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Historical trends of polychlorinated biphenyls and alkylphenols recorded in core sediments from the intertidal areas of the Yellow Sea and Bohai Sea

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ABSTRACT

Historical records of polychlorinated biphenyls (PCBs) and alkylphenols (APs) were reconstructed from intertidal zones of the Yellow and Bohai Seas over the past 80 years. Concentrations of PCBs (1.50–6.47 ng g^{-1} organic carbon (OC)) and APs (8.42–13.8 ng g^{-1} OC) in Dangjin, South Korea, peaked in the 1970s and subsequently declined. Conversely, levels in Tianjin and Dandong, China, have continued to increase in recent decades (PCBs: 0.53–6.1 ng g^{-1} OC; APs: 2.61–42.7 ng g^{-1} OC). These divergent trends align with regulatory enforcement: levels in South Korea declined following the implementation of regulations in 1979 and 2003, while the continued increase in China, despite regulation in 1974 and 2011, points to unregulated sources. Estimated fluxes of PCBs and APs from the intertidal zone to offshore areas decreased by approximately 83% and 57%, respectively. This study provides baseline data for assessing long-term pollution trends in intertidal environments.

1. Introduction

Sediments acts as a major repository for anthropogenic pollutants, providing valuable natural archives that record historical contamination. Reconstructing the distribution of stored contaminants allows us to trace pollution history in specific regions. In addition, determining sediment age through radionuclide analysis with vertical distribution data yields insights into both contaminant trajectories and environmental transitions linked to industrial and energy development (Cui et al., 2013). While many previous pollution studies have focused on lakes, rivers, estuaries, and coastal areas, intertidal zones have received comparatively less attention (Duan et al., 2013; Guerra et al., 2019; Zhang et al., 2014). Intertidal zones, which are heavily impacted by anthropogenic activities and serve as a crucial link between riverine and coastal systems, are essential for understanding the fate of pollutants in coastal ecosystems. However, most previous studies have concentrated on spatiotemporal distribution and potential ecological risk rather than on historical records of contaminants and their function as dynamic buffer zones at the land–sea interface (Li et al., 2022).

Polychlorinated biphenyls (PCBs) and alkylphenols (APs) are well-known pollutants with a wide range of applications, such as dielectric liquids, heat transfer fluids, and plasticizers for PCBs and surfactants, paints, and pesticides for APs. These pollutants are released into the environment during industrial processes and, in the case of PCBs, also through fossil fuel combustion and waste incineration (Lin et al., 2023). Due to their harmful environmental impacts, PCBs and APs have been subject to extensive regulatory control globally (Acir and Guenther, 2018; Safe, 1994). PCBs have been banned since the 1970s, representing compounds that have been regulated for a long time, while APs have been banned since the mid-2000s, representing more recently regulated pollutants.

The timeline of regulation has varied between countries, particularly between South Korea and China. In South Korea, the use of PCBs in the electrical industry was first regulated in 1979, with a complete ban on production, import, and use by 1996. In China, PCBs regulation began in 1974, focusing on their use in electrical capacitors, followed by broader regulations on PCB pollution control and hazardous waste incineration in 1991 and 1999, respectively. However, an e-waste import ban was not

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implemented until 2017. Nonylphenols (NPs), a major subgroup of APs, have been regulated as endocrine-disrupting chemicals since the 2000s. South Korea banned the use of NPs in household detergents, inks, and paints in 2006, extending the ban to industrial detergents, textile, and leather processing by 2016. In China, restrictions on the import and export of NPs were established in 2011, with a prohibition on their use as pesticide additives in 2022 and as cosmetic ingredients in 2023.

The timing and scope of these regulations have differed between the two nations. For instance, South Korea banned the recycling of existing PCB-containing products, whereas China allowed the recycling and disposal of e-waste for copper, iron, and gold (Shi et al., 2019). Since 2016, NPs have been banned in all industries with a high potential for direct discharge into water systems in South Korea, while in China, they have only been banned as additives in certain industrial fields (Zhao et al., 2024). These regulatory discrepancies may lead to contrasting outcomes in pollution reduction, despite the adoption of broadly similar objectives.

The Yellow and Bohai Seas, semi-enclosed areas bordered by the Korean Peninsula and eastern China, represent highly urbanized and industrialized regions (Hoagland and Jin, 2006). The coastal and estuarine areas of the Yellow and Bohai Seas are of great socioeconomic and ecological importance for both countries. Numerous rivers discharge into the Yellow and Bohai Seas, carrying pollutants from industrial complexes and metropolitan areas. The degradation of the marine environment due to various contaminants, including PCBs, APs, and other persistent toxic substances (PTSs), has been widely reported in estuaries, coastal areas, and offshore regions of these seas (Meng et al., 2017; Kim et al., 2024). Previous studies have identified several hotspots, including Siheung in South Korea and Huludao, Tianjin, Yingkou, and Nantong in China, where sediments are heavily polluted by industrial discharges, fuel combustion, and vehicle emissions (Hong et al., 2010; Kim et al., 2020; Yoon et al., 2020). While the spatial distribution and sources of pollutants have been assessed, long-term historical patterns, especially at the large marine ecosystem (LME) scale, remain understudied. The Yellow Sea is a vital, interconnected marine environment for both countries, and joint assessments of PTS pollution levels and regulatory impacts in this region are crucial. Although conducting such transboundary research presents challenges, understanding the full scope of historical pollution and the effectiveness of regulations in this shared marine ecosystem is essential.

Over the past several decades, development in South Korea and China has exacerbated PCBs and APs pollution in the intertidal zones of the Yellow and Bohai Seas. However, few studies have investigated historical records to assess the effectiveness of pollution regulations in both countries. This study hypothesizes that historical concentrations of PCBs and APs in sediment cores were influenced by environmental regulations, leading to a subsequent decrease in levels. The specific objectives were to: (1) reconstruct historical records of PCBs and APs, (2) track changes in pollution sources, (3) compare temporal contamination trends between two countries, and (4) assess the flux and transport of PCBs and APs. Results from this study are expected to provide crucial insights into the long-term impacts of regulatory policies and inform future strategies for managing the Yellow and Bohai Seas.

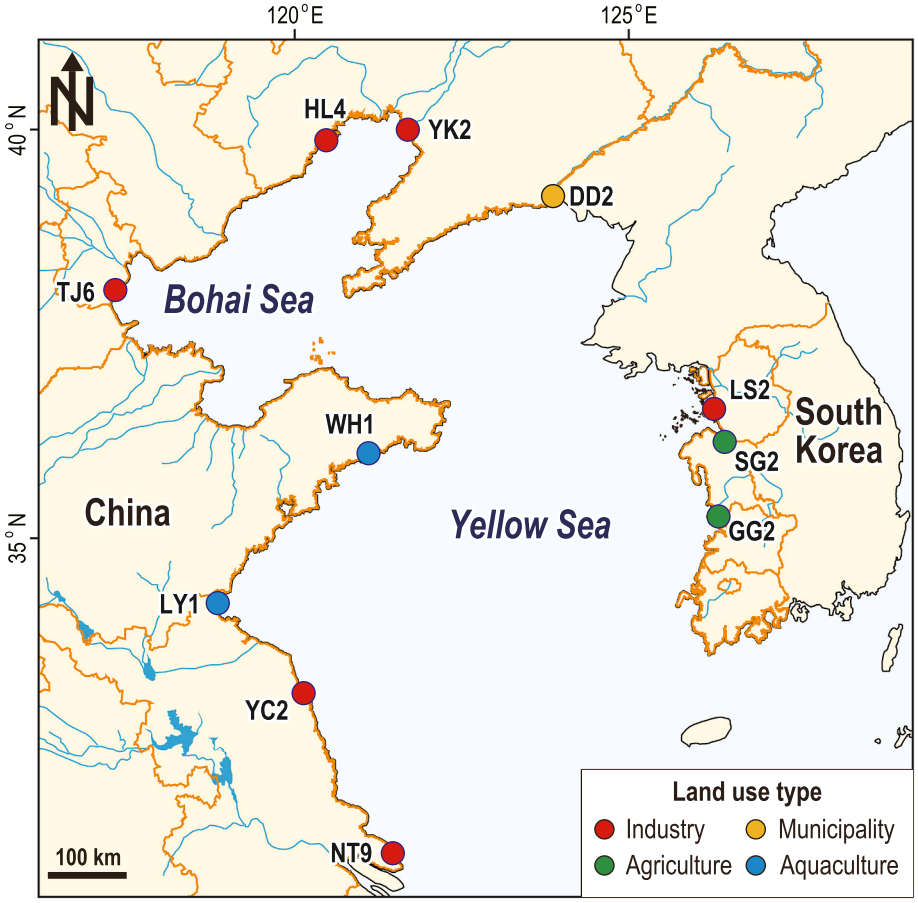


Fig. 1. Map showing the sediment core sampling stations in the intertidal zone from the Yellow and Bohai Seas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Study area

Eleven sediment cores were collected from the intertidal zones of the Yellow Sea and Bohai Sea in 2018, covering seven provinces in South Korea and China (Fig. 1). Sampling stations were selected to represent regions where undisturbed sediments and relatively high concentrations of PCBs and APs were expected, based on previous research (Yoon et al., 2020). Selection criteria included PTS concentrations in surface sediments, sediment grain size, and land use types. Stainless steel core samplers (600 mm in height) were used for sediment collection. Sediment cores were sectioned at 5 cm intervals, followed by freeze-drying, homogenization, and sieving through a 2-mm mesh prior to analysis.

2.2. Quantification of PCBs and APs

The analytical protocol for PCBs and APs in sediments followed previously reported methods (Yoon et al., 2017; Kim et al., 2021). Briefly, 10 g of sediment was extracted using a Soxhlet extractor with 350 mL of dichloromethane (DCM, Burdick & Jackson, Muskegon, MI) after the addition of surrogate standards. The extract was concentrated using a rotary evaporator and solvent-exchanged with hexane (Burdick & Jackson). Activated copper (Sigma Aldrich, Saint Louis, MO) was added to remove elemental sulfur from the extracts. The extracts were then purified and fractionated using 8 g of activated silica gel (70-230 mesh, Sigma Aldrich) columns. PCBs were eluted with 30 mL of hexane, and APs were eluted with 50 mL of 40% of acetone in DCM. The eluents were concentrated under a stream of nitrogen gas, and an internal standard was added before instrumental analysis. Concentrations were determined using gas chromatography (Agilent 7890B GC, Agilent Technologies, Santa Clara, CA) coupled with a 5977B mass selective detector (MSD, Agilent Technologies). Detailed data for the target compounds, method detection limit (MDL), and instrument conditions are provided in Tables S1 and S2.

2.3. Core dating and flux calculation

Bulk density, total organic carbon (TOC), and ^{210}Pb data were obtained from a previous study (Yoon et al., 2023). Sediment chronologies were re-evaluated using the serac package in R, which applies the constant flux–constant sedimentation (CFCS) model within a Monte Carlo simulation framework to estimate mass accumulation rates (MAR) along with associated means and standard deviations (Bruel and Sabatier, 2020). Layer-specific sediment accumulation rates (SARs) were calculated by normalizing MAR with dry bulk density at corresponding depth. The conventional log-linear CFCS model exhibited poor linearity in several cores, and the constant rate of supply (CRS) model, which assumes that excess ^{210}Pb reaches equilibrium at depth, was not applicable due to the lack of clear equilibrium in our profiles. Consequently, we employed a bulk density-based CFCS model using mass depth, which has been shown to be a robust alternative when classical assumptions are not fully met (Barsanti et al., 2020; Sanchez-Cabeza and Ruiz-Fernández, 2012). Among the eleven sampling stations, valid excess ^{210}Pb data were obtained at four stations: TJ6, DD2, and YC2 in China and SG2 in South Korea. The MAR across these cores ranged from 0.57 to 2.24 g cm^{-2} y^{-1}, and the corresponding SAR, calculated by dividing MAR ranged from 0.28 to 1.25 cm y^{-1}. These values are consistent with previously reported sedimentation rates in the Yellow and Bohai Seas, supporting the reliability of the updated chronology (Liu et al., 2010; Wang et al., 2008). The deposition flux (F) of PCBs and APs was calculated using the following Eq. (1):

$$F = C_x \times p_x \times S \quad (1)$$

Where S is the SARs in core sediment (cm y^{-1}), p_x is the bulk density at depth x in sediment (g cm^{-3}), and C_x is the concentration of PCBs or APs at depth x (ng g^{-1}).

2.4. Data analyses

Concentrations of PCBs and APs were normalized by TOC to account for regional variation. Original concentrations were presented for comparisons with previous studies. Statistical analyses were performed using SPSS 25.0 and PRIMER 6 software. Cluster analysis was conducted based on Euclidean distance, and the Kruskal-Wallis test with Bonferroni correction was applied owing to non-parametric dispersion. Principle component analysis (PCA) was used to identify the source of PCBs, with a Kaiser-Meyer-Olkin (KMO) value of 0.69 and Bartlett's test significance level of $P < 0.01$. Regression curves were applied to assess historical trends and compositional changes in contaminant concentrations over time.

3. Results and discussion

3.1. Vertical distribution of PCBs

PCBs were detected in most samples with a detection frequency of 92.1%, and the vertical distribution of PCBs showed an irregular pattern depending on both region and depth (Fig. S2). In South Korea, PCB concentrations ranged from <MDL to 11.9 ng g^{-1} OC (mean: 2.4 ng g^{-1} OC), while in China, they ranged from <MDL to 326 ng g^{-1} OC (mean: 12.8 ng g^{-1} OC). The highest concentrations were observed at HL4 (mean: 161 ng g^{-1} OC), exceeding those at other stations by >30-fold. Huludao is known as a pollution hotspot, contaminated by various pollutants, including metals and dioxins (Naile et al., 2011; Zheng et al., 2008). A previous study also reported higher PCB concentrations in river sediments in Huludao compared to this study (Lu et al., 2021). The elevated PCB level at HL4 suggested a direct influence of PCB leakage from industrial activities in the area. Other stations with relatively high PCB concentrations included LS2 (mean: 4.72 ng g^{-1} OC), TJ6 (mean: 2.63 ng g^{-1} OC), and YK2 (mean: 2.46 ng g^{-1} OC), all located in industrial areas. PCB concentrations in industrial areas were significantly higher than those in municipalities, agricultural areas, and particularly aquaculture zones ($P < 0.01$), underscoring the dominant contribution of industrial emissions.

The historical distribution of PCBs showed contrasting trends between South Korea and China (Fig. 2a). In South Korea, relatively low concentrations were recorded before the 1960s at SG2, corresponding to the pre-industrialization era. Concentrations peaked in the 1970s, followed by a gradual decline into the 2000s. This decline corresponded with regulatory milestones, beginning with restrictions and followed by a complete ban, ultimately reaching the lowest levels in the sediment core. These trends align with previous studies from other regions in South Korea (Choi et al., 2001; Kim et al., 2008), demonstrating the effectiveness of the regulatory measures. In contrast, the historical trend in China (stations TJ6, DD2, and YC2) showed an increase. PCB concentrations were relatively low or stable until the 1990s, after which they began to rise. This upward trend has been corroborated by studies in Chinese rivers, estuaries, and coastal regions (Pan et al., 2012; Wu et al., 2019; Zhao et al., 2016). Despite regulatory efforts, the continued increase suggests limited effectiveness, likely due to unregulated or unaddressed sources. Following the 2017 ban on PCBs use from recycled e-waste in China, it may take additional time before significant reductions in PCB concentrations are observed.

3.2. Vertical distribution of APs

APs were detected in all samples, with vertical distribution patterns varying between South Korea and China (Fig. S1). AP concentrations ranged from 5.31 to 76.6 ng g^{-1} OC (mean: 17.7 ng g^{-1} OC) in South Korea and from 2.61 to 73.3 ng g^{-1} OC (mean: 16.2 ng g^{-1} OC) in China.

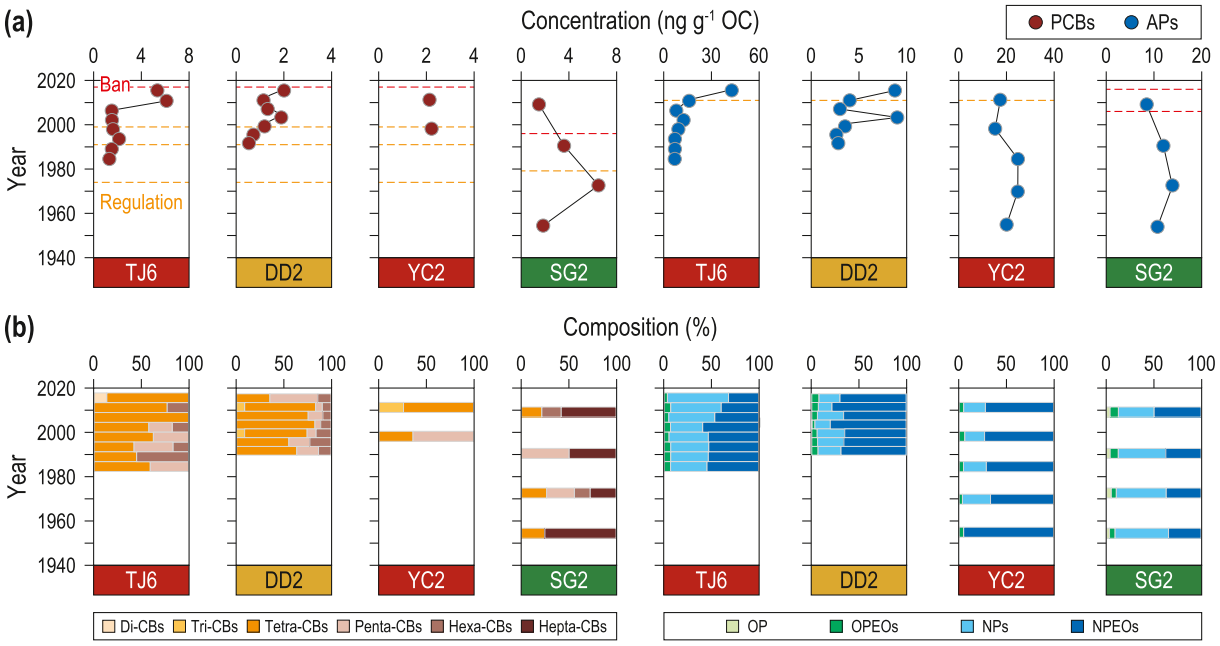


Fig. 2. (a) Historical distribution and (b) relative composition of PCBs and APs in four stations. Regulations and bans of PCBs and APs are indicated by orange and red dotted lines, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Relatively high concentrations of APs were observed at HL4 (mean: 46.7 ng g^{-1} OC), LS2 (mean: 33.1 ng g^{-1} OC), and WH1 (mean: 26.2 ng g^{-1} OC), all of which are located in industrial and aquaculture areas. These stations exhibited significantly elevated AP levels compared to agricultural and municipal areas ($P < 0.01$) (Fig. S3), suggesting greater use of APs in industrial detergents and aquaculture operations (Moon et al., 2009; Hook et al., 2018). AP concentrations at LS2 in South Korea were found to be 2.4 to 101 times lower than those reported in previous studies from 1998 and 2008 (Khim et al., 1999; Hong et al., 2010). Meanwhile, concentrations at HL4 and WH1 in China were only 1.3 to 1.5 times lower than levels reported in 2005 (Wang et al., 2010). These differences likely reflect variations in national policy implementation and enforcement, which can be further clarified using dated sediment cores.

The historical distribution of APs mirrored the trends observed for PCBs, with distinct patterns emerging between South Korea and China (Fig. 2a). At station SG2 in Korea, AP concentrations have shown a recent decreasing trend, with relatively stable levels over the past 80 years. This decline persisted despite the urban development and industrial expansion following the 1970s, indicating the impact of regulatory interventions. In contrast, AP concentrations at stations TJ6, DD2, and YC2 in China have continued to rise, even after the introduction of regulations. This suggests that the full effects of regulations introduced later in China have not yet been realized. Similar increasing trends have been observed in Dianchi Lake and the Pearl River Estuary in China (Chen et al., 2019; Wang et al., 2012). This pattern is also consistent with observations in core sediments from other developing countries, such as the Philippines and Thailand, where environmental regulations were implemented later (Kwan et al., 2014). These findings imply that the long-term impact of environmental regulations on AP concentrations in China may require additional time to manifest.

3.3. *Changes in compositions and potential sources of PCBs and APs*

The compositional profiles of PCBs and APs varied irregularly across different land use types (Fig. S2). Low-chlorinated PCBs (LCl-CBs; di- to tetra-CBs) were generally predominant, while high-chlorinated PCBs (HCl-CBs; penta- to hepta-CBs) were more prominent at LY1, LS2, SG2, and GG2. The dominance of LCl-CBs indicates combustion sources such as municipal waste incinerators and steelworks, whereas elevated proportions of HCl-CBs suggest contributions from PCB-based products, particularly near port-associated areas (Hong et al., 2005; Ikonomou et al., 2002). PCA results supported the dominance of combustion sources, with technical PCB input identified only at station HL4, where the highest PCB concentrations were observed (Fig. 3a). The localized nature of HCl-CBs, which tend to accumulate near their sources, contrasted with the more mobile LCl-CBs, capable of long-range transport (Ashley and Baker, 1999). These patterns imply that most intertidal areas are distant from primary PCB sources, with combustion dominating, except at HL4, where direct product usage is evident.

Alkylphenol ethoxylates (APEOs) were more prevalent than NPs and octylphenol (OP) in China, whereas NPs and OP were dominant in South Korea. The presence of APEOs in core sediments implied direct discharge of untreated wastewater or insufficient wastewater treatment (Ferguson et al., 2003). Anaerobic/anoxic/oxic biological reactions in the secondary treatment process of sewage treatment plants (STPs) are known to be effective in removing phenol compounds (Nie et al., 2012). Although effluents from STPs in the Haihe River showed slight increases in NP, approximately 70% of NPEOs were removed, indicating partial but incomplete treatment efficacy (Yu et al., 2009). Thus, the results of this study suggested that the sampling stations in China are less affected by STPs or that the treatment capacity is insufficient compared to that of the STPs in Korea (Duong et al., 2010). In addition, the persistence and stability of APEOs in sediments can be attributed to the slow decomposition of these nonionic surfactants under anaerobic conditions and their high adsorption capacity (Corada-Fernández et al., 2013).

The historical composition of the PCBs revealed more regional than temporal differences between Korea and China (Fig. 2b). The proportion of HCl-CBs has remained relatively high over the past 80 years at SG2 in Korea, while LCl-CBs have increased at TJ6, DD2, and YC2 in China. The LCl/HCl-CB ratio highlighted these trends (Fig. S4), indicating the influence of PCB products at SG2 and combustion sources at TJ6, DD2, and YC2. PCA results showed mixed sources at SG2, with both PCB products and combustion sources, likely due to its long-term port activities (Fig. 3b). At the Chinese stations (TJ6, DD2, and YC2), combustion sources persisted across all periods, indicating that regional rather than temporal differences drive PCB source variation. Similar findings have been reported in studies from the Pearl River Delta, Haizhou Bay, and

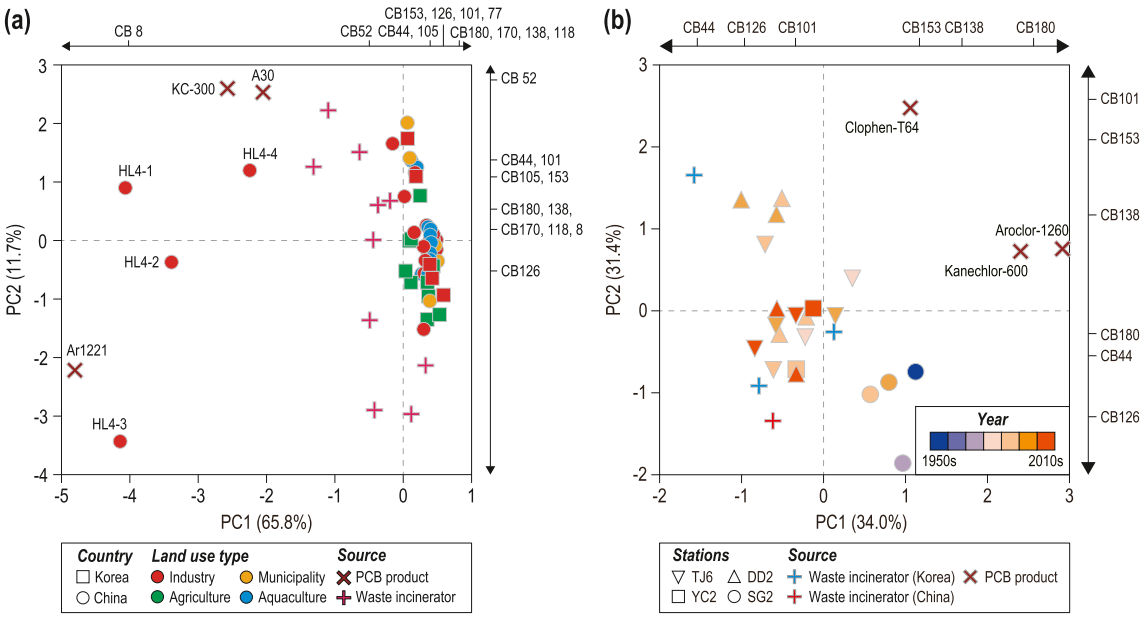
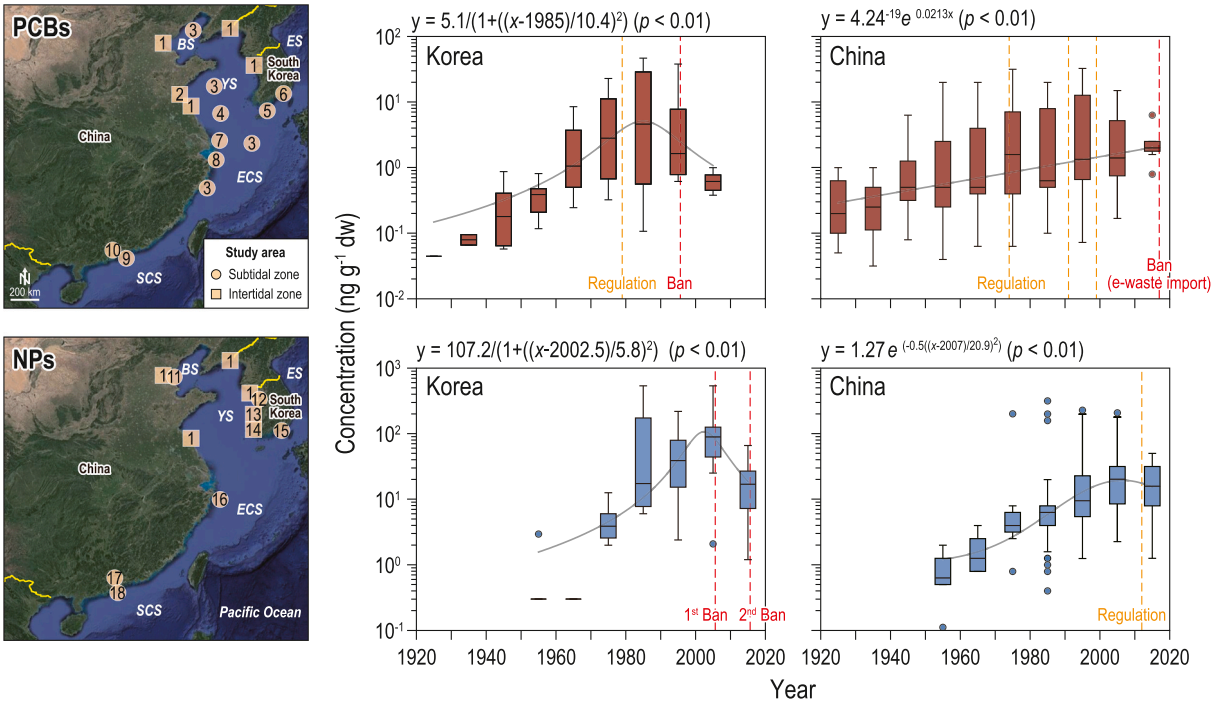


Fig. 3. PCA results in (a) all core sediments and (b) dated core sediments from the Bohai and Yellow Seas. Source profiles of PCBs referred from Ikonomou et al. (2002); Ishikawa et al. (2007); Shi et al. (2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the Korea Strait, where source compositions remained relatively constant over time (Guerra et al., 2019; Mai et al., 2005; Zhang et al., 2014). Clear shifts in PCB sources were observed mainly around the 1940s and 1950s, coinciding with the introduction of PCB products (Huo et al., 2017; Yang et al., 2012). Spatially, various PCB sources have been identified, including e-waste, combustion, PCB products, and unintentional PCBs (UP-PCBs) in coastal areas (Lin et al., 2023), as well as petrochemicals, paint, and polymer sealants in air and soil (Mao et al., 2021; Zhao et al., 2020). However, understanding historical source variations in coastal areas remains complex.

Over the past 80 years, NPs have been dominant in South Korea, while APEOs have been more prevalent in China since the 1960s.



1. This study; 2. Zhang et al., 2014; 3. Wu et al., 2019; 4. Zhang et al., 2009; 5. Guerra et al., 2019; 6. Hong et al,. 2003; 7. Duan et al., 2013; 8 Yang et al., 2012; 9. Wei et al., 2008; 10. Mai et al., 2005; 11. Jin et al., 2008; 12. Hong et al., 2010; 13. Jeon et al., 2017; 14. Kim et al., 2020; 15. Moon et al., 2009; 16. Bian et al., 2010; 17. Chen et al., 2019; 18. Peng et al., 2007.

Fig. 4. Mini-review of studies investigating the historical records of PCBs and NPs in Korea and China from the Bohai, Yellow, East China, and South China Seas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Anaerobic degradation of APEOs is known to take over 60 years in areas such as the Fraser River Delta, Canada (Shang et al., 1999). APEOs can be protected from microbial degradation by adsorption onto inorganic solids coated with organic matter (Kvestak and Ahel, 1995). But the anaerobic degradation of APEOs has also been reported in estuarine and coastal areas and may occur due to various factors, such as organic carbon content, oxygen supply, temperature, and adapted microorganisms (Hong et al., 2010; Lara-Martin et al., 2006). Achieving a complete understanding of APEOs degradation under anaerobic conditions remains a challenge.

3.4. Implications for difference in temporal trends

A comprehensive review of historical records from the Bohai, Yellow, East China, and South China Seas was carefully conducted to evaluate the temporal changes in PCBs and NPs deposition in marine environments between South Korea and China (Bian et al., 2010; Chen et al., 2019; Duan et al., 2013; Guerra et al., 2019; Hong et al., 2003; Hong et al., 2010; Jeon et al., 2017; Jin et al., 2008; Kim et al., 2020; Kim et al., 2008; Mai et al., 2005; Moon et al., 2009; Peng et al., 2007; Wei et al., 2008; Wu et al., 2019; Yang et al., 2012; Zhang et al., 2009; Zhang et al., 2014) (Fig. 4 and Table 1). Due to limited historical data for OP and APEOs, only NPs were considered.

The temporal trends of PCB concentrations exhibited notable differences between South Korea and China. In South Korea, PCB concentrations increased until the 1980s and began to decline after 1990, suggesting that the restrictions implemented in 1979 led to a delayed but eventual reduction in PCB levels. By 2000, a general decline was observed, following the 1996 ban. These findings suggest that it took approximately a decade for regulatory actions to translate into measurable environmental improvements. In contrast, PCB concentrations in China continued to rise until the 2010s, indicating that regulations were less effective. Although a temporary decrease was observed in the 1980s following the 1974 regulation, concentrations resumed their upward trend in the 1990s and persisted despite subsequent regulations and bans until 2017. This persistent increase is likely due to a reduction in intentionally produced PCBs (IP-PCBs) being offset by the rising contributions of UP-PCBs. UP-PCBs, which are by-products of industrial thermal processes such as cement, metallurgy, pigments, and paint industries, have increased alongside growing iron ore consumption (Cui et al., 2013; Wu et al., 2019). UP-PCB is expected to continue to occur, and effective control strategies will be essential to reverse this trend in China (Zhao et al., 2017).

The temporal trends of NPs in both countries showed similar patterns, but with a time lag of about a decade. In South Korea, NP concentrations rose rapidly until the 2000s, followed by a sharp decline in the 2010s after their use was banned in 2006 and 2016. In China, NP concentrations also increased until the 2000s, but the rate of increase slowed following the introduction of regulations in 2011. These trends suggest positive impacts of NP regulations, along with supporting policies such as improved wastewater treatment and factory closure targeting high-risk dischargers (Kim et al., 2020; Chen et al., 2019). Similar decreasing trends have been observed in cetaceans in the South China Sea, top predators that reflect the long-term accumulation of pollutants, further demonstrating that regulatory policies have effectively reduced NP emissions (Guo et al., 2023). Overall, while the effectiveness of environmental regulations has been demonstrated in South Korea, ongoing monitoring of PCBs and NPs in China will be necessary to fully evaluate the long-term impact of their policy measures.

3.5. Historical flux and transport mechanisms

The deposition fluxes of PCBs and NPs in intertidal and offshore areas of the Yellow and Bohai Seas have generally increased over the past 80 years, although the trends differ slightly between regions (Fig. 5a and Table 2). In intertidal areas, the historical flux of PCBs has steadily increased since the 1950s. On the other hand, offshore areas showed an increase in flux until the 1970s, followed by a decline, and then a renewed increase from the 1990s to the present. This recent uptick suggests elevated emissions of UP-PCBs, which have been rising since the 1990s, resulting in greater PCB inflows into offshore areas compared to earlier periods (Wu et al., 2019). The predominance of LCl-CBs in surface sediments of the Yellow and Bohai Seas during the 2010s, with UP-PCBs accounting for 76%, supports the finding of a relatively high PCBs influx in offshore areas (Yu et al., 2023). The historical flux of NPs has also consistently increased in both intertidal and coastal areas of the Bohai Sea, indicating that the influx of NPs continues to increase in China. Although historical data suggested a gradual decrease in NP influx, recent evidence remains insufficient to fully assess current fluxes to Bohai Sea, highlighting the need for continued monitoring.

The distribution of PCBs between intertidal and offshore areas varies regionally, with differences in the composition of PCB congeners

Table 1
Comparison of the historical distribution of PCBs and NPs in core sediment collected from Bohai, Yellow, East China, and South China Seas.

Regions	Year (dated)	PCBs (ng g^{-1} dw) Min.–Max. (mean)	NPs (ng g^{-1} dw) Min.–Max. (mean)	References
Masan Bay	1940s–1990s	0.30–46.8 (11.2)		Hong et al. (2003)
Haizhou Bay[a]	1950s–2010s	1.30–9.90 (4.36)		Zhang et al. (2014)
Yangtze River Estuary	1920s–2000s	0.04–0.77 (0.20)		Duan et al. (2013)
Coast of Hongkong	1900s–2000s	0.03–6.20 (2.09)		Wei et al. (2008)
Yellow River Estuary	1920s–2000s	0.10–14.7 (7.68)		Yang et al. (2012)
Pearl River Estuary	1990s–1990s	0.10–32.0 (11.4)		Mai et al. (2005)
Inner shelf of ECS	1950s–1990s	0.17–1.21 (0.49)		Wu et al. (2019)
Bohai Sea (offshore)	1950s–2010s	0.28–2.15 (0.76)		
Yellow Sea (offshore)	1900s–2000s	0.11–0.92 (0.53)		
East China Sea (offshore)	1950s–1990s	0.06–0.71 (0.36)		
Yellow Sea (offshore)	1920s–1990s	0.04–0.18 (0.09)		Zhang et al. (2009)
Korea Strait (offshore)	1910s–2010s	0.05–1.01 (0.44)		Guerra et al. (2019)
Pearl River Estuary	1960s–2010s		2.80–48.3 (17.7)	Chen et al. (2019)
Bohai Bay	1940s–1990s		0.11–9.50 (2.93)	Jin et al. (2008)
Yangtze River Estuary	1970s–2000s		0.80–25.0 (6.52)	Bian et al. (2010)
Pearl River Estuary	1950s–2000s		1.50–700 (216)	Peng et al. (2007)
Masan Bay	1950s–2000s		0.30–109 (21.6)	Moon et al. (2009)
Lake Shihwa	1980s–2000s		6.00–540 (141)	Hong and Shin (2009)
West Coast of Korea[a]	2010s		1.20–66.0 (19.9)	Jeon et al. (2017); Kim et al. (2020)
Bohai bay (TJ6)[a]	1980s–2010s	0.66–2.70 (1.34)	1.31–9.27 (3.29)	This study
Korea Bay (DD2)[a]	1990s–2010s	1.38–4.44 (2.65)	1.30–3.43 (2.13)	
Yancheng Coast (YC2)[a]	1950s–2010s	0.80–0.86 (0.83)	1.12–1.51 (1.28)	
Asan bay (SG2)[a]	1950s–2000s	0.42–1.93 (0.89)	2.11–2.97 (2.51)	

[a] Samples were collected from tidal flats.

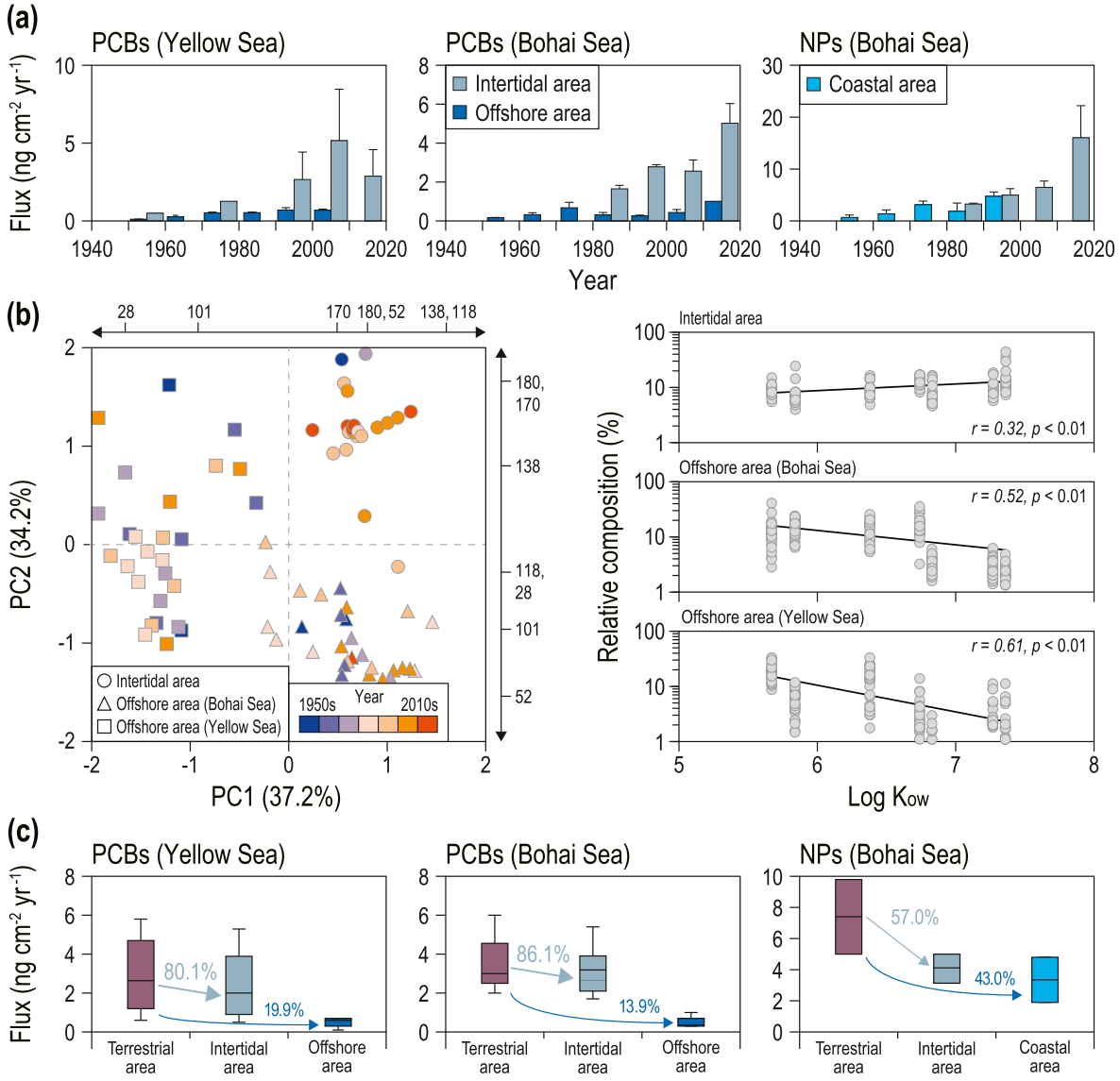


Fig. 5. (a) Deposition flux of PCBs and NPs in the Yellow and Bohai Seas. (b) PCA results for the distributions of PCBs and relative composition according to log K_{ow} in the intertidal zone and offshore areas. (c) deposition flux of PCBs and NPs from terrestrial to offshore areas in the Yellow and Bohai Seas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regardless of the period (Fig. 5b). PCA results indicate that HCl-CBs dominate in intertidal areas, while LCl-CBs are more prevalent offshore in the Yellow and Bohai Seas, with notable differences in the dominant congener. HCl-CBs tend to deposit in the intertidal zone due to their strong adsorption to particles, driven by their high log K_{OA} values (Thibodeaux et al., 1993). On the other hand, LCl-CBs, being more volatile, are more likely to be transported through the atmosphere (Anderson and Hites, 1996), a trend also observed in offshore areas of the Yellow Sea (Kim et al., 2024). Tri-CBs and di-CBs are the most common in the Bohai Sea and Yellow Sea, respectively, indicating that less chlorinated congeners tend to migrate further offshore. The relative composition of PCBs in intertidal and offshore areas is influenced by the log K_{OW} values of PCBs, with more pronounced effects observed further offshore ($P < 0.01$). In addition, the congener patterns of PCBs in offshore areas are likely affected by atmospheric reactions with hydroxyl radicals during long-range transport (Mulder et al., 2015).

If PCBs and NPs were transported solely through the water column from terrestrial to offshore areas, a substantial amount would accumulate in the intertidal zone (Fig. 5c). The intertidal zone plays a crucial role in reducing pollutant flux, with a 57.0% reduction in flux into coastal areas and approximately 83.1% into offshore areas. These findings are consistent with flux reductions observed for PAHs in the Bohai and Yellow Seas in a previous study (Yoon et al., 2023). However, since this analysis excludes atmospheric inputs, which are a significant source of offshore PCB contamination, the rate of decline in the intertidal zone is likely underestimated, particularly for highly volatile compounds such as LCl-CBs. In offshore areas of the Yellow and Bohai Seas, atmospheric inputs account for 56.6% to 62.9% of total PCB inflows (Yu et al., 2023). Considering atmospheric contributions, the reduction of PCBs in the intertidal zone may increase by approximately 10%. Given the incomplete understanding of contaminant flux and transport mechanisms within the intertidal zone, future studies should quantitatively evaluate its role as a pollutant buffer.

4. Conclusions

This study comprehensively assessed the historical trends, fluxes, and transport mechanisms of PCBs and APs across the LME scale in the Yellow and Bohai Seas. The findings reveal contrasting national trends: while AP concentrations have declined in both countries, and PCB levels

Table 2
Comparison of the deposition flux of PCBs and NPs in core sediment reported from Bohai and Yellow seas in Korea and China.

Region	Year (dated)	PCBs (ng cm^{-2} y^{-1}) Min.–Max. (mean)	NPs (ng cm^{-2} y^{-1}) Min.–Max. (mean)	References
Inner shelf of ECS	1950s–1990s	0.20–1.13 (0.45)		Wu et al. (2019)
Bohai Sea (offshore)	1950s–2010s	0.16–1.07 (0.38)		
Yellow Sea (offshore)	1900s–2000s	0.11–0.87 (0.50)		
East China Sea (offshore)	1950s–1990s	0.04–0.15 (0.08)		
Bohai Bay	1940s–1990s		0.09–5.76 (2.27)	Jin et al. (2008)
Bohai bay (TJ6)[a]	1980s–2010s	1.53–6.43 (3.10)	3.07–23.2 (7.68)	This study
Korea Bay (DD2)[a]	1990s–2010s	2.52–8.33 (5.02)	2.47–6.44 (4.05)	
Yancheng Coast (YC2)[a]	1950s–2010s	0.60–0.64 (0.62)	0.91–1.12 (1.01)	
Asan bay (SG2)[a]	1950s–2000s	0.50–1.31 (0.79)	1.10–1.63 (1.40)	

[a] Samples were collected from tidal flats.

have continued to rise in China. These differences highlight the variable effectiveness of environmental regulations in the two nations and suggest that PCB sources in China are not yet adequately controlled. The study also underscores the increasing fluxes of these pollutants into intertidal and offshore areas, with the intertidal zone functioning as a critical buffer that limits pollutant transfer to offshore waters. However, the absence of independent chronological markers represents a limitation in validating the sediment age model. The quantitative attribution of historical PCB sources also remains uncertain, and limited data from the intertidal zone constrains evaluations of decomposition processes and transport dynamics. The historical records of PCBs and APs presented here provide a scientific basis for evaluating current regulatory outcomes and identifying policy gaps. Overall, our findings offer essential baseline information for developing targeted environmental management strategies and enhancing regulatory frameworks to address persistent contaminants in the marine environment.

CRediT authorship contribution statement

Seo Joon Yoon: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Junghyun Lee:** Visualization, Investigation, Formal analysis. **Youngnam Kim:** Formal analysis, Data curation. **Bong-Oh Kwon:** Project administration, Investigation. **Wenyou Hu:** Project administration, Investigation, Funding acquisition. **Tieyu Wang:** Project administration, Investigation, Funding acquisition. **Seongjin Hong:** Writing – review & editing, Visualization, Supervision, Conceptualization. **Jong Seong Khim:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2025.118043.

Data availability

Data will be made available on request.

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<Supplementary Materials>

Historical trends of polychlorinated biphenyls and alkylphenols recorded in core sediments from the intertidal areas of the Yellow Sea and Bohai Sea

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Supplementary Tables

Table S1. Target compounds, abbreviations, target ions in the instrumental analysis, method detection limits, and recovery of surrogate standards.

Target compounds	Abbreviations	Target ions (m/z)		Method detection limit (ng g^{-1} dw)
		Quantification ion	Confirmation ion	
Polychlorinated biphenyls (PCBs)				
2,4'-Dichlorobiphenyl	CB8	222	224	0.23
2,4,4'-Trichlorobiphenyl	CB28	256	258	0.34
3,4,4'-Trichlorobiphenyl	CB37	256	258	0.17
2,2',3,5'-Tetrachlorobiphenyl	CB44	292	290	0.25
2,2',4,5'-Tetrachlorobiphenyl	CB49	292	290	0.22
2,2',5,5'-Tetrachlorobiphenyl	CB52	292	290	0.16
2,3,4,4'-Tetrachlorobiphenyl	CB60	292	290	0.29
2,3',4,4'-Tetrachlorobiphenyl	CB66	292	290	0.30
2,3',4',5-Tetrachlorobiphenyl	CB70	292	290	0.12
2,4,4',5-Tetrachlorobiphenyl	CB74	292	290	0.16
3,3',4,4'-Tetrachlorobiphenyl	CB77	326	256	0.14
2,2',3,3',4-Pentachlorobiphenyl	CB82	338	340	0.30
2,2',3,4,5'-Pentachlorobiphenyl	CB87	292	290	0.21
2,2',4,4',5-Pentachlorobiphenyl	CB99	326	328	0.18
2,2',4,5,5'-Pentachlorobiphenyl	CB101	326	324	0.20
2,3,3',4,4'-Pentachlorobiphenyl	CB105	326	324	0.16
2,3,4,4',5-Pentachlorobiphenyl	CB114	326	328	0.19
2,3',4,4',5-Pentachlorobiphenyl	CB118	326	328	0.35
3,3',4,4',5-Pentachlorobiphenyl	CB126	360	362	0.25
2,2',3,3',4,4'-Hexachlorobiphenyl	CB128	440	442	0.23
2,2',3,4,4',5'-Hexachlorobiphenyl	CB138	360	362	0.15
2,2',4,4',5,5'-Hexachlorobiphenyl	CB153	360	362	0.17
2,3,3',4,4',5-Hexachlorobiphenyl	CB156	360	362	0.22
2,3,3',4,4',6-Hexachlorobiphenyl	CB158	326	328	0.32
2,3,4,4',5,6-Hexachlorobiphenyl	CB166	394	396	0.17
3,3',4,4',5,5'-Hexachlorobiphenyl	CB169	360	362	0.27
2,2',3,3',4,4',5-Heptachlorobiphenyl	CB170	394	396	0.25
2,2',3,4,4',5,5'-Heptachlorobiphenyl	CB180	394	396	0.3
2,2',3,4,4',5',6-Heptachlorobiphenyl	CB183	360	362	0.17
2,2',3,4',5,5',6-Heptachlorobiphenyl	CB187	394	396	0.20
Alkylphenols (APs)				
4-*tert*-Octylphenol	OP	207	221	0.08
4-*tert*-Octylphenol monoethoxylate	OP1EO	251	265	0.09
4-*tert*-Octylphenol diethoxylate	OP2EO	295	309	0.09
Nonylphenols	NPs	207	221	0.89
Nonylphenol monoethoxylates	NP1EOs	251	265	0.45
Nonylphenol diethoxylates	NP2EOs	295	309	0.88
Surrogate standards		**Quantification ion**	**Confirmation ion**	**Surrogate recovery (%, mean ± SD)**
Polychlorinated biphenyls (PCBs)				
^{13}C-labeled CB 28		268	270	105 ± 8
^{13}C-labeled CB 52		304	302	98 ± 7
^{13}C-labeled CB 101		326	328	104 ± 7
^{13}C-labeled CB 153		372	374	110 ± 8
^{13}C-labeled CB 138		360	362	111 ± 7

^{13}C-labeled CB 180		406	408	112 ± 6
^{13}C-labeled CB 209		510	512	111 ± 7
Alkylphenols (APs)				
Bisphenol A-d16	BPA-d16	368	386	75 ± 16

Table S2. Instrumental conditions of the gas chromatograph equipped with a mass selective detector for analyzing polychlorinated biphenyls (PCBs) and alkylphenols (APs).

GC/MSD system	**Agilent 7890B GC and 5977B MSD**
Column	DB-5MS UI (30 m long, 0.25 mm i.d., 0.25 μm film thickness)
Gas flow	1 mL/min He
Injection mode	Splitless
Injection volume	2 μL
Injector temperature	300 °C
Ionization	EI mode (70 eV)
MS temperature	180 °C
Detector temperature	230 °C
Oven temperature	60 °C (hold 1 min) →
(PCBs)	5 °C min^{-1} to 140 °C (hold 1 min) →
	30 °C min^{-1} to 200 °C (hold 1 min) →
	4 °C min^{-1} to 250 °C (hold 5 min) →
	10 °C min^{-1} to 300 °C (hold 1 min)
(APs)	60 °C (hold 5 min) →
	10 °C min^{-1} to 100 °C →
	20 °C min^{-1} to 300 °C (hold 6 min)

Supplementary Figures

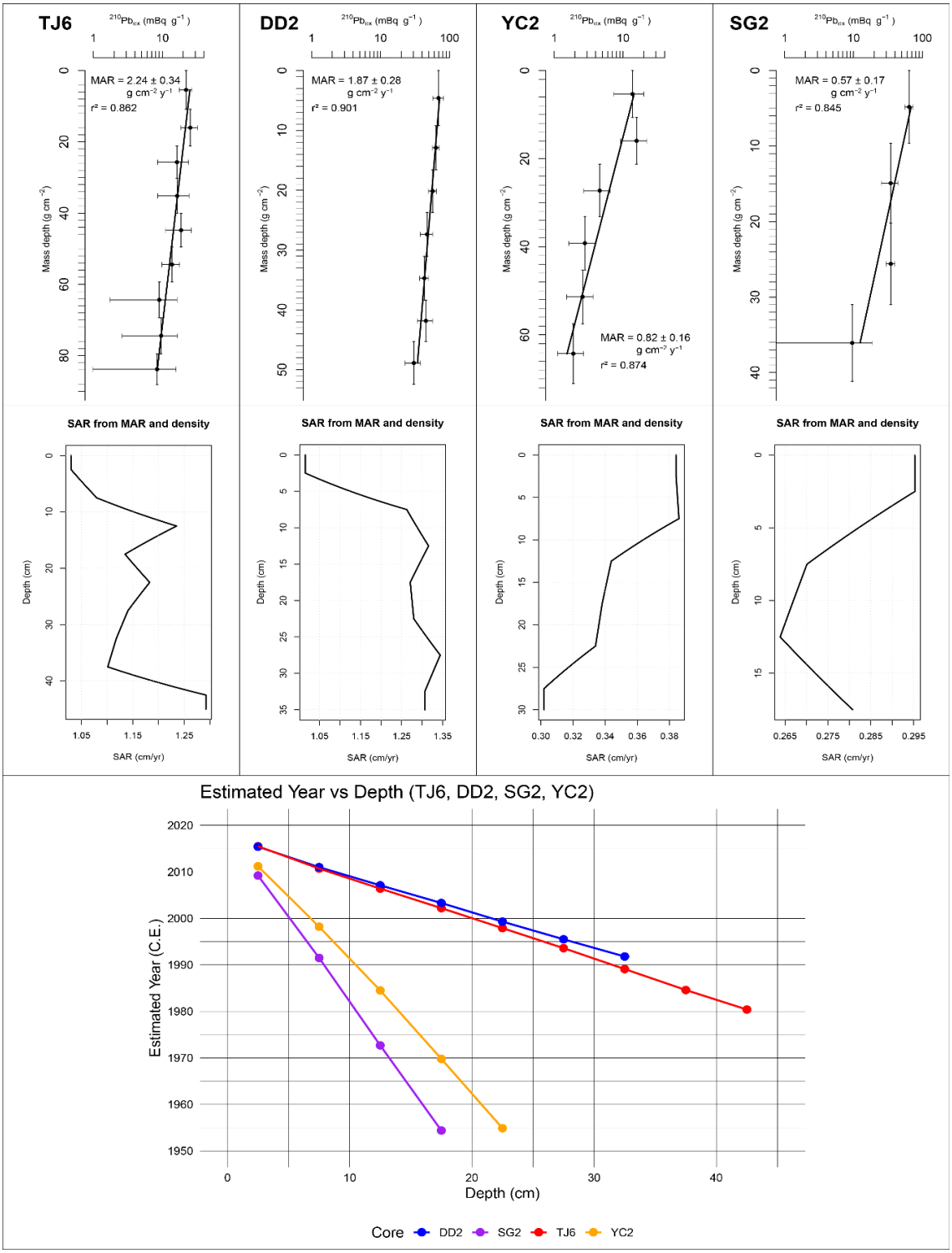

Fig. S1. Depth profiles of $^{210}Pb_{ex}$, sedimentation rate (SAR) from MAR and density, and estimated year in intertidal sediment cores of the Yellow and Bohai Seas.

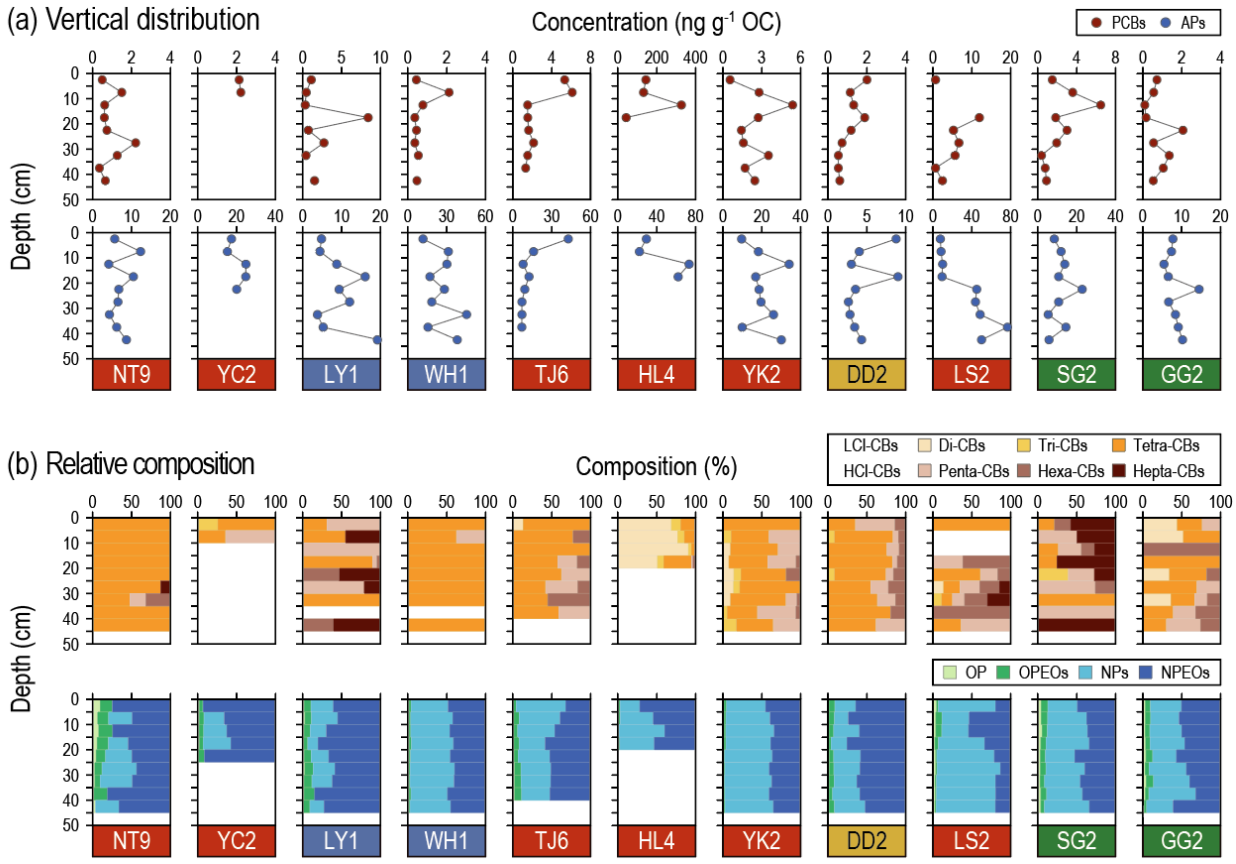

Fig. S2. (a) Vertical distribution and (b) relative composition of PCBs and APs in intertidal sediment cores collected from the Yellow and Bohai seas.

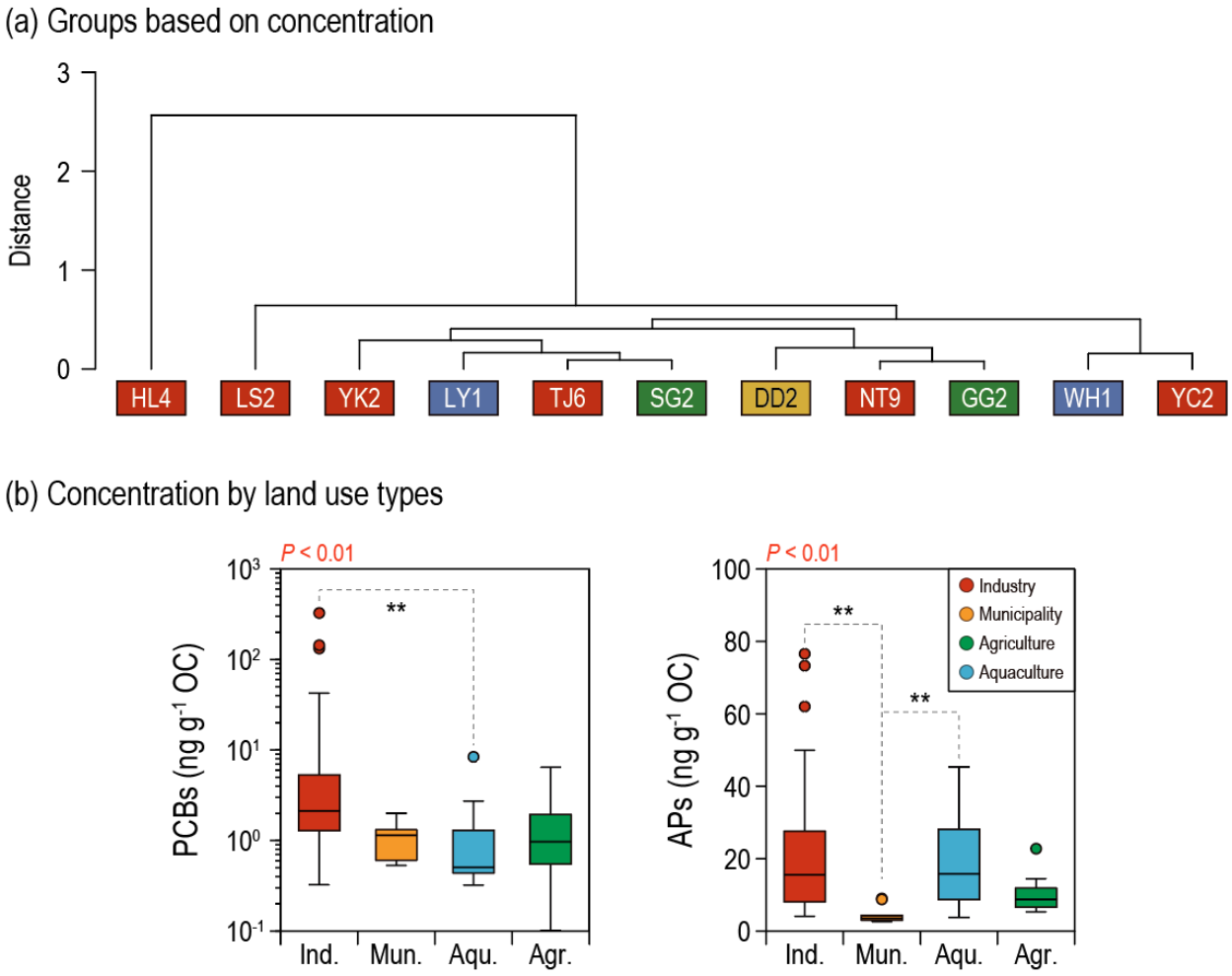

Fig. S3. Results of **(a)** cluster analysis and **(b)** box plot of PCBs and APs to land-use types.

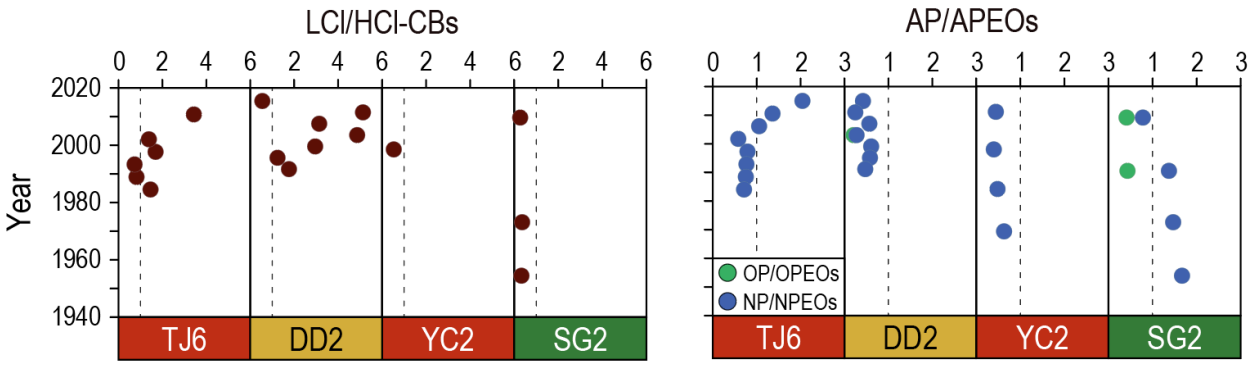

Fig. S4. Historical ratios of low-chlorinated CBs & high-chlorinated CBs and alkylphenols & alkylphenol ethoxylates.