were analyzed by a gas chromatography system (6890N; Agilent) with a high-resolution mass spectrometer (JMS-800D; JEOL, Tokyo).

2.4. Sample extraction for POPs in the particulate matter

Weighed particulate matter samples were transferred to a 33-mL volume cell for ASE. Thereafter, 50 ng mL^{-1} of POPs clean-up spike (100 μL^{-1}) prepared from # ES-5261-1.2 POPs Clean-up Spike (Cambridge Isotope Laboratories) as a surrogate was added to the mixture. The POPs in the particulate matter samples were extracted by three cycles of acetone (for Dioxins Analysis Grade: Kanto Chemical) with the above-described ASE system under 100°C and 1500 psi. The extracts were concentrated to 50 mL using the rotatory evaporator and NVC-1100, and the concentrated extract was transferred to a separating funnel. The concentrated extract was shaken at 300 rpm for 10 min and left standing for 10 min at room temperature in the separating funnel.

After the extracts were dehydrated with anhydrous sodium sulfate, the extracts were transferred to a pear-shaped flask and concentrated to 2–3 mL with the rotary evaporator. Next, 1 g of sodium sulfate anhydrous (for pesticide residue and PCB Analysis Grade; Kanto Chemical Co.) was stuffed into a pretreatment cartridge (12-mL SPE tube, Si/44% H_2SO_4/Si SPE Tube 54040-U; Merck), and the cartridge was lined by introducing 10 mL hexane.

Each extract was loaded to the cartridge, and the POPs in the extract were successively eluted by the introducing 50 mL of hexane. Purified POPs in the extracts were concentrated to

3–4 mL by the rotary evaporator. The extracts were then transferred to a spits glass and concentrated under a nitrogen gas flow. The volume of the extract was then filled up to 0.5 mL by hexane and added to 20 μL of MBP-15 (50 ng mL^{-1}; Wellington) and MBP-70 (50 ng mL^{-1}; Wellington). The POPs concentrations in the extract sample were analyzed by the gas chromatograph and（6890N: Agilent）with a high-resolution mass spectrometer (JMS-800D: JEOL）.

2.5. Sample analyses

Concentrations of POPs in the extracts were analyzed based on Tsurukawa et al., 2011, with minor modifications. The above-described gas chromatograph coupled with the high-resolution mass spectrometer was used for determining the concentrations of the POPs in the sediment samples. The capillary column used for the analysis was an HT8-PCB column (60 m × 0.25 mm i.d.; SGE Analytical Science, Victoria, Australia). The column oven temperature was controlled at 120°C and increased to 180°C at 20°C min^{-1}, then to 210°C at 2°C min^{-1}, and to 280°C at 5°C min^{-1} before reaching 330°C at 20°C min^{-1} and held for 18 min. The 2-μL sample was injected in splitless mode, and the He carrier gas flow rate was 1.5 mL min^{-1}. The inlet temperature, ion source temperature, and interface temperature were kept at 260°C. Electron ionization (EI) mass spectra were recorded at 38 eV electron energy with an ionization current of 400 μA and a detector voltage of 300V.

All procedural blanks were extracted in the same manner as the samples below the method quantification limits (MQLs). The MQLs (signal-to-noise ratio of 10) ranged from 0.007 to 0.63 ng g^{-1} dry weight for the sediment samples and from 0.03 to 0.63 ng g^{-1} dry weight for the particulate matter samples. The matrix spike recoveries for all analytes, HCHs, HCB, DDTs, and CHLs were 86%–115% with a mean standard deviation (MSD) of 6.9% for the sediment samples and 67%–104% with 8.5% MSD for the particulate matter samples.

3. Results and Discussion

3.1. Hexachlorocyclohexane isomers (HCHs) in the sediment samples

The concentrations of ΣHCHs in the sediments from Seto Inland Sea ranged from <0.003 to 1.20 ng g^{-1} (**Table 2**). The concentrations at the innermost area of Osaka Bayat Stations O-1 (0.99 ng g^{-1}), O-2 (1.20 ng g^{-1}), and O-M1 (0.39 ng g^{-1}) were high compared to the other stations (<0.003–0.24 ng g^{-1}). Compared to the recently obtained concentrations of ΣHCHs in the sediments from different areas around the world (**Table 3**), the surface sediments in the Seto Inland Sea were not significantly contaminated by HCHs.

Technical HCH contains 60%–70% α-HCH, 5%–12% β-HCH, 10%–12%, γ-HCH, and 6%–10% δ-HCH. It is also available in its pure form as lindane (>99% γ-HCH; Jiang et al.

2009). The composition of HCHs in the sediment samples that we collected from the Seto Inland Sea were 20.0%–46.6% for α-HCH, 24.0%–57.5% for β-HCH, and 10.6%–46.3% for γ-HCH (**Fig. 2**). The proportion of β-HCH was relatively high except at Stations A-M1, A-2, and K-1. This was attributed to β-HCH's resistance to biodegradation (Dannenberger 1996). Thus, the relatively higher percentages of β-HCH in the present sediment samples indicated no new HCH sources in the Seto Inland Sea. In contrast, γ-HCH (lindane) accounted for 39.0%–46.3% of the total HCHs at Stations A-M1, A-2, and K-1.

The ratio of α-HCH/γ-HCH reflects the source of HCH, and the reported α-HCH/γ-HCH values varied from 0.54 to 5.85 for technical HCHs and 0 for lindane (Zhang et al. 2003). The α-HCH/γ-HCH value in the sediments from the Seto Inland Sea ranged from 0.5 to 4.4 (**Table 2**), indicating that the HCHs in the present sediment samples originated from the mixture of technical HCHs and lindane (Iwata et al. 1995).

3.2. Hexachlorobenzene (HCB) in the sediment samples

The HCB concentrations in the sediment samples collected from the Seto Inland Sea ranged from <0.007 to −0.25 ng g^{-1} (**Table 2**). The HCB concentrations at the innermost area of Osaka Bay, i.e., at Stations O-1 (0.14 ng g^{-1}) and O-2 (0.25 ng g^{-1}) were high compared to those at the other 13 stations (<0.007−0.07 ng g^{-1}). Our comparison of the HCB levels in marine sediments with those in studies conducted at various sites around the world is summarized in **Table 3**. The reported HCB concentrations in the sediments from those different sites were 0.005–0.097 ng g^{-1}, which indicates that the sediment samples from the Seto Inland Sea (except for those from the innermost area of Osaka Bay) were not contaminated by HCB.

The emission sources of HCB are thought to be impurities in pesticides (e.g., HCH, pentachlorophenol [PCP], and dimethyl tetrachlorterephthalate [DCPA]) and from the incineration of municipal and hazardous waste (Bailey 2001). Because HCH and PCP are no longer allowed to be used as pesticides in Japan, the atmospheric deposition due to the combustion of solid waste might also be a source of HCB in the innermost area of Osaka Bay (Teil et al. 2004; Rossini et al. 2005).

3.3. Dichlorodiphenyltrichloroethane and its metabolites (DDTs) in the sediment samples

The concentrations of ΣDDTs in the sediment samples from the Seto Inland Sea ranged from 0.01 to 2.51 ng g^{-1} (**Table 4**). The higher concentrations of ΣDDTs in the sediment samples from the Seto Inland Sea were detected in the innermost area of Osaka Bay — i.e., at Stations O-1 (2.28 ng g^{-1}), O-2 (2.51 ng g^{-1}), and O-M1 (1.32 ng g^{-1}) and A-M1 (1.18 ng g^{-1}) and HA-M1 (0.81 ng g^{-1}). Compared to the concentrations of DDTs in the sediments from different areas worldwide (**Table 3**), the surface sediments from the Seto Inland Sea were at a lower pollution level.

DDT can be transformed to DDD and DDE, which were more un-degradable (Dannernbereger 1996). The DDT composition ratios in the sediment samples that were collected from the Seto Inland Sea varied from 0% to 13.8% for o,p'-DDE, 19.5%–100% for p,p'-DDE, 0%–11.0% for o,p'-DDD, 0%–38.8% for p,p'-DDD, 0%–13.6% for o,p'-DDT, and 0%–43.3% for p,p'-DDT (**Fig. 3**). DDEs and DDD accounted for 41.1%–64.3% and 35.3%–48.3%, respectively, except at Stations A-M1 and B-1. At Station B-1, only p,p'-DDE was quantified. In contrast, p,p'-DDT accounted for 43.3% of the total DDTs at Station A-M1. A small ratio (0~0.49) of p,p'-DDT/(p,p'-DDE + p,p'-DDD) indicates historical DDT, whereas a value that is greater than 1.0 indicates fresh application (Jiang et al. 2009). The ratios of p,p'-DDT/(p, p'-DDE + p,p'-DDD) in the sediments ranged from <0.12 to 0.27 (smaller than 1) with the exception of Station A-M1 (1.2), indicating that most of the DDT detected in the sediments were from historical applications of DDT (**Table 4**).

The ratio of o,p'-DDT/p,p'-DDT can also be used to distinguish DDT pollution caused by technical DDT from DDT pollution caused by dicofol (Li et al. 2008; Yang et al. 2008). Generally, the o,p'-DDT/p,p'-DDT value ranges from 0.2 to 0.3 in technical DDT and from 1.3 to 9.3 or higher in dicofol (Qiu et al. 2005). In the present study, the ratios of o,p'-DDT/p,p'-DDT were all <0.48, suggesting that the DDT in the sediments originated from technical DDT

(**Table 4**).

3.4. Chlordane isomers (CHLs) in the sediment samples

The concentrations of ΣCHLs were 0.01–0.48 ng g^{-1} (**Table 5**). The concentrations of ΣCHLs at the innermost area of Osaka Bay, Stations O-1 (0.45 ng g^{-1}), O-2 (0.48 ng g^{-1}), and O-M1 (0.12 ng g^{-1}) were also high compared to those at the other stations (0.01–0.08 ng g^{-1}). The contamination levels of CHLs in the sediment samples from the innermost area of Osaka Bay were higher than those in other countries (**Table 3**).

A ratio of trans-chlordane/cis-chlordane >1.0 is generally indicative of aged chlordane (Jiang et al. 2009), because cis-chlordane degrades more easily than trans-chlordane in the environment. The ratio of most of the sediment samples from the Seto Inland Sea were >1.0 (**Table 5**), implying that CHLs in those sediments were generally attributed to aged chlordane.

3.5. The factors controlling the concentrations of POPs in surface sediments

In Japan, the uses of lindane, DDT, and chlordane as pesticides expired in 1971. Moreover, the uses of lindane and chlordane are prohibited and the use of DDT is regulated under the POPs Convention as noted in the Introduction. Our present analyses demonstrated that the concentrations of POPs in sediments at the innermost area of Osaka Bay (Stations O-

1, O-2, and O-M1) were high compared to the concentrations at other parts of the Seto Inland Sea. The concentrations of POPs (dissolved phase) in seawater from the Seto Inland Sea and river water ranged from 1 to 10000 pg L^{-1}, and the HCH concentration was especially high (by 100 times) compared to the concentrations of other POPs (Tsuno et al. 2007). Especially, the concentrations of POPs (dissolved phase) in river water approximately ranged from 0.7 to 1000 pg L^{-1}(Tsuno et al. 2007), indicating that the terrigeneous load in the Seto Inland Sea thus remained one of the sources of the POPs observed in the present study.

The carbon and nitrogen isotopes corresponding to the $\delta^{13}C$ and $\delta^{15}N$ of the sediment collected from the Seto Inland Sea ranged from −21.41 to −20.31 and from 5.28 to 8.79, respectively (Asaoka et al., submitted). The average isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) for marine particulate organic matter (POM) collected from each station were -23.0 to -17.4 and 5.59 to 10.0, respectively. The isotope ratios of $\delta^{13}C$ and $\delta^{15}N$ of the sediment accorded well with those of marine POM. The organic matter in the surface sediments thus originated from marine POM. Notably, at the innermost area of Osaka Bay, which is adjacent to major metropolitan and industrial areas (catchment area: 10,140 km^2, population 16 million), are significantly affected by terrigenous loads from the Yodo River (catchment area: 8,240 km^2, yearly averaged discharge: 267.51 m^3 s^{-1}). High primary productivity was therefore observed due to the nutrients' enrichment (Nakai et al. 2018).

The coastal fronts of Osaka Bay concentrate persistent and lipophilic toxic chemicals due to the amassment of oily substances and particles including plankton (Tanabe et al. 1991). The phytoplankton biological pump with bioaccumulation is a major driver of POPs' export to sediments (Nizzetto et al. 2012). Hence, it was believed that the phytoplankton biological pump with bioaccumulation derived from high primary productivity increased the concentration of POPs in surface sediments at the innermost area of Osaka Bay. Microplastics are also hypothesized to act as a carrier for POPs in marine ecosystems (Koelmans et al. 2013; Rodrigues et al. 2019).

The concentrations of POPs in the marine POM in the surface layer of the Seto Island Sea are listed in **Table 6**. Chlordane isomers were detected in marine POM collected from almost all sampling stations, and DDE was detected from Osaka Bay. HCHs and HCB were not detected in the marine POM; this is because HCH isomers were distributed in seawater due to their higher water solubility compared to DDTs (Wurl et al. 2006).

In the present study, we calculated the POPs' sedimentation fluxes from both the concentrations of POPs in POM and the POM sedimentation flux measured in prior investigations (Matsuda et al. 1977; Hoshika et al. 1983, 1994; Hoshika 2008) near our present sampling stations (**Table 7**). The sedimentation fluxes of HCHs, HCB and DDTs were small except at Stations O-1 (DDTs; 9.1 pg cm^{-2} y^{-1}) and O-4 (DDTs; 17 pg cm^{-2} y^{-1}), indicating that the sedimentation might not significantly affect the concentration of these pollutants in surface sediment. The sedimentation flux of the CHLs ranged from <0.12 to 46 pg cm^{-2} y^{-1}.

The ratios of POPs concentrations in the marine POM to the concentrations in marine sediments are shown in **Table 8**. The ratios of HCHs, HCB, and DDTs (except Stations O-1 and O-4) were smaller than 1, suggesting that these pollutants in the marine POM might not affect the concentration of POPs in the surface sediments. This result is consistent with the sedimentation flux results. In the case of DDTs at Stations O-1 and O-4, approx. 30% and 100% respectively of the POPs in the surface sediments were derived through the adsorption process to the marine POM in the water column. This is because the concentration of DDTs in the marine POM at Stations O-1 and O-4 were 0.78 and 0.88 ng g^{-1}, respectively, which is higher compared to the other stations. At Station O-4, one of the highest sedimentation fluxes (0.93 g cm^{-2} y^{-1}) in the Seto Inland Sea was reported (Hoshika 2008). The ratio of CHLs ranged from 0.5 to 150, revealing that the ratio was higher than 1 at most of the stations. Although the average concentrations of CHLs in the seawater and fresh water around the Seto Inland Sea were similar to those of HCHs and DDTs, we observed a high concentration of CHL in the marine POM. The distribution coefficient between marine POM and seawater (K_d) has been roughly calculated from the observed POP concentrations in marine POM divided by the average concentrations of the POPs in water in Japan (Ministry of the Environment, Japan

2005). The K_d that we calculated were <0.05 for HCHs, <0.95 for HCB, <0.16–14 for DDTs, and <0.35–22 for CHLs. More CHLs were thus distributed to the marine POM compared to the other pollutants. This implies that the source of CHLs in the marine POM is not only the terrigeneous load but also atmospheric deposition (Bidleman et al. 2002; Murayama et al. 2003). CHLs were still being used in Japan as an insecticide for termites in the mid-1980s. The volatilization of soil residues influences the atmospheric levels in remote regions (Bidleman et al. 2002). The CHLs in air are uniformly distributed on the global scale, indicating the possibility of a continuous emission of CHLs from third-world as well as developed countries at the middle latitudes (Tanabe 2016). We thus speculate that CHLs in air that were removed by atmospheric deposition were adsorbed on the marine POM.

In contrast, our analyses demonstrated that the concentrations of HCHs, HCB, and DDTs in the sediments were higher than those in the marine POM (**Table 8**). Another factor involved in the control of the concentration of POPs in surface sediments is resuspension. The resuspension process in estuarine and near-coastal environments may act as a source of contaminants such as POPs to the overlying water column (Eggleton and Thomas 2004; Wu et al. 2016; Liu et al. 2017) Resuspension tends to enhance the transfer of organic pollutants in the benthic food chain (Charles et al. 2005). In the present study, the mud contents ranged from 60% to 99.1% except at Stations A-2, B-1, HA-1 and K-1 (Setouchi Net). Because it is easy to resuspend sediments in the fine fraction of sediment with high percentages of mud (Matthai et al., 2001), it appears that resuspension increased the concentrations of HCHs, HCB, and DDTs in the surface sediment with the release of these historically contaminated pollutants that had accumulated in a lower layer.

The POPs concentrations in the sediments from the Seto Inland Sea were positively correlated with the refractory organic matter concentration in the sediments (coefficient of determination; $r^2 = 0.674–0.884$, **Fig. 4**) In contrast, the POPs concentrations in the sediments were not correlated with the labile or semi-labile organic matter concentrations in the sediments ($r^2 = 0.0017–0.177$). This result shows that POPs were strongly adsorbed on the refractory organic matter. We found that approx. 93% of the refractory organic matter in sediments collected from Seto Inland Sea was categorized into humin (Asaoka et al., submitted). POPs are thought to be adsorbed by hydrophobic interaction, charge transfer complexes, and π-π stacking on humin (Fukushima et al. 2011). Thus, the spatial distribution of POPs in the surface sediments from Seto Inland Sea depends on the concentration of humin in the sediments.

As shown in **Tables 2, 4**, and **5**, the POPs in the sediment samples that we collected from the Seto Inland Sea originated mainly from historical application. Our present findings thus also support the release of historically adsorbed POPs on the refractory organic matter through resuspension. Positive correlations were also revealed among the HCHs, DDTs, CHLs and

HCB (r^2 = 0.841–0.947, **Fig. 5**). These correlations suggest that these organic pollutants had a similar fate in the sediments.

4. Conclusion

Although in Japan the use of lindane and chlordane is now prohibited and that of DDT is regulated, the concentrations of POPs in atmospheric and aquatic environments are decreasing slowly, consistent with the reduction of primary emissions. However, our analyses show that the concentrations of these pollutants in surface sediments from the Seto Inland Sea (which reflect the current load of POPs) are not uniformly distributed in the sea. The concentrations were especially high at the innermost area of Osaka Bay compared to other parts of the sea. In the case of HCHs, HCB, and DDTs which were adsorbed on refractory organic matter in the sediments, resuspension is thought to have increased the concentrations in surface sediment with the release of historically contaminated pollutants that had accumulated in a lower layer. Our findings also indicate that atmospheric deposition affects the concentration of CHLs in the surface sediments. These mechanisms might decelerate the decrease of the POP concentrations in surface sediments even though an extensive reduction of primary emissions has been conducted worldwide.

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Figure captions

Fig. 1. Sampling stations in the Seto Inland Sea, Japan.

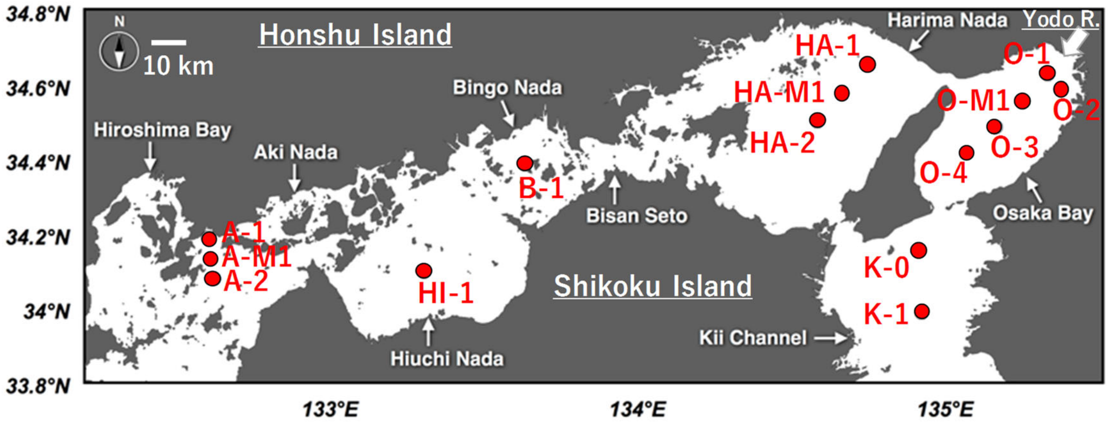
Fig. 2. Composition of HCHs in sediments collected from the Seto Inland Sea.

Fig. 3. Composition of DDTs in sediments collected from the Seto Inland Sea.

Fig. 4. Correlations between the log concentrations of POPs and refractory organic matter in the sediments collected from Seto Inland Sea.

Fig. 5. Correlations among POPs in the sediments collected from the Seto Inland Sea.

Figures



Map of sampling stations were drawn using software for the analysis and visualization of oceanographic and meteorological data sets, Ocean Data View ver. 4.7.10.

Fig. 1 Sampling stations in the Seto Inland Sea, Japan

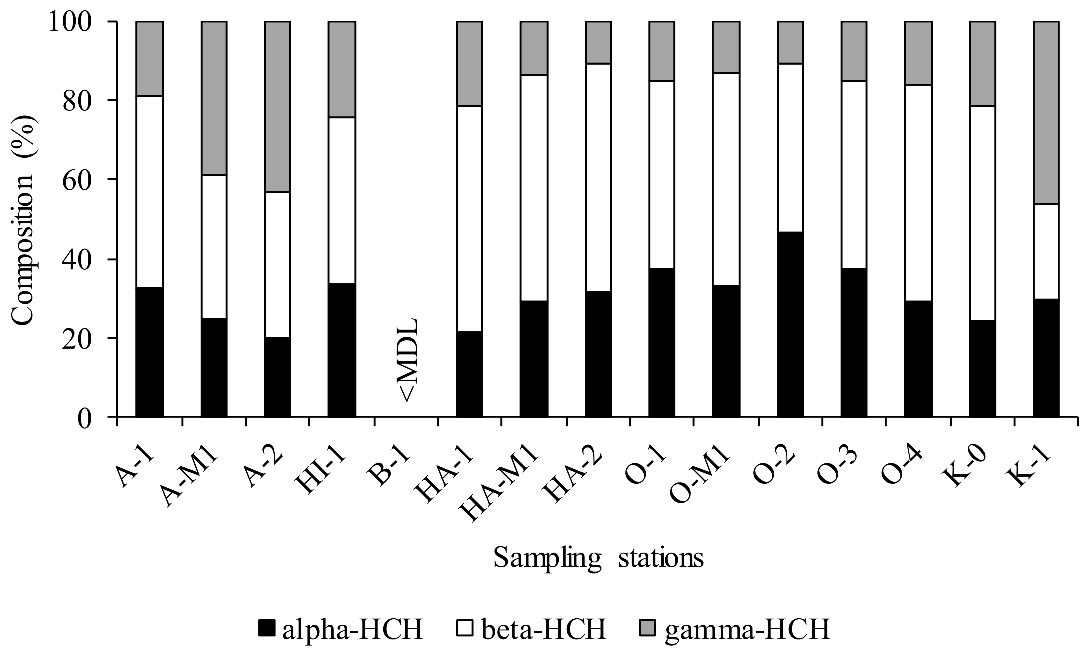


Fig.2 Composition of HCHs in sediments collected from the Seto Inland Sea

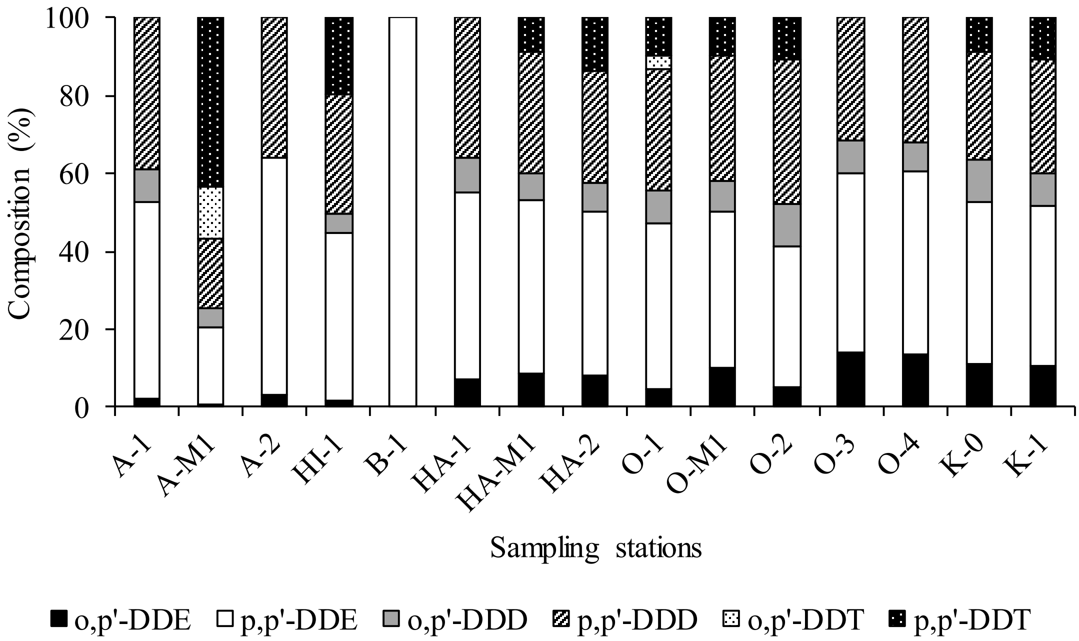


Fig.3 Composition of DDTs in sediments collected from the Seto Inland Sea

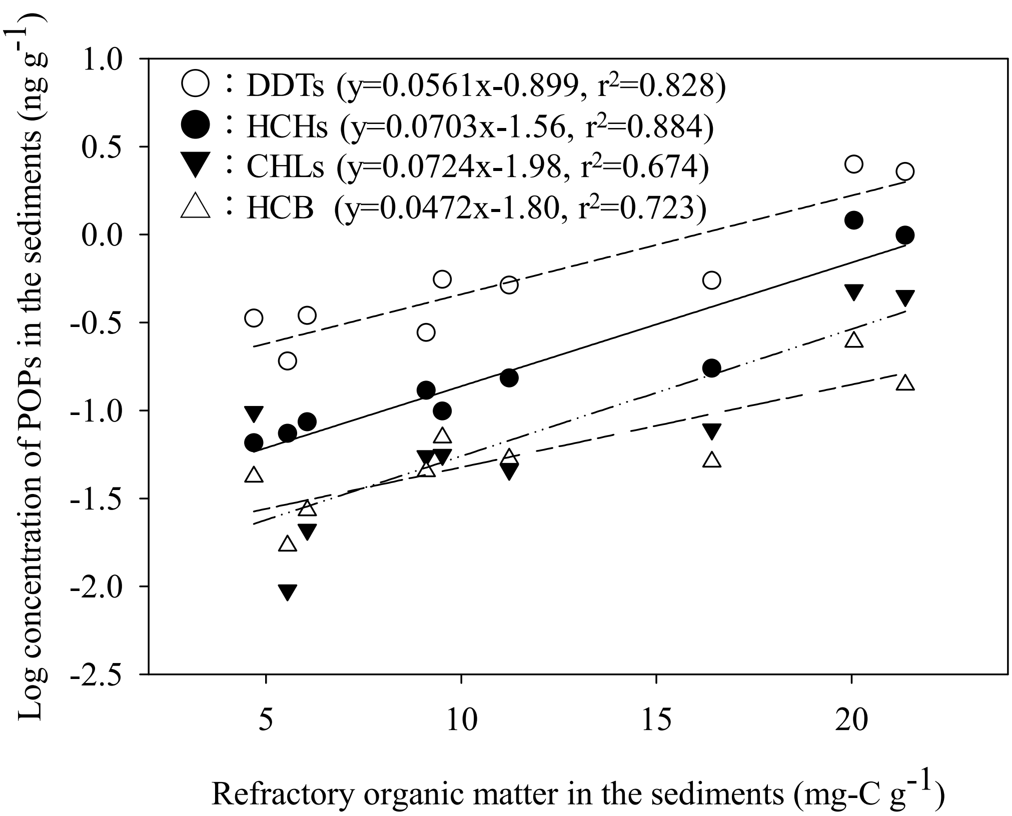
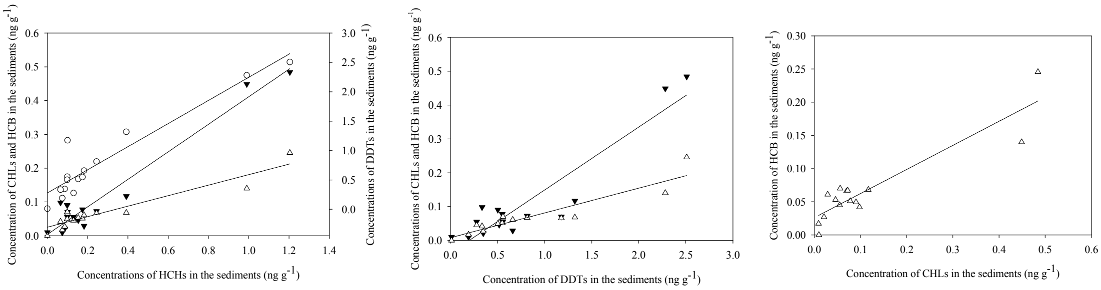


Fig. 4 Corrections between the log concentrations of POPs and refractory organic matter in the sediments collected from the Seto Inland Sea



○:DDTs y=1.97X+0.279 (r^2=0.892)
▼:CHLs y=0.408+0.0039 (r^2=0.947)
△:HCB y=0.156X+0.0254 (r^2=0.878)

▼:CHLs y=0.186-0.0371 (r^2=0.857)
△:HCB y=0.0732X+0.008 (r^2=0.847)

△:HCB y=0.363X+0.026 (r^2=0.841)

Fig. 5 Corrections among POPs in the sediments collected from the Seto Inland Sea

Table 1. Sampling stations at the Seto Inland Sea, Japan

Station	Latitude	Longitude	POPs	Degradation study	Carbon and nitrogen isotopes	Marine POM	Sampling date
A-1	34-12.0'N	132-36.0'E	○	○	○	○	Jul.4 in 2016, Jul. 3 in 2017
A-M1	34-09.0'N	132-37.0'E	○	–	–	○	Jul. 4 in 2016, Jul. 3 in 2017
A-2	34-06.0'N	132-38.0'E	○	○	○	○	Jul. 4 in 2016, Jul. 3 in 2017
HI-1	34-06.7'N	133-18.2'E	○	○	○	○	Nov. 14 in 2016, Jul. 3 in 2017
B-1	34-23.7'N	133-38.1'E	○	○	○	○	Nov. 16 in 2016, Jul. 6 in 2017
HA-1	34-40.0'N	134-45.0'E	○	○	○	○	Jul. 7 in 2016, Jul. 6 in 2017
HA-M1	34-35.0'N	134-40.0'E	○	–	–	○	Jul. 7 in 2016, Jul. 6 in 2017
HA-2	34-30.0'N	134-35.0'E	○	○	○	○	Jul. 7 in 2016, Jul. 6 in 2017
O-1	34-40.0'N	135-20.0'E	○	○	○	○	Jul. 6 in 2016, Jul. 5 in 2017
O-M1	34-35.0'N	135-15.0'E	○	–	–	–	Jul. 6 in 2016, Jul. 5 in 2017
O-2	34-36.5'N	135-22.5'E	○	○	○	–	Jul. 6 in 2016
O-3	34-30.0'N	135-10.0'E	○	○	○	○	Jul. 6 in 2016, Jul. 5 in 2017
O-4	34-25.0'N	135-05.0'E	○	–	–	○	Jul. 6 in 2016, Jul. 5 in 2017
K-0	34-10.0'N	134-55.0'E	○	–	–	○	Jul. 5 in 2016, Jul. 4 in 2017
K-1	34-00.0'N	134-55.0'E	○	○	○	–	Jul. 5 in 2016

○：Sediments and marine POM were collected for each study; –: Sediments and marine POM were not collected

Table 2. Concentrations (ng g^{-1} dry weight) of HCHs and HCB in surface sediments from the Seto Inland Sea

Station	α-HCH	β-HCH	γ-HCH	Σ HCHs	α-HCH/γ-HCH	HCB
A-1	0.05	0.07	0.03	0.15	1.7	0.05
A-M1	0.03	0.04	0.04	0.10	0.6	0.07
A-2	0.03	0.05	0.06	0.13	0.5	0.05
HI-1	0.03	0.04	0.02	0.10	1.4	0.07
B-1	<MDL	<MDL	<MDL	<MDL	–	<0.007
HA-1	0.02	0.04	0.02	0.07	1.0	0.02
HA-M1	0.07	0.14	0.03	0.24	2.2	0.07
HA-2	0.06	0.10	0.02	0.17	2.9	0.05
O-1	0.37	0.47	0.15	0.99	2.5	0.14
O-M1	0.13	0.21	0.05	0.39	2.5	0.07
O-2	0.56	0.52	0.13	1.20	4.4	0.25
O-3	0.03	0.04	0.01	0.09	2.5	0.03
O-4	0.05	0.10	0.03	0.18	1.8	0.06
K-0	0.02	0.05	0.02	0.10	1.2	0.05
K-1	0.02	0.02	0.03	0.07	0.6	0.04
MDL	0.002	0.003	0.002	–	–	0.002

MDL: method detection limit.

Table 3. Concentrations (ng g^{-1} dry weight) of POPs in sediments from different areas around the world

Location	Year	Σ HCHs	HCB	Σ DDTs	Σ CHLs	Reference
Seto Inland Sea, Japan	2016–2017	<0.003-1.20	<0.007–0.25	0.01–2.51	0.01–0.48	This study
Bering Sea	2008	0.19–0.56	–	0.68–2.34	0.03–0.12	Jin et al. 2017
Bering Strait	2012	–	0.012–0.097	0.0006–0.116	0.002–0.021	Ma et al. 2015a
Kongsfjorden, Svalbard	2009	0.007–0.1	–	–	0.001–0.022	Ma et al. 2015b
Hong Kong coast	2008	4.24–15.5	–	1.59–9.57	–	Wang et al. 2014
Chukchi Sea	2012	–	0.014–0.052	0.007–0.083	0.003–0.007	Ma et al. 2015a
Iceland Station	2012	–	0.005–0.010	0.012–0.098	ND–0.003	Ma et al. 2015a
Sarno river and estuary, Italy	2008	0.018–1.47	–	0.027–2.09	–	Montuori et al. 2014
Nagaon wetland, India	2011	142–743	–	154–932	–	Mishra et al. 2013
English Bay, Canada	2011	0.0659	0.0424	0.688	0.0452	Morales-Caselle et al. 2017
Liaohe Estuary, China	2014	0.13–4.77	–	0.11–3.54	–	Li et al. 2017
Coastal areas of central Vietnam	2013–2014	0.491–22.6	–	0.441–26.7	–	Tham et al. 2019

Table 4. Concentrations (ng g^{-1} dry weight) of DDTs in surface sediments from the Seto Inland Sea

Station	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	Σ DDTs	p, p'-DDT /(p, p'-DDE + p, p'-DDD)	o,p'-DDT /p,p'-DDT
A-1	0.01	0.26	0.04	0.20	<MDL	<0.063	0.52	<0.14	–
A-M1	0.01	0.23	0.06	0.21	0.16	0.51	1.18	1.2	0.31
A-2	0.01	0.17	<MDL	0.10	<MDL	<0.063	0.28	<0.23	–
HI-1	0.01	0.24	0.03	0.17	<MDL	0.11	0.56	0.27	<0.15
B-1	<MDL	0.01	<MDL	<0.007	<MDL	<MDL	0.01	–	–
HA-1	0.01	0.09	0.02	0.07	<MDL	<MDL	0.19	<0.12	–
HA-M1	0.07	0.36	0.06	0.25	<MDL	0.073	0.81	0.12	<0.23
HA-2	0.05	0.23	0.04	0.16	<MDL	0.074	0.55	0.19	<0.23
O-1	0.11	0.97	0.19	0.71	0.08	0.22	2.28	0.13	0.37
O-M1	0.13	0.53	0.11	0.42	<MDL	0.13	1.32	0.14	<0.13

O-2	0.13	0.91	0.27	0.94	<MDL	0.27	2.51	0.15	<0.06
O-3	0.05	0.16	0.03	0.11	<MDL	<MDL	0.35	<0.07	–
O-4	0.09	0.31	0.05	0.21	<MDL	<0.063	0.66	<0.12	–
K-0	0.06	0.21	0.05	0.14	<MDL	0.04	0.50	0.13	<0.39
K-1	0.04	0.14	0.03	0.10	<MDL	0.04	0.33	0.15	<0.48
MDL	0.002	0.001	0.002	0.002	0.02	0.019	–	–	–

MDL: method detection limit.

Table 5. Concentrations (ng g^{-1} dry weight) of chlordanes in surface sediments from the Seto Inland Sea

Station	heptachlor	trans-Chl	cis-Chl	oxy-Chl	trans-nonachlor	cis-nonachlor	ΣCHLs	trans-chlordane /cis-chlordane
A-1	<MDL	0.03	0.02	<MDL	<MDL	<MDL	0.05	1.4
A-M1	<MDL	0.04	0.03	<MDL	<MDL	<MDL	0.07	1.1
A-2	<MDL	0.03	0.02	<MDL	<MDL	<MDL	0.06	1.3
HI-1	<MDL	0.03	0.03	<MDL	<MDL	<MDL	0.06	1.1
B-1	0.01	<MDL	<MDL	<MDL	<MDL	<MDL	0.01	–
HA-1	0.01	<0.013	<0.017	<MDL	<MDL	<MDL	0.01	–
HA-M1	0.01	0.03	0.04	<MDL	<MDL	<MDL	0.07	0.8
HA-2	0.03	0.03	0.02	<MDL	<MDL	<MDL	0.08	1.5
O-1	<MDL	0.12	0.12	<MDL	0.11	0.10	0.45	1.0
O-M1	<MDL	0.06	0.06	<MDL	<0.053	<0.057	0.12	1.0
O-2	<MDL	0.14	0.13	<MDL	0.12	0.09	0.48	1.1
O-3	<MDL	0.02	<0.017	<MDL	<MDL	<MDL	0.02	–
O-4	<MDL	0.03	<MDL	<MDL	<0.053	<0.057	0.03	–
K-0	<MDL	0.03	0.03	<MDL	<0.053	<MDL	0.06	1.1
K-1	<MDL	0.03	0.03	<MDL	<0.053	<MDL	0.07	0.9
MDL	0.002	0.004	0.005	0.014	0.016	0.017	–	–

Table 6. Concentrations of POPs (ng g^{-1}) in marine particulate organic matter collected from the Seto Inland Sea

Station	α-HCH	β-HCH	γ-HCH	HCB	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT	heptachlor	trans-chl	cis-chl	oxy-chl	trans-nonachlor	cis-nonachlor
A-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.51	0.39	<MDL	0.32	<MDL
A-M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.38	0.46	<MDL	0.06	<MDL
A-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.40	0.64	<MDL	0.02	<MDL
HI-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.93	0.37	<MDL	<MDL	<MDL
B-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.72	0.46	<MDL	0.32	<MDL
HA-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.75	0.43	<MDL	<MDL	<MDL
HA-M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.85	0.58	<MDL	<MDL	<MDL
HA-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
O-1	<MDL	<MDL	<MDL	<MDL	<MDL	0.78	<MDL	<MDL	<MDL	<MDL	<MDL	1.35	1.12	<MDL	<MDL	<MDL
O-3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.61	0.77	<MDL	<MDL	<MDL
O-4	<MDL	<MDL	<MDL	<MDL	0.18	0.70	<MDL	<MDL	<MDL	<MDL	<MDL	0.47	0.53	<MDL	0.20	<MDL
K-0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.99	0.71	<MDL	0.40	<MDL

MDL	0.02	0.03	0.02	0.02	0.02	0.01	0.02	0.02	0.17	0.19	0.02	0.04	0.05	0.14	0.16	0.17

Table 7. Sedimentation flux (pg cm^{-2} y^{-1}) of POPs in the Seto Inland Sea

Station	HCHs	HCB	DDTs	CHLs
A-1	<0.2	<0.2	<0.04	8.2
A-M1	<0.1	<0.1	<0.02	3.4
A-2	<0.1	<0.1	<0.03	5.9
HI-1	<0.2	<0.2	<0.05	11
B-1	<0.6	<0.6	<0.16	39
HA-1	<0.2	<0.2	<0.05	9.4
HA-M1	<0.1	<0.1	<0.02	4.9
HA-2	<0.1	<0.1	<0.04	<0.12
O-1	<0.4	<0.4	9.1	46
O-3	<0.4	<0.4	<0.12	26
O-4	<0.7	<0.7	17	37
K-0	<0.04	<0.04	<0.01	<4.0

Table 8. The ratio of POPs concentrations in marine particulate organic matter to those of the marine sediments

Station	HCHs	HCB	DDTs	CHLs
A-1	<0.1	<0.4	<0.02	25
A-M1	<0.2	<0.3	<0.01	13
A-2	<0.2	<0.4	<0.04	18
HI-1	<0.2	<0.3	<0.02	22
B-1	–	–	<1	150
HA-1	<0.3	<1.0	<0.05	120
HA-M1	<0.1	<0.3	<0.01	21
HA-2	<0.1	<0.4	<0.02	0.5
O-1	<0.02	<0.1	0.3	5.5
O-3	<0.2	<0.7	<0.03	69
O-4	<0.1	<0.3	1	40
K-0	<0.2	<0.4	<0.02	35