

# **Deposition records of persistent organic pollutants and black carbon in dated sediment cores from China marginal seas: implications for terrestrial sources and transport processes**

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## **Abstract**

Black carbon (BC) and persistent organic pollutants (POPs) were analyzed from three sediment cores collected offshore in the East China Marginal Seas. The results showed steadily increasing or stable BC concentrations and fluxes. By contrast, time trends of POPs fluxes were consistent with historical records of commercial production and use in China. Although the POP inventories decreased significantly with increase in offshore distance, the relatively consistent trends for individual POPs in different sea areas confirmed that the main sources are derived from mainland China and that atmospheric input was an important contribution. POPs concentrations decreased by 59-91% during transport from the Yellow Sea to the remote East China Sea and deposition to the sediment. This suggests that the source signal for POPs may be preserved under stable depositional environments, even though only a fraction of those pollutants

are buried in open sea sediments.

Key words: POPs; BC; depositional fluxes; inventory; transport processes; East China Marginal Seas

Highlight:

BC and POPs were analyzed from three sediment cores collected offshore in the ECMSs.

Compared with BC, there was a significant loss of POPs during transport in the atmosphere and water column.

Source signals may be better preserved although only a fraction is buried in the sediment.

## 1. Introduction

Sources of persistent organic pollutants (POPs) have been regulated by the Stockholm Convention that came into force through joint international collaboration in 2001 (Ofenvironment, 2013). However, in spite of bans and controls, legacy POPs (e.g. HCHs, DDTs, PCBs, PBDEs) can still be detected in environmental media at locations remote from their sources (Li et al., 2014). In addition to these historical residues, with the boom in manufacturing and e-waste recycling, emerging organic contaminants of concern have been emitted in China and widely detected in various environmental media (Zhao et al., 2017, 2019). Organic contaminants can enter the coastal environment through riverine inputs and atmospheric deposition (Wurl and Obbard, 2005). Some compounds with strong hydrophobicity have a high affinity to sorb to suspended particulate organic matter and to sediment. Thus, marine sediment is an important sink for many organic contaminants including legacy POPs (Hu et al., 2011).

Records derived from the chemical analysis of sediment cores are useful to trace the history of pollutant emissions (Guo et al., 2006). This approach assumes that (1) the fluxes of chemical deposition to the sediment are proportional to the environmental emission for a given chemical and (2) the source signal, environmental transport and transformation processes remain consistent over the period captured by the sediment archive. However, the variability in environmental conditions during pollutant transport from source to sink is often overlooked, and may even lead to misinterpretation of emission histories, especially in estuaries and offshore areas where the sedimentary environment is more complicated (Latimer et al., 1999; Lin et al., 2016). The combination of high-resolution multi-sedimentary records in a specific regional environment can effectively reveal the characteristics of spatiotemporal variability, which can provide a better understanding of dynamic changes after transport, and important controlling factors. For example, surveys using multiple sediment cores in the Yangtze River Estuary and offshore, have found that estuarine sedimentary environments are influenced by enhanced soil erosion associated

with extreme flood events and large scale transformation of land use. In estuaries the huge amount of sediment input and rapid deposition processes obscure the source signal, while sediment records in more distal areas correspond to historical source signals (Lin et al., 2016). Since fine particulate matter can often be transported farther with cycles of re-suspension and deposition, mass inventories of total organic carbon (TOC), HCHs and DDTs remain relatively constant while sedimentation rate decreases with sediment transport distance. Thus TOC or fine particulate matter may be considered significant potential factors influencing the distribution and preservation of source signals of organic contaminants within this heterogeneous environmental system (Hu et al., 2011).

The East China Marginal Seas (ECMSs) include, from north to south, the Bohai Sea (BS), the Yellow Sea (YS) and the East China Sea (ECS).. The coastal region of ECMSs is an economically highly developed area with heavy industrial and agricultural activities and widespread chemical use and emission (Li et al., 1999). For instance, black carbon (BC) emission inventories indicate that regions of the Bohai Rim and Yangtze River Delta Economic Circle have the highest emission intensities in China (Wang et al., 2012). Driven by the East Asian monsoon, the continental shelves of ECMSs are downwind of the Asian continental outflow in spring and winter, and a large number of organic pollutants (e.g. POPs, BC and polyaromatic hydrocarbons), transported through atmosphere, are deposited in these marginal seas (Hu et al., 2016). The objective of this study is to evaluate the spatial variability in chemical records and emission histories derived from sediment cores collected from different sites within the ECMSs. Temporal and spatial variations in depositional fluxes and concentrations of chemicals deposited to the sediment under the control of riverine input were analyzed for legacy POPs, to provide a better understanding of the factors controlling source signal change after long-range atmospheric transport. Furthermore, we include BC data as well as TOC since its sorption capacity of is much higher. Similar to POPs, BC is mainly derived from terrestrial anthropogenic emissions and may be used to effectively assess the loss

of POPs in the atmosphere and water column from source to sink.

## 2. Materials and methods

### 2.1. Sampling

Three sediment cores (Figure 1) were collected between 2007 and 2013 from the central BS (core M7: 39°32'N, 120°27'E), South YS (core F0306: 34°59'N, 122°30'E) and southwestern Cheju Island ECS (core FFJ103: 31°40'N, 125°52'E). The mud deposition center was selected as the sample drilling point. The three cores were stored at 4°C before being taken to the laboratory where they were cut into 1 cm sections along their lengths using a stainless steel cutter. Core segments were packed in aluminum foil, freeze-dried and stored at -20°C until analysis.

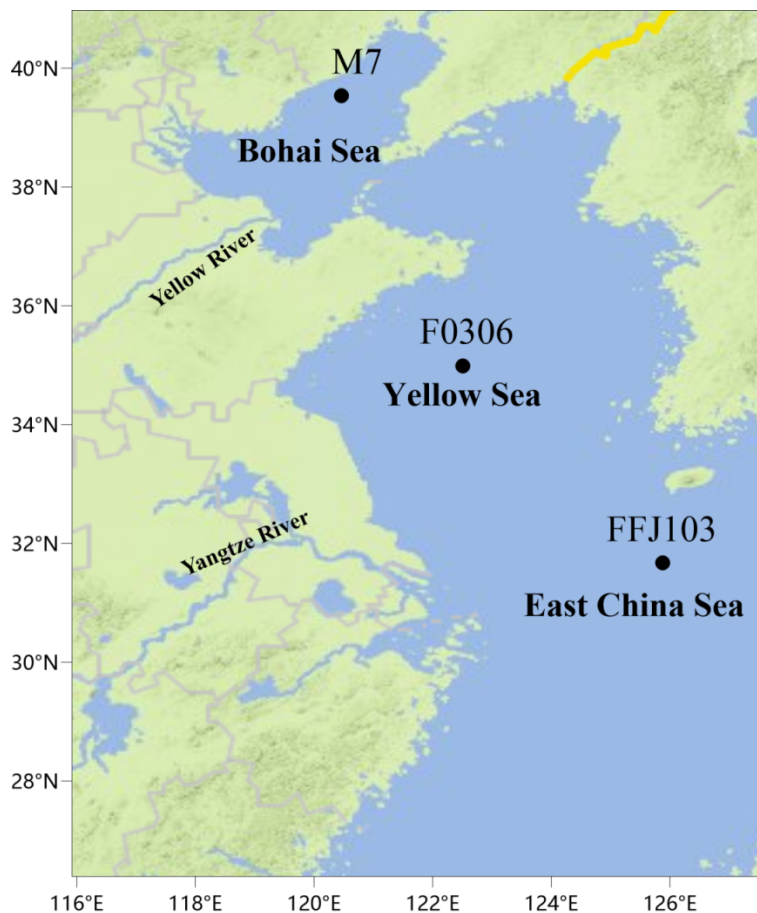


Figure 1. Coring sites M7, F0306, and FFJ103 in the East China Marginal Seas.

### 2.2. $^{210}\text{Pb}$ dating

Core dating for M7, F0306 and FFJ103 using  $^{210}\text{Pb}$  gamma spectrometry is presented elsewhere (Li et al., 2016) but included in Supplementary Information Text S1. The mean sedimentary rates of M7, F0306 and FFJ103 were 0.64 cm/year, 0.53 cm/year and 0.33 cm/year, respectively (Li et al., 2016) (Figure S1). The relative error for this method was less than 6%. Vertical variation in grain composition was small in all three cores, suggestive of a relatively stable environment in the coring areas (Figure S2). Based on this, the average sedimentation rate and chronology for each site was calculated using a constant flux-constant sedimentation rate model.

### 2.3. Organic pollutant analysis and quality control

The details of organic analysis and quality control are present in Supplementary Information Text S2. Briefly, approximately 10 g of each core sample (freeze-dried and homogenized) were supplemented with surrogate compounds (TcmX and PCB209) in a Soxhlet apparatus and then extracted with dichloromethane for 48 h, with activated copper granules added to the round bottom flask. The concentrated extracts were cleaned up and fractionated by elution with 50 mL of a 1:1 (v:v) dichloromethane/n-hexane mixture through a sulfuric acid modified silica gel column. The eluent was again concentrated under a gentle nitrogen stream. Internal standards (penta-chloronitrobenzene and BDE-77) were added prior to instrumental analysis. The specific analytical instruments and associated parameters for DDTs, HCHs, PCBs and PBDEs were presented previously (Li et al., 2016; Lin et al., 2016; Wu et al., 2019).

For HCHs and DDTs analysis, the surrogate recoveries for TcmX and PCB209 in sediment samples were  $79 \pm 10\%$  and  $97 \pm 13\%$ , respectively. The reported HCH and DDT concentrations were not recovery-corrected. The method detection limits for these pesticides were assigned as the average field blank value and three times the standard deviation of the blanks, and were 0.005–0.01 ng/g. For PCBs analysis, the average recoveries of the surrogates in the sediment samples were  $78.6 \pm 10.3\%$  for TcmX and  $96.5 \pm 12.8\%$  for PCB209.

The reported PCB concentrations were not adjusted for surrogate recoveries. The relative percent differences (RPDs) of PCBs (sum of 27 congeners) in duplicate samples were less than 15%. For PBDEs analysis, the detection limits were 50 pg/g for BDE-209 and 0.5 pg/g for other individual PBDE congeners. The average recoveries for spiked blanks were  $88.0 \pm 8.5\%$ ; and the average surrogate recoveries were  $86.7 \pm 9.7\%$ .

#### 2.4. Black carbon analysis

Wet-chemical treatment combined with a thermal optical reflectance (TOR) method was adopted to quantify elemental carbon (EC). Briefly, sediment samples were freeze-dried and homogenized (<80 mesh). Hydrochloric (HCl) and hydrofluoric (HF) acids were then used to eliminate metals, metal oxides, inorganic carbonates, and silicates. The residues were suspended in deionized water, and filtered through 47-mm-diameter quartz fiber filters (prefired at 450°C for 4 hours) which were then dried in a constant temperature and humidity environment. The EC was analyzed on a Thermal/Optical Carbon Analyzer (Desert Research Institute, model 2001). A 0.544 cm<sup>2</sup> circular punch was used for carbon quantification. The oven is heated under 100% He to produce four organic carbon fractions at four different temperature stages. The analysis was transferred to a mixture of O<sub>2</sub> (2%) and He (98%) where the three EC fractions (defined as EC1, EC2, and EC3) were produced at 580, 740, and 840°C respectively. The pyrolysis of organic carbon (POC) occurred in an atmosphere of 100% He and is reflected by the decrease in the laser reflection signal. In the second O<sub>2</sub>/He stage, POC similar to the original EC fraction was oxidized. Based on the IMPROVE protocol, BC was calculated as EC1+EC2+EC3-POC (Fang et al., 2018; Han et al., 2007). The difference determined from replicate analyses was <5% for BC.

#### 2.5. Grain size

One gram of freeze-dried sample was soaked in 10 ml 5% H<sub>2</sub>O<sub>2</sub> for 24

hours to remove organic components and the sample was then dispersed ultrasonically for 30 seconds using the built-in ultrasonic oscillator. A Mastersizer2000 laser particle size analyzer (Malvern Instruments, United Kingdom) was used to analyze the particle size distributions of the sediment samples. The measurement range was 0.02-2000  $\mu\text{m}$ , the resolution was 0.01 $\Phi$ , and the relative error on repeat samples was less than 3%. Standard particle size classifications were used (clay < 4 $\mu\text{m}$ ; silt is 4-63 $\mu\text{m}$ ; sand > 63 $\mu\text{m}$ ). The three cores were all dominated by clay and silt, with a small amount of sand (Figure 2, S2 and S3).

## 2.6. The analysis of total organic carbon

One gram of freeze dried sample was soaked in 10 ml 4 M hydrochloric acid three times (3 x 8 hours) to remove the carbonate fraction. The acid was discarded and the sample washed to neutral and dried overnight at 60 °C. Prepared samples of 1-10 mg were put in the elemental analyzer (Vario EL-III Elemental Analyzer) to measure TOC. Replicate analysis of one sample (n = 6) showed the analytical precision to be  $\pm 0.02$  wt%.

## 2.7. Flux and inventory calculation

Concentrations measured for sediment cores were used to estimate the flux of net deposition of chemicals to each segment (i) of the cores (Equation (1)):

$$\text{Net flux}(\text{ ng/cm}^2/\text{y} ) = C_i \times R_i \times \rho_i \quad (1)$$

where  $C_i$  (ng/g) is the measured POPs concentration,  $\rho_i$  (g/cm<sup>3</sup>) is the dry bulk density and  $R_i$  (cm/y) is the sedimentation rate.

Chemical inventories were calculated by (Equation (2)):

$$\text{Inventory}(\text{ng/cm}^2) = \sum C_i \times \rho_i \times d_i \quad (2)$$

where  $d_i$  is the sample thickness (cm) of core segment i.

## 3. Results and discussion



### 3.1. BC and TOC

The down-core variation of BC and TOC depositional fluxes in the sediment cores are shown in Figure 2 and Table S1. The BC concentrations in M7, F0306 and FFJ103 ranged from 0.61-1.68, 0.7-1.43 and 0.97-1.59 mg/g, respectively while the flux ranges were 0.34-0.79, 0.28-0.55 and 0.21-0.34 mg/cm<sup>2</sup>/yr, respectively. Fluxes of BC deposition reached a first peak in the mid-1980s (M7, F0306 and FFJ103 were 0.76, 0.55 and 0.32 mg/cm<sup>2</sup>/yr, respectively) after which they declined for a short time. However, since the mid-1990s, an increasing trend was observed in all three sediment cores, due to the fast development of industrialization and urbanization in China.

The TOC concentrations ranged from 4.0-7.2, 5.4-9.6 and 4.4-6.3 mg/g in M7, F0306 and FFJ103, respectively (Table S1), while the TOC fluxes ranged from 2.3-3.7, 2.1-3.6 and 1.0-1.3 mg/cm<sup>2</sup>/yr, respectively. The vertical profiles showed an increasing trend, but there was no great down-core change in TOC fluxes. This relatively stable depositional environment is confirmed by grain size profiles (Figure S2). The grain size composition of the three sediment cores showed good consistency, with the largest proportion comprising silt, followed by clay, and sand having the lowest content. Under the presence of cyclonic eddies, in particular the convergence of cold cyclonic eddies, sediments gradually settle to the center of the marine basins to form the central mud (Cheng et al., 2004). Hence pollutants with high particle affinities can be co-transported by ambient currents to central areas of the YS and ECS where fine-grained particles and their associated pollutants are continuously deposited (Cheng et al., 2004; Hu et al., 2011).

The inventories of BC in M7, F0306 and FFJ103 were 36.63, 23.88 and 14.98 mg/cm<sup>2</sup>, respectively indicating a seaward decreasing trend largely related to deposition rate. This decreasing trend is more obvious for TOC and the relative value of TOC/BC is 63% in FFJ103 compared with that in F0306. This means that despite there being a contribution from marine-derived organic matter, TOC has suffered a significant loss at the remote site, confirming that black carbon

particles are more stable than organic carbon particles during transport to their final depositional area.

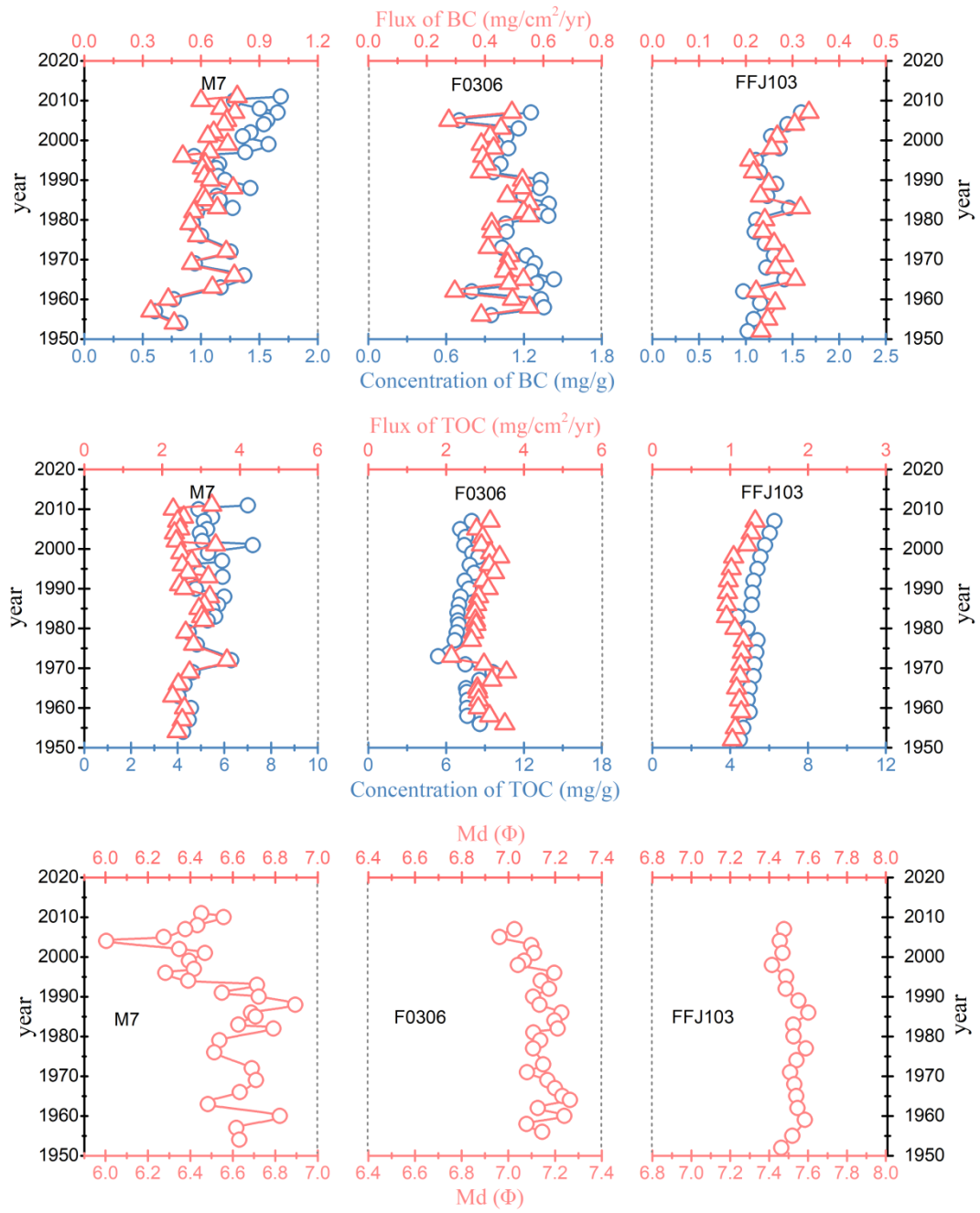


Figure 2. The concentrations and fluxes of TOC and BC, as well as grain size in cores M7, F0306, and FFJ103

### 3.2. Temporal trends in HCHs, DDTs, PCBs and PBDEs fluxes

The temporal trends of PCBs, DDTs, HCHs, 8PBDEs (sum of BDE -28, -47, -99, -100, -138, -153, -154, -183,) and BDE-209 fluxes after 1950 are shown in Figure 3 and S4 (in Supplementary Information). The peak fluxes and inventories of the three cores are shown in Figure 4. The PCBs fluxes to sites M7, F0306 and FFJ103 were in the ranges 0.16-1.07, 0.11-0.86 and 0.04-0.15 ng/cm<sup>2</sup>/yr, respectively. These fluxes increase from the base of the cores, and reach a first peak in the mid-1970s (PCB peak concentrations in M7, F0306 and FFJ103 were 1.07, 0.58 and 0.12 ng/cm<sup>2</sup>/yr, respectively). After these initial peaks, PCB fluxes declined by 82% and 71% in cores M7 and FFJ103 respectively (Figure 3), before increasing once more. This trend agrees with PCB manufacture in China from 1965 to 1974 (Mai et al., 2005). Increases in PCB fluxes were observed in all three sediment cores from the mid-1980s (or the early 1990s) and, overall, PCBs fluxes in the surface sediments of the cores averaged 60% higher than their peaks in the 1970s. Since the mid-1980s, PCB fluxes have not shown any downward trend and this may be associated with unintentionally produced PCBs from e-waste (Zhao et al., 2017) resulting in continuous inputs, especially in East China. Additional contributions may be derived from volatilization of pigment/painting sources and the metallurgical industry. These are the most important sources of unintentionally produced PCBs nationally, with a combined contribution of more than 60%, particularly in Shandong province (Zhao et al., 2019).

The first peak in DDT concentrations was observed in the period 1975-1986 and a similar trend can be observed with HCHs. These trends are consistent with the uses of DDTs and HCHs in China between 1950 and 1980s, after which the two pesticides were officially banned in 1983 (Li et al., 2001). Before their phase-out, deposition fluxes of HCHs and DDTs increased by factors of 11 and 10, 6 and 6, and 4 and 7 for cores M7, F0306 and FFJ103, respectively, implying overwhelming technical source inputs. The fluxes of DDTs and HCHs showed second peaks around 1990 in M7 (1.29 and 0.56 ng/cm<sup>2</sup>/yr, respectively), but no

such a peak was observed in F0306 and FFJ103. Overall, DDT and HCH continued to decline, indicating that sources of emission to the atmosphere are gradually decreasing (Lin et al., 2012).

The fluxes of 8PBDEs and BDE-209 have been continuously increasing since the 1980s. The fluxes have increased rapidly since 1990 and there has been no clear sign of decline until recently. The highest values in core M7 occurred in the subsurface layer, while in cores F0306 and FFJ103 they occurred at the surface. Similar to PCBs, there is almost no sign of recent decline in PBDE fluxes, suggesting ongoing emissions of these pollutants. These include confirmed sources such as e-waste recycling sites in the coastal region of eastern China (Wang et al., 2011) as penta-BDE and octa-BDE are used as additives in many electrical and electronic products, textiles, plastics, building materials and furnishings to reduce flammability (Martin et al., 2004; Siddiqi et al., 2003).

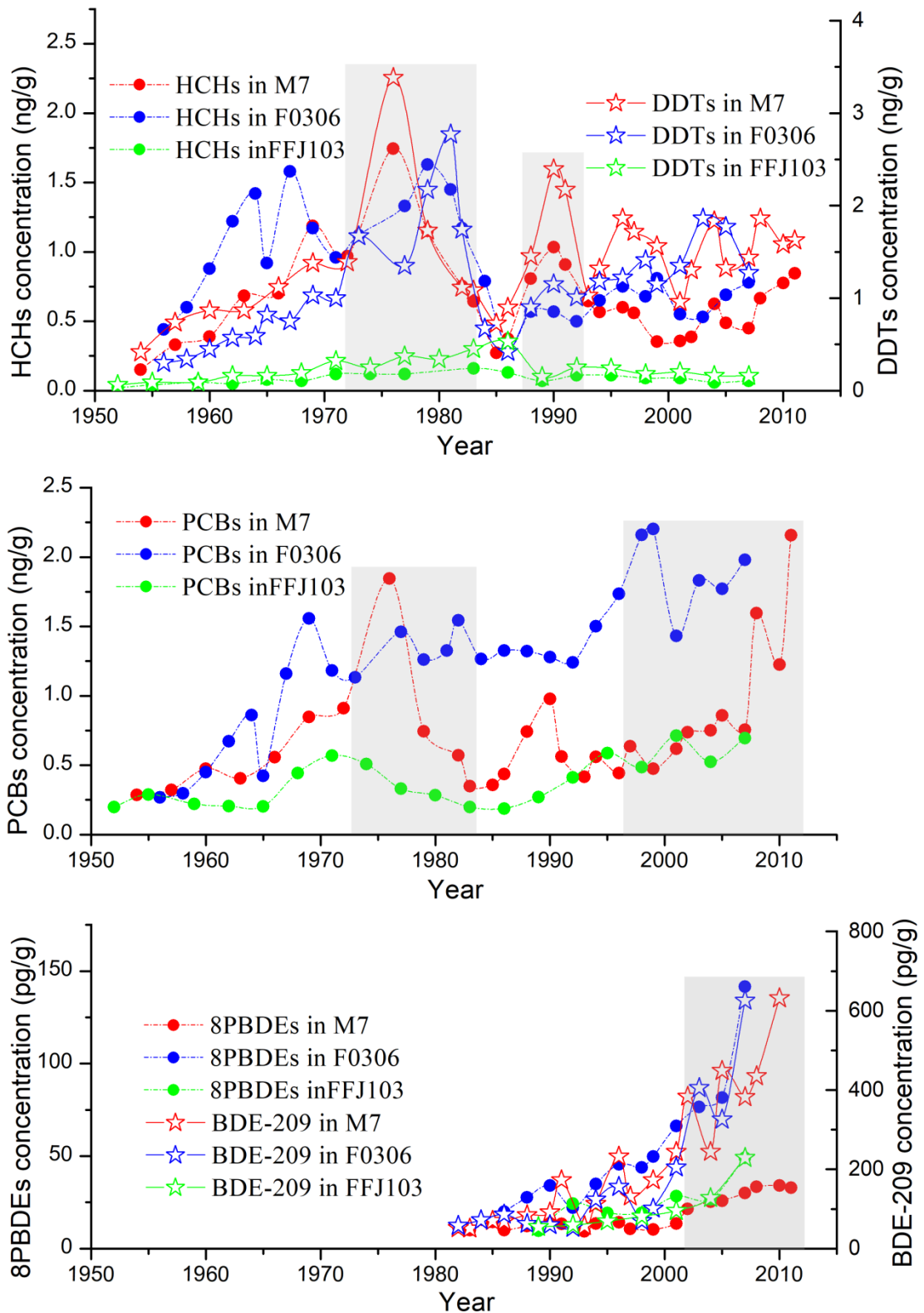


Figure 3. The temporal trends of DDTs, HCHs, PCBs, 8PBDEs and BDE-209 concentration in M7, F0306, and FFJ103.

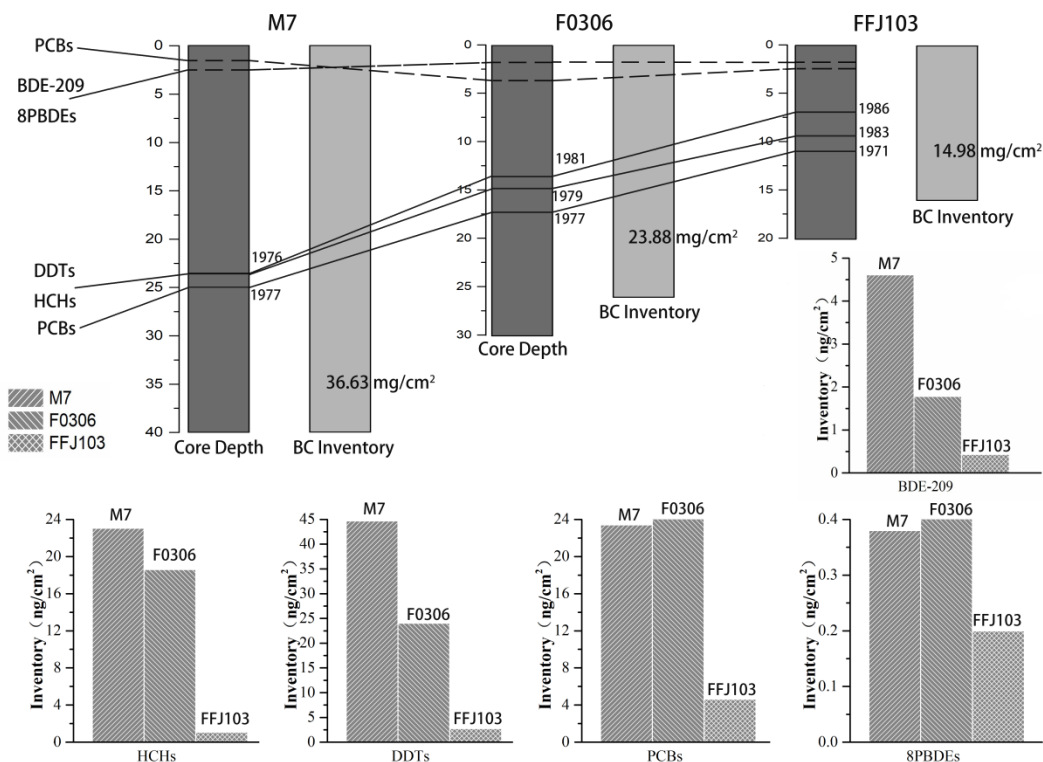


Figure 4. The inventory and peak fluxes of POPs and BC in M7, F0306, and FFJ103

There have been many studies on the deposition records of POPs in lakes, estuaries and open seas in China, and these show peak inputs to these archives generally coinciding with historical records of production and use, as well as events corresponding to the control of POPs-containing products in China (Li et al., 2016; Yang et al., 2020; Zhang et al., 2002).

The temporal trends in the contaminant fluxes from the marginal sea cores are consistent with trends determined from sediment cores taken from lakes and estuaries in China, indicating that these chemicals mainly originated from terrestrial sources. Besides the influence of source emissions, Zhang et al. (2002) found enhanced soil runoff from large-scale land transformation processes had transported pesticides from soil to aquatic sedimentary systems, and which may be responsible for the second peak of HCH and DDT pollutants around 1990. In this study, the lack of a peak in more remote sediment cores after the ban on DDT and HCH, indicated that these areas were beyond the direct impact of riverine lateral transport. Unlike DDTs and HCHs, the sedimentary fluxes of PCBs and

PBDEs in all the cores display increasing trends or strong recoveries in concentrations since the 1990s, again confirming they are not related to riverine inputs.

The influence of long range atmospheric transport to the central BS has been clearly illustrated by Qin et al. (2011). Due to the combination of a limited rate of coastal surface runoff and the circulation system in the coastal BS, there is only a weak exchange of suspended sediments and water between these two areas. As a result, atmospheric deposition may be an important source of POPs to the central BS. A strong atmospheric outflow from the Asian continent occurs in late winter and spring, and its impact may be far greater than runoff output, even in the region of southwestern Cheju Island in ECS (Wilkening et al., 2000; Zhang et al., 1992). Thus, the sediment burden closely follows estimated time trends of consumption and emission of POPs in China, and allows the reconstruction of atmospheric POPs deposition histories from these remote sea areas.

Fang et al.'s (2018) findings also indicate that atmospheric deposition and riverine input dominate more than 80% of the BC flux into BS, and that sequestration to sediments dominated their removal (70%). Thus, BC sediment inventories can be used as a very good reference indicator in this study. Taking POP/BC in BS (M7) as a reference, the relative values of POP/BC in YS (F0306) ranged from 82% (DDTs) to 174% (PCBs), respectively (Table S2). PCBs (174%) and 8PBDEs (167%) were highly enriched in the F0306 region, showing the extra contribution of relatively high pollution from Jiangsu and Shandong provinces upwind. This also further confirms the continuous input of pollutants, especially from East China.

### 3.3. Spatial variation between POPs and BC/TOC inventories and their implications for transport processes

The net fluxes of ... at in the surface sediments, their ranges in the three cores, as well as the inventories at each site, are shown in Table S1. In the three



cores, the analyzed POPs and BC had the lowest sediment inventories at FFJ103 which is 400 km away from the continent. The BC inventory ratio between the two cores FFJ103/F0306 is 0.60, equivalent to a deposition rate ratio of 0.62. By comparison, the inventory ratios of individual POPs between the two cores (FFJ103/F0306) were, for HCHs, 0.06, DDTs 0.11, PCBs 0.17, 8PBDEs 0.26 and BDE-209 0.24. As BC has considerable resistance to degradation during transport (Coppola et al., 2018) and as there is no additional input of BC over the sea between YS and ECS, a reasonable explanation for these results is that these POPs have been lost during transport in the atmosphere and water column. Clearly, loss would be expected to be greater for more volatile and water-soluble compounds (e.g HCHs and DDTs), resulting in a reduced availability for burial in more remote mud areas, while the loss of compounds with stronger sorption to particulate matter or BC is relatively small. For example, 8PBDEs and BDE209 with stronger sorption to particulate matter are more inclined to be buried in the sediment (Mai et al., 2005).

Taking POP/BC in F0306 as a reference, the relative values of POP/BC in FFJ103 range from 9% (HCHs) to 41% (8PBDEs). Hence, about 9%, 18%, 28%, 41%, 38% of HCHs, DDTs, PCBs, 8PBDEs and BDE-209 respectively are being buried in ECS sediments compared with the POP inventories in the YS. This suggests that the source signal may be preserved, although only a small part of the pollutants end up buried in the open sea sediments. For the core M7, grain size measurements show that sand content had a large fluctuation (Figure 2). In F0306 sand content stabilized at < 10%, and there was a negligible sand component in FFJ103 (Figure S2). This indicates that sandy sediment was not the main carrier of POPs, and that these pollutants may be more sorbed onto fine particles (silt or clay), organic or carbonaceous particles during transport.

The POPs not deposited to the sediments may be considered lost to the atmosphere and water column and our estimates of these are shown in Figure 5. HCHs, DDTs, PCBs, 8PBDEs and BDE-209 decreased by 91%, 82%, 72%, 59%, and 62%, respectively from F0306 to FFJ103. The sediment sampling locations

(in YS and ECS) were about 60-65 m deep and the central YS and ECS locations are dominated by cold water masses resulting in cyclonic circulations accompanied by upwelling at their centers (Shi et al., 2002; Cheng et al., 2004). The process of net sediment transport patterns in this area can also be obtained by grain-size analysis of surface sediments, to determine where fine-grained particles and their associated pollutants are ultimately deposited (Shi et al., 2002; Cheng et al., 2004). Thus, we estimated POPs losses from the water column using particle settling rates. In general, the settling rate of fine particles in a water body follows an exponential relationship with the size of the particle, and the depths of sediment below water surface (60-65 m). According to Stokes' Law, for particles with a median size of  $5.5\mu\text{m}$  (as for FFJ103), the corresponding average deposition rate is 0.65 m/day, and therefore the residence time of the particles in the water column at FFJ103 is about 100 days. This is consistent with results obtained from  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  (Nozaki et al., 1991; Fang et al., 2013). We estimated that POP losses from the water column at FFJ103 were 46% HCHs, 40% DDTs, 36% PCBs, 17% 8PBDEs and 17% BDE-209, respectively (Figure 5). Furthermore, we believe that loss in the water column may be underestimated. Taking DDTs and HCHs as an example, it was noted that the peaks of these two groups in the remote sediment cores (relative to the nearshore sediment cores) were significantly dispersed (Figure 4), indicating a degree of resuspension at the sediment-water interface. This differentiation is especially obvious in the open sea area where there is a low sedimentation rate. Compared with HCHs, DDTs have a stronger sorption to particulates and can move upwards as particles are resuspended and then re-deposited. This characteristic increases the residence time of DDTs in the water column. For HCHs, it seems that only a small fraction returns to the sediments after being released into the water during the resuspension process due to their higher solubility. This results in HCHs being more efficiently removed from the water column due to their uptake and metabolism within the aquatic food web.

During long-range atmospheric transport, the aerosol concentration

decreases rapidly as the air mass diffuses (Jaward et al., 2004). At the same time, due to the dry and wet deposition, atmospheric particulate matter, and hence particulate-phase concentrations of POPs, also continues to decrease (Zhang et al., 2007). In this study, the proportion of loss from the atmosphere ranges from 36 to 45% (Figure 5; exclude the sediment and water column fractions), which is consistent with previous monitoring results from land-source atmospheric transport of heavy metals and POPs (Lammel et al., 2007; Wang et al., 2017)

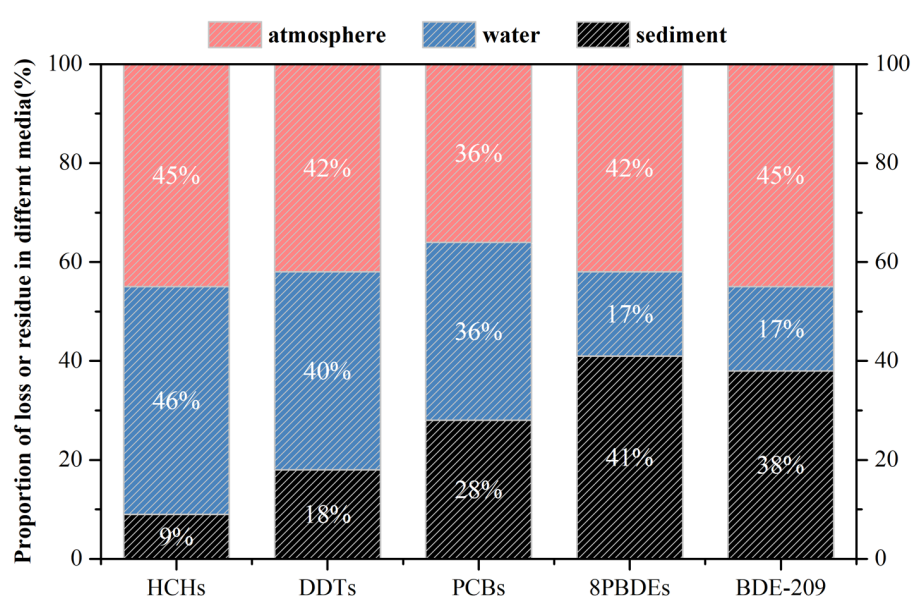


Figure 5. Proportions of POPs lost during atmospheric transport and to the water column, and the residue in sediment from site F0306 (YS) to site FFJ103 (ECS)

BC could strongly affect the distribution and transport of POPs (Fang et al., 2015; Hung et al., 2011). Loss from the water column (rather than from the atmosphere) is the main factor behind the variation in the sediment fluxes of different pollutants and partly explains how changes in the sedimentary environment affect the source signal. Hence, the presence of BC in stable depositional environments is probably significant for the good preservation of pollutant source signals. Importantly, observations have shown that emissions of POPs associated with combustion processes, and hence with the same source as

BC, may be considered unexchangeable once absorbed (Zhao et al., 2019). Therefore, an increase in BC emission may lead to more POPs adsorption onto carbonaceous particles, reduced degradation in the atmosphere and in the water column, eventually leading to enhanced burial in sediments. The increasing atmospheric emission of BC may therefore change the transport, fate and depositional fluxes of POPs.

#### 4. Conclusions

In this study, three sediment cores were collected from relatively open sea areas of China, and stable depositional environments were indicated by BC, TOC and grain size analyses. Although a seaward decreasing trend in inventories was observed, the temporal patterns of POPs within the cores were consistent with those of lakes and estuaries in China, indicating that the sources in the region were mainly derived from mainland terrestrial sources.

BC can be used as an important reference to reveal the level of degradation of organic pollutants during source-to-sink transport. Our estimates show that HCHs, DDTs, PCBs, 8PBDEs and BDE-209 decreased by 91%, 82%, 72%, 59%, and 62%, respectively, during atmospheric transport from the Yellow Sea to the relatively remote East China Sea and in the water column. Furthermore, our data suggest that even though only a small fraction of the pollutants end up deposited to, and buried in, these open sea sediments, the source signal can be well preserved under such stable depositional environments. The role of BC in the preservation of terrestrial POPs source signals in marine systems deserves further study.

#### Acknowledgments

The authors would like to thank Xianming Zhang for their valuable comments. This work was supported by the National Natural Science Foundation of China (42076205, 41103046), and the Taishan Scholar Program (TSQN20182117).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2011.03.001>

### Refs:

- Cheng, P., Gao, S., Bokuniewicz, H. (2004) Net sediment transport patterns over the Bohai Strait based on grain size trend analysis, *Estuarine, Coastal and Shelf Science* 60(2), 203-212, doi:10.1016/j.ecss.2003.12.009.
- Coppola, A.I., Wiedemeier, D.B., Galy, V., Haghipour, N., Hanke, U.M., Nascimento, G.S., Usman, M., Blattmann, T.M., Reisser, M., Freymond, C.V. (2018) Global-scale evidence for the refractory nature of riverine black carbon. *Nature Geoscience*, 584-589, doi: 10.1038/s41561-018-0159-8.
- Fang, Z., Yang, W., Zhang, X., Fan, D., Ma, Q., Zhang, R., Zheng, M., Qiu, Y. (2013) Sedimentation and lateral transport of <sup>210</sup>Pb over the East China Sea Shelf. *J Radioanal Nucl Chem* 298, 739–748. <https://doi.org/10.1007/s10967-013-2561-4>.
- Fang, Y., Chen, Y.J., Lin, T., Hu, L.M., Tian, C.G., Luo, Y.M., Yang, X., Li, J., Zhang, G. (2018) Spatiotemporal Trends of Elemental Carbon and Char/Soot Ratios in Five Sediment Cores from Eastern China Marginal Seas: Indicators of Anthropogenic Activities and Transport Patterns. *Environmental Science & Technology* 52, 9704-9712, doi: 10.1021/acs.est.8b00033.
- Fang, Y., Chen, Y.J., Tian, C.G., Lin, T., Hu, L.M., Huang, G.P., Tang, J.H., Li, J., Zhang, G. (2015) Flux and budget of BC in the continental shelf seas adjacent to Chinese high BC emission source regions. *Global Biogeochemical Cycles* 29, 957-972, doi: 10.1002/2014gb004985.
- Guo, Z.G., Lin, T., Zhang, G., Yang, Z.S., Fang, M. (2006) High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. *Environmental Science & Technology*, 5304-5311, doi: 10.1021/es060878b.
- Guo, Z.G., Lin, T., Zhang, G., Zheng, M., Zhang, Z.Y., Hao, Y.C., Fang, M. (2007) The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River Estuary coastal sea for the past century. *Science of The Total Environment* 386, 33-41, doi: 10.1016/j.scitotenv.2007.07.019.
- Han, Y.M., Cao, J.J., Chow, J.C., Watson, J.G., An, Z.S., Jin, Z.D., Fung, K., Liu, S.X. (2007) Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere* 69, 569-574, doi: 10.1016/j.chemosphere.2007.03.024.
- Hu, L., Lin, T., Shi, X., Yang, Z.S., Wang, H.J., Zhang, G., Guo, Z. (2011) The role of shelf mud depositional process and large river inputs on the fate of organochlorine pesticides in sediments of the Yellow and East China seas. *Geophysical Research Letters* 38, L03602, doi: 10.1029/2010gl045723.
- Hu, L.M., Shi, X.F., Bai, Y.Z., Qiao, S.Q., Li, L., Yu, Y.G., Yang, G., Ma, D.Y., Guo, Z.G. (2016) Recent organic carbon sequestration in the shelf sediments of the Bohai Sea and Yellow Sea, China. *Journal of Marine Systems* 155, 50-58, doi: 10.1016/j.jmarsys.2015.10.018.
- Hung, C.C., Gong, G.C., Ko, F.C., Lee, H.J., Chen, H.Y., Wu, J.M., Hsu, M.L., Peng, S.C., Nan, F.H., Santschi, P.H. (2011) Polycyclic aromatic hydrocarbons in surface sediments of the East China Sea and their relationship with carbonaceous materials. *Marine Pollution Bulletin* 63, 464-470, doi: 10.1016/j.marpolbul.2011.03.001.

- Jaward, F.M., Barber, J.L., Booij, K., Dachs, J., Lohmann, R., Jones, K.C. (2004) Evidence for dynamic air-water coupling of persistent organic pollutants over the open Atlantic Ocean. *Environmental Science & Technology* 38, 2617, doi: 10.1021/es049881q.
- Lammel, G., Ghim, Y.-S., Grados, A., Gao, H., Hühnerfuss, H., Lohmann, R. (2007) Levels of persistent organic pollutants in air in China and over the Yellow Sea. *Atmospheric Environment* 41, 452-464, doi: 10.1016/j.atmosenv.2006.08.045.
- Latimer, J.S., Davis, W.R., Keith, D.J. (1999) Mobilization of PAHs and PCBs from In-Place Contaminated Marine Sediments During Simulated Resuspension Events. *Estuarine, Coastal Shelf Science* 49, 577-595, doi: 10.1006/ecss.1999.0516.
- Li, X.M., Gao, Y., Wang, Y.W., Pan, Y.Y. (2014) Emerging Persistent Organic Pollutants in Chinese Bohai Sea and Its Coastal Regions. *The Scientific World Journal* 2014, 608231, doi: 10.1155/2014/608231.
- Li, Y.F., Cai, D.J., Shan, Z.J., Zhu, Z.L. (2001) Gridded Usage Inventories of Technical Hexachlorocyclohexane and Lindane for China with 1/6° Latitude by 1/4° Longitude Resolution. *Archives of Environmental Contamination Toxicology* 41, 261, doi: 10.1007/s002440010247.
- Li, Y.F., Cai, D.J., Singh, A. (1999) Historical DDT use trend in China and usage data gridding with 1/4° by 1/6° longitude/latitude resolution. *Advances in Environmental Research* 2, 497-506.
- Li, Y.Y., Lin, T., Hu, L.M., Feng, J.L., Guo, Z.G. (2016) Time trends of polybrominated diphenyl ethers in East China Seas: Response to the booming of PBDE pollution industry in China. *Environment International* 92-93, 507-514, doi: 10.1016/j.envint.2016.04.033.
- Lin, T., Li, J., Xu, Y., Liu, X., Luo, C.L., Cheng, H.R., Chen, Y.J., Zhang, G. (2012) Organochlorine pesticides in seawater and the surrounding atmosphere of the marginal seas of China: Spatial distribution, sources and air-water exchange. *Science of The Total Environment* 435-436, 244-252, doi: 10.1016/j.scitotenv.2012.07.028.
- Lin, T., Nizzetto, L., Guo, Z.G., Li, Y.Y., Li, J., Zhang, G. (2016) DDTs and HCHs in sediment cores from the coastal East China Sea. *Science of The Total Environment* 539, 388-394, doi: 10.1016/j.scitotenv.2015.09.010.
- Qin, Y.W., Zheng, B.H., Lei, K., Lin, T., Hu, L.M., Guo, Z.G. (2011) Distribution and mass inventory of polycyclic aromatic hydrocarbons in the sediments of the south Bohai Sea, China, *Marine Pollution Bulletin* 62, 371-376, doi:10.1016/j.marpolbul.2010.09.028.
- Mai, B.X., Zeng, E.Y., Luo, X.J., Yang, Q.S., Zhang, G., Li, X.D., Sheng, G.Y., Fu, J.M. (2005) Abundances, Depositional Fluxes, and Homologue Patterns of Polychlorinated Biphenyls in Dated Sediment Cores from the Pearl River Delta, China. *Environmental Science & Technology* 39, 49-56, doi: 10.1021/es049015d.
- Martin, M., Lam, P.K., Richardson, B.J. (2004) An Asian quandary: where have all of the PBDEs gone? *Marine Pollution Bulletin* 49, 375-382, doi: 10.1016/j.marpolbul.2004.05.015.
- Nozaki, Y., Tsubota, H., Kasemsupaya, V., Yashima, M., Naoko, I. (1991) Residence times of surface water and particle-reactive <sup>210</sup>Pb and <sup>210</sup>Po in the East China and Yellow seas. *Geochimica et Cosmochimica Acta* 55(5), 1265-1272, doi: 10.1016/0016-7037(91)90305-O.
- Ofenvironment, D. (2013) Stockholm Convention on Persistent Organic Pollutants. 47, 187-196.
- Siddiqi, M.A., Laessig, R.H., Reed, K.D. (2003) Polybrominated diphenyl ethers (PBDEs): new pollutants-old diseases. *Clin Med Res* 1, 281-290, doi: 10.3121/cmr.1.4.281.
- Shi, X., Chen, F. C., Liu, Y. G., Reng, H., Wang H. Y., (2002) Trend analysis of sediment grain size and sedimentary process in the central South Yellow Sea, *Chinese Science Bulletin* 47(14), 1202-1207, doi:10.1007/bf02907610.

- Wang, C.L., Zou, X.Q., Zhao, Y.F., Li, Y.L., Song, Q.C., Wang, T., Yu, W.W. (2017) Distribution pattern and mass budget of sedimentary polycyclic aromatic hydrocarbons in shelf areas of the Eastern China Marginal Seas. *Journal of Geophysical Research: Oceans* 122, 4990-5004, doi: 10.1002/2017jc012890.
- Wang, J.X., Lin, Z.K., Lin, K.F., Wang, C.Y., Zhang, W., Cui, C.Y., Lin, J.D., Dong, Q.X., Huang, C.J. (2011) Polybrominated diphenyl ethers in water, sediment, soil, and biological samples from different industrial areas in Zhejiang, China. *Journal of Hazardous Materials* 197, 211-219, doi: 10.1016/j.jhazmat.2011.09.078.
- Wang, R., Tao, S., Wang, W., Liu, J., Shen, H., Shen, G., Wang, B., Liu, X., Li, W., Huang, Y., Zhang, Y., Lu, Y., Chen, H., Chen, Y., Wang, C., Zhu, D., Wang, X., Li, B., Liu, W., Ma, J. (2012) Black Carbon Emissions in China from 1949 to 2050. *Environmental Science & Technology* 46, 7595-7603, doi: 10.1021/es3003684.
- Wilkening, K.E., Barrie, L.A., Marilyn, E. (2000) Trans-Pacific Air Pollution. *Science* 290, 65-67, doi: 10.1126/science.290.5489.65.
- Wu, Z.L., Lin, T., Li, A., Zhou, S.S., He, H., Guo, J.H., Hu, L.M., Li, Y.Y., Guo, Z.G. (2019) Sedimentary records of polychlorinated biphenyls in the East China Marginal Seas and Great Lakes: Significance of recent rise of emissions in China and environmental implications. *Environmental Pollution* 254, 112972, doi: 10.1016/j.envpol.2019.112972.
- Wurl, O., Obbard, J. (2005) Organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in Singapore's coastal marine sediments. *Chemosphere* 58, 925-933, doi: 10.1016/j.chemosphere.2004.09.054.
- Yang, R.Q., Xie, T., Wang, P., Li, Y.M., Zhang, Q.H., Jiang, G.B. (2020) Historical trends of PCBs and PBDEs as reconstructed in a lake sediment from southern Tibetan Plateau. *Journal of Environmental Sciences* 98, 31-38, doi: 10.1016/j.jes.2020.04.030.
- Zhang, G., Li, J., Cheng, H.R., Li, X.D., Xu, W.H. (2007) Distribution of Organochlorine Pesticides in the Northern South China Sea: Implications for Land Outflow and AirSea Exchange. *Environmental Science & Technology* 41, 3884-3890, doi: 10.1021/es070072r.
- Zhang, G., Parker, A., House, A., Mai, B.X., Li, X.D., Kang, Y.H., Wang, Z.S. (2002) Sedimentary Records of DDT and HCH in the Pearl River Delta, South China. *Environmental Science & Technology* 36, 3671-3677, doi: 10.1021/es0102888.
- Zhang, J., Huang, W.W., Liu, S.M., Liu, M.G., Yu, Q., Wang, J.H. (1992) Transport of particulate heavy metals towards the China Sea: a preliminary study and comparison. *Marine Chemistry* 40, 161-178, doi: 10.1016/0304-4203(92)90021-2.
- Zhao, S.Z., Breivik, K., Liu, G.R., Zheng, M.H., Jones, K.C., Sweetman, A.J. (2017) Long-Term Temporal Trends of Polychlorinated Biphenyls and Their Controlling Sources in China. *Environmental Science & Technology* 51, 2838-2845, doi: 10.1021/acs.est.6b05341.
- Zhao, S.Z., Jones, K.C., Li, J., Sweetman, A.J., Zhang, G. (2019) Evidence for Major Contributions of Unintentionally Produced PCBs in the Air of China: Implications for the National Source Inventory. *Environmental Science & Technology* 54, 2163-2171, doi: 10.1021/acs.est.9b06051.