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Historical record of polychlorinated biphenyls (PCBs) in the continental shelf of the Korea Strait

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H I G H L I G H T S

- The depositional history of PCBs was studied in the continental shelf of the Korea Strait.
- Two depositional periods were identified, before and after the mid 1980s.
- PCBs temporal trends parallel PCBs consumption in the region for the period 1956–1983.
- Unexpected increase in PCBs occurred in 1990s–2010, probably due to secondary regional emissions.
- Kanechlor 300, Kanechlor 400, Aroclor 1242 and regional steel plants seem the most probable sources.

A R T I C L E I N F O

Keywords:

Historical record

Sediment

¹³⁷Cs

Polychlorinated biphenyls (PCBs)

Source apportionment

Korea strait

A B S T R A C T

The vertical distribution of PCBs was measured in a dated core from the continental shelf of the Korea Strait. The historical trend of deposition and fluxes of individual and total PCB agreed well with the dynamics of historical tendencies of PCBs consumption in South Korea up to mid 1980 and a peak of total PCBs of 810 ng kg⁻¹ was recorded at the turn of the 1960s. A second period of deposition, when concentrations of total PCB up to 1007 ng kg⁻¹ were reached, was evidenced between 1989 and 2010 after the ban of PCBs. Sediments deposited in 1990s–2010, and sediments deposited in the period of maximum PCBs use (1956–1983) are both enriched in the less chlorinated homologue groups (tri- and tetrachlorobiphenyls) and congener PCB 118. However, the ratio of dioxin like PCBs, and dichloro- and hexachloro homologue groups disclosed compositional variations between the two time periods. Source analysis suggested that PCBs in the sediment record mainly originated from Kanechlor 300, Kanechlor 400 and Aroclor 1242 technical mixtures overlapped by secondary/unintentional combustion sources from regional steel making processes in the last decades (1990s–2010).

1. Introduction

Polychlorinated biphenyls (PCBs) are legacy pollutants targeted by the Stockholm Convention on Persistent Organic Pollutants (POPs), issued by the United Nations Environmental Programme (UNEP), that are widely distributed in the global biogeosphere. These compounds were highly employed from the 1930s to the

1970s in a wide variety of applications, including dielectric fluids in capacitors and transformers, heat transfer and hydraulic fluids, lubricating oils, and as additives in paints and surface coatings, sealants, and plastics. The ubiquitous distribution of these compounds in the biogeosphere results from a combination of their physicochemical properties and the hydrological, geophysical, and biogeochemical parameters of the environment. In the ocean, hydrophobic contaminants including PCBs are scavenged from the water column by settling organic rich particles, and a fraction eventually sinks to deep waters and sediments (Sobek and Gustafsson, 2014). Monitoring and modelling of PCBs distribution and inventories suggest that shelf sediments in the North Pacific and the Arctic, as well as in the North Atlantic represent a globally

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significant repository and permanent sink of PCBs (Armitage et al., 2013; Jonsson et al., 2003; Ma et al., 2015). The accumulation of PCBs in continental shelves is heterogeneous depending on the geographical location and dynamics of sedimentation fluxes, as well as circulation including deep water formation (Salvadó et al., 2019; Sobek and Gustafsson, 2014). After production and direct emissions of PCBs have been halted at global level, a substantial chronological decrease of PCBs has been detected in deep sea and continental shelf sediments in the Palos Verde shelf (Taylor et al., 2019), the San Francisco Bay (Venkatesan et al., 1999), the Strait of Georgia (Johannessen et al., 2008), the Yellow Sea and the East China Sea (Cai et al., 2016; Pan et al., 2012), and the Arctic Ocean (Brown et al., 2009). Conversely, an unlike decline or even an increase of PCBs levels has been observed in 21st century sedimentary records in the Gulf of Thailand and Philippines (Kwan et al., 2014), Central Vietnam (Tri et al., 2016), the Baltic Sea (Sobek et al., 2015) as well as the Arctic fjords (Pouch et al., 2017) most probably due to emissions from secondary sources. Hence, the quantification of PCBs in continental shelves is important to understand the long term behavior and sinks of PCBs once the primary sources are exhausted and the secondary sources predominate.

From 1961 to 1996, South Korea underwent a period of rapid economic development turning into a booming industrial society. Industrialization, while important for the economic growth and development of the Korean society, resulted in emissions of PCBs to air, soil, freshwater and marine waters, and environmental and health issues (Shin et al., 2011; Nguyen et al., 2016; Kim and Yoon, 2014; Kim et al., 2008). This work aims to evaluate the past and contemporary levels of PCBs in a dated sediment core from the continental shelf of the Korea Strait to reconstruct the historical trends, fluxes and potential primary and secondary sources of these contaminants over the last century.

2. Materials and methods

2.1. Study area

The Korea Strait, connected to the Yellow Sea in the west and to the East Sea (Sea of Japan) in the east, is a submerged epicontinental sea between Korea and Japan. The continental shelf adjacent to the southeastern Korean peninsula is a flat shelf area (depth < 150 m) with thick accumulation of land derived clastic sediments that can be clearly separated from the northeastern slope region which is connected to the deeper (>1000 m) East Sea. Recent sediment accumulation occurs mainly in the inner shelf region forming a typical nearshore mud belt, while most of the outer shelf and Korea Strait regions are covered with relict sands (Cho et al., 1999). The major source of terrigenous fine grained sediments are the Seomjin and Nakdong Rivers, which are dispersed along the south and southeast inner shelf of the Korean peninsula (Park et al., 1999). The ocean current system on the shelf area of the Korea Strait is dominated by the Tsushima Warm Current (TWC) flowing northeastward, whose seasonality and origin from the Taiwan Current or as a branch of Kuroshio current is still debated (Isobe, 1999; Park et al., 2013), and the Korean Coastal Current which flows northeastward along the southern coastline contributing to the dispersal of fine grained sediments supplied by rivers (Isobe, 1999; Kim et al., 2001).

2.2. Sample collection and processing

A sediment core was collected using a piston corer (Fig. 1) at 28 m depth from the continental shelf of the Korea Strait (34°21,081' N and 127°35,786' E) in July 2010 aboard the research

vessel R/V Tamgu 7. The sediment core was sectioned immediately onboard at 3 cm intervals using stainless steel plates down to 60 cm, and then every 5 cm down to the bottom of the core. All samples were wrapped in aluminum foil, and stored at 4 °C onboard immediately after sectioning. Sediments were then transported to the laboratory, where they were freeze dried and passed through a 2 mm sieve for dating and chemical analysis.

2.3. Analytical methods

Freeze dry sediment samples were extracted in a Soxhlet apparatus with 200 mL acetone and toluene (1:9, v/v) for 20 h (ultra residue analysis, J.T. Baker, Phillipsburg, NJ, USA). Concentrated extracts were spiked with ¹³C labelled surrogate internal standards for PCBs (68A LCS and 68A IS) and purified by passing through a multilayer silica gel column (Fig. S1, Supplementary Material).

The quantitation of PCBs was performed using a high resolution gas chromatograph (HP6890 Agilent Technologies, USA), and a high resolution mass spectrometer (JMS700D, JEOL, Japan). An HT8 PCB capillary column (50 m × 0.22 mm × 0.25 μm) was used for separation of the 209 PCB congeners using helium as a carrier gas (1 mL min⁻¹). The temperature of the injector was kept constant at 290 °C, while the samples were injected (1 μL) in splitless mode. The GC oven was programmed to start from 90 °C (1 min hold) to 170 °C (at 20 °C min⁻¹), then ramped to 290 °C (at 3.5 °C min⁻¹) and finally to 320 °C (at 4.5 °C min⁻¹, 4 min hold). The mass spectrometer was operated under positive EI conditions (40 eV) with a resolution of 10,000 mass to charge ratio (*m/z*). The PCBs were monitored in the selected ion monitoring mode. The concentrations of peaks were determined by isotope dilution quantification.

For the analysis of the PCB congeners, a standard solution M 1668A 1 5 0.01X (Accu Standard, USA) was used. All labelled internal standards were detected with no interferences. Solvents injected before and after the injection of standards showed negligible contamination or carryover. Procedural blanks were processed in the same way as the samples and they were less than limits of detection (LOD) of target compounds. The LOD values for sediment samples were found to be 0.04–0.08 ng kg⁻¹ for individual PCBs.

Toxic Equivalency Quotients (TEQ) concentrations for dioxin like PCBs (dl PCBs) (IUPAC numbers #77, #81, #105, #114, #118, #123, #126, #156, #157, #167, #169, and #189) were calculated using the WHO toxic equivalency factor (TEF) reevaluated in 2005 (Van den Berg et al., 2006):

$$TEQ = \sum_{i=1}^n C_i \times TEF_i$$

where TEQ is the total toxic equivalent (ng kg⁻¹), *C_i* is the residuals of PCBs in sediments (ng kg⁻¹), TEF_{*i*} is the toxic equivalency factor of individual dl PCBs.

The measured concentrations of PCBs are expressed on a dry weight basis. For this purpose, water content was determined by using separate subsamples (~2 g) that were dried at 105 °C to a constant weight. Porosity was subsequently calculated, assuming a mineral density of 2.6 g cm⁻³, and loss on ignition (LOI) determined using the weight difference between the ignited and non ignited (dried) samples.

2.4. Age dating

Sub samples (~40–50 g) were measured for ²¹⁰Pb, ²¹⁴Pb (a daughter isotope of ²²⁶Ra, used to compute ²¹⁰Pb excess), and ¹³⁷Cs

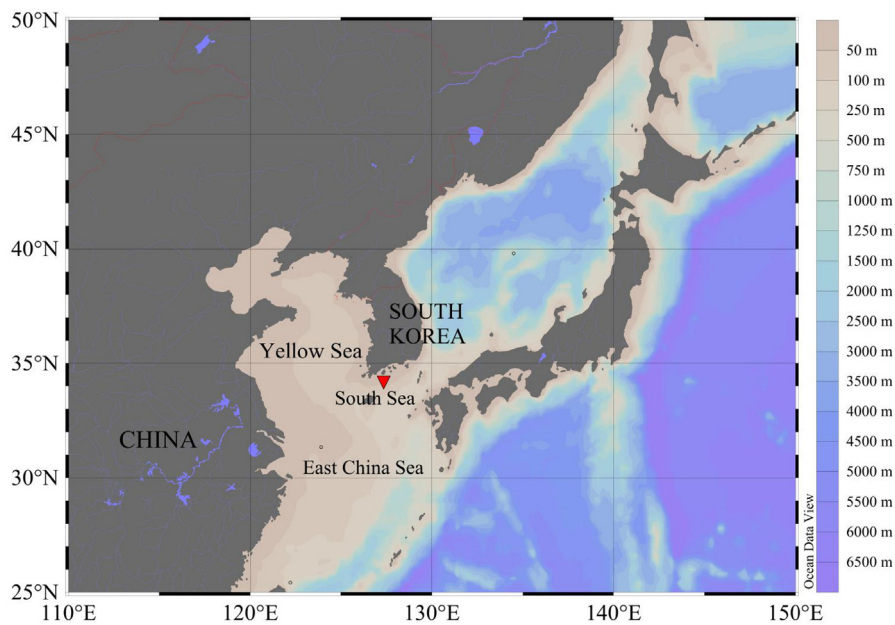


Fig. 1. Location map and bathymetry of the Korea Strait. The triangle represents the sampling station located in the continental shelf of the Korea Strait where the sediment core was taken for this study.

by γ ray spectrometry using an n type coaxial HPGe detector with a 22.6% nominal relative efficiency, and a resolution of 1.9 keV at 1.33 MeV (^{60}Co). Samples were sealed in Petri dishes and, after at least three weeks, were counted for a live time of 172800 s.

^{210}Pb chronologies were constructed using the Constant Flux (CF) dating model (Robbins, 1978), which assumes a constant flux of ^{210}Pb to the sediment, and variable accumulation rates (Sanchez Cabeza and Ruiz Fernandez, 2012); ^{210}Pb ages and accumulation rate uncertainties were estimated with Monte Carlo simulation (Sanchez cabeza and Ruiz Fernandez, 2014). Detailed information on the radiometric technique and dating method is provided in the Supplementary Material (Table S1 and Fig. S2).

Fluxes ($\text{ng cm}^{-2} \text{y}^{-1}$) were estimated as $C_i r \rho_i$, where C_i is the concentration of individual and total PCBs ($\sum \text{PCBs}$) in sediment layer i (ng g^{-1}), r is the SAR in the sediment core (cm y^{-1}) and ρ_i is the dry mass bulk density of the sediment layer i (g cm^{-3}).

2.5. Multivariate statistical analysis

The homologue and dioxin like congener ratios of PCBs in the sediment layers and in several potential sources were compared by principal component analysis (PCA), carried out using the software PRIMER 6. Discriminant analysis, carried out using the software Past 3.21, was used to contrast sediment layers grouped in time periods.

3. Results and discussion

3.1. Age dating

The investigated ~ 1 m sediment core from the continental shelf of the Korea Strait covers over a century sediment accumulation dating back 117 ± 12 years (1890s–2010) (Fig. S2, Supplementary Materials), with mass and sediment accumulation rates of $1.4 \pm 1.0 \text{ cm y}^{-1}$ and $1.3 \pm 0.3 \text{ g cm}^{-2} \text{ y}^{-1}$ (mean \pm standard deviation of all sediment layers). ^{210}Pb derived mass and sediment accumulation rates (MAR $0.2\text{--}14 \text{ g cm}^{-2} \text{ y}^{-1}$; SAR $0.2\text{--}1.8 \text{ cm y}^{-1}$) are consistent with values previously reported for along shelf

deposits in the East China Sea (Su and Huh, 2002; Liu et al., 2006), and in the Chonsu and Masan Bays (Lee et al., 2012; Moon et al., 2009), but higher than shelf deposits accumulating in the southeastern Korea Strait (Park et al., 1999), in the southwestern Sea of Japan (Hong et al., 1997), and in the Yellow and East China Seas (Lim et al., 2007).

The vertical distribution of ^{137}Cs reflects a steady deposition and accumulation of sediment overtime with a subsurface maximum, and a penetration depth of ~ 30 cm; however, no clear fallout peak could be identified in our sediment record to corroborate ^{210}Pb chronology. This tendency is frequently observed in regional seas adjacent to the Korean Peninsula (i.e. East China/Yellow Sea, East Sea/Sea of Japan), where much of the ^{137}Cs is confined in the surface or near surface layers of the sedimentary column followed by a decreasing trend with depth (Duran et al., 2004; Pettersson et al., 1999). The ^{137}Cs concentrations and total integrated inventory are low ($< 5 \text{ Bq/kg}$ and 0.05 Bq cm^{-2}) and comparable to levels detected in seabed sediments from the Asian Pacific regional seas (Duran et al., 2004; Park et al., 2004; Su and Huh, 2002) prior to the Fukushima accident, which occurred in March 2011 in Japan (Kusakabe et al., 2013). The ^{137}Cs inventory radioactivity decay corrected to 1 July 1998 ($716 \pm 143 \text{ Bq m}^{-2}$) was lower than the integrated atmospheric fallout value of 2780 Bq m^{-2} for 35° N latitude published by (UNSCEAR, 1982, 1977).

It should be pointed out that the lack of a precise chronological marker makes our time frames approximate; nevertheless, a significant positive correlation between $^{210}\text{Pb}_{\text{xs}}$ calculated at different depths and LOI content ($r 0.728$, $n 32$, $p < 0.001$) suggests that concentrations of $^{210}\text{Pb}_{\text{xs}}$ at the time of deposition was affected by organic matter content. The weight loss on ignition (LOI), used as a proxy for total organic carbon content, is given in Table S2 and Fig. S3 (Supplementary Materials). The lowest LOI values are found below 65–70 cm depth, corresponding to sediments deposited prior to the mid 1950s, then increase up to maximum values at the end of the 1970s. After the Korean War (1950–1953), the coastal zone of South Korea has experienced a wide range of engineered coastal modifications including construction of seawalls that eliminated vast tidal flats and extensive land reclamation, that altered the

transport of sediment and organic matter (Williams et al., 2014). These changes could have been associated with the supply of higher amounts of organic matter from terrigenous sediments to the continental shelf of the Korea Strait from the 1960s to the end of the 1970s. A sharp drop in LOI content was marked at 40–45 cm depth (1983 ± 1.5) concomitant with the construction of the Nak dong River estuary barrage (1983–1987), that in turn, caused water and sediment flux restricted within the lower estuary (Woo et al., 2018). This unambiguous fact is reflected by a decreasing trend of LOI in the sediment record from 1983 ± 1.5 onward (Fig. S3, Supplementary Materials). In the absence of specific chronological markers, the LOI profile in the historical record from the Korea Strait is consistent with the ^{210}Pb chronology.

3.2. Vertical profiles of polychlorinated biphenyls

The sedimentary record of individual and total PCBs compounds deposited in the continental shelf of the Korea Strait covering the time of maximum consumption and reaching back to their introduction phase is presented in Fig. 2 and Tables S2 and S3 (Supplementary Material).

The total concentrations of PCBs in the historical sediment record range from 45 to 1007 ng kg^{-1} . These results are 10–100 times lower than the measured PCBs concentrations in shelf sediments of the Baltic Sea, the Mediterranean Sea, the Aegean and Marmara Sea; however, these low levels compared well with PCBs concentrations detected in sediments from the continental shelves of North Atlantic, the Pacific, and the Arctic Oceans and deep sediments from the Asian seas (Table 1). With reference to Asian regional seas, estuarine and coastal areas of the Bohai Sea and the Yellow Sea bordering China and South Korea are more severely contaminated by PCBs than the sediments from the continental shelf of the Korea Strait (Meng et al., 2017 and references therein).

Among the individual dl PCBs, PCB 118 was found the most abundant (freq. 100%) and measured at the highest concentration ranging from 0.19 to 10.8 ng kg^{-1} ; hence, considering the sum of dl PCBs ($1.15\text{--}21.5 \text{ ng kg}^{-1}$) this compound dominated in the whole time period of the historical sediment record. The individual PCBs concentration distribution is, in decreasing order (mean \pm standard deviation of all sediment layers): PCB 118 ($3.38 \pm 2.93 \text{ ng kg}^{-1}$) > PCB 105 ($1.46 \pm 1.17 \text{ ng kg}^{-1}$, freq. 100%) > PCB 77 ($0.81 \pm 0.70 \text{ ng kg}^{-1}$, freq. 94%) > PCB 156 ($0.58 \pm 0.50 \text{ pg g}^{-1}$, freq. 97%), whereas other dl PCBs are less represented (Table S3 and Fig. 2). These predominant congeners are the most important dl PCBs found in commercial Kanechlor formulations (Takasuga et al., 2005). The WHO TEQ values calculated for individual dl PCB congeners vary from 0.001 to 0.046 ng TEQ kg^{-1} , and are approximately 10–1000 times lower than levels found in sediments from heavily industrialized bays in the southern Korean Peninsula ($0.07\text{--}5.40 \text{ ng TEQ kg}^{-1}$; Moon et al., 2008).

The depth profiles of individual and total PCBs concentrations and depositional fluxes show a very similar shape throughout the entire sediment core. ΣPCBs levels remained low below 70 cm depth ($45\text{--}117 \text{ ng kg}^{-1}$ and $0.05\text{--}0.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$, respectively), i.e. until the onset of their exponential increase (ca 1960), and peaked to $> 1000 \text{ ng kg}^{-1}$ ($1.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$) just below the surface (~ 2003).

Two points of significant change were observed in the individual and total PCBs profiles and fluxes, both occurring in the second half of the twentieth century. The first observed increase in ΣPCBs above background occurred in the late 1950s, briefly reaching $>200\text{--}810 \text{ ng kg}^{-1}$ ($0.2\text{--}0.6 \text{ ng cm}^{-2} \text{ yr}^{-1}$) in the period between the 1960s and mid 1980s, then declining by the end of 1980s (100 ng kg^{-1} and $0.1 \text{ ng cm}^{-2} \text{ yr}^{-1}$, respectively) to pre 1960s levels. The most pronounced shift in PCBs concentrations occurred at the beginning of the 1990s, when individual and total PCBs began to increase simultaneously reaching the highest levels over the last century. PCBs in recently deposited sediments (1990–2010) display concentrations and fluxes 2–3 times higher than those recorded in peak years between 1960s and 1985 ($720 \pm 200 \text{ ng kg}^{-1}$ and $1.0 \pm 0.3 \text{ ng cm}^{-2} \text{ yr}^{-1}$, and $440 \pm 200 \text{ ng kg}^{-1}$ and $0.4 \pm 0.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$, respectively).

The presence of some trace level congeners in the sediment prior to the industrial production of PCBs was detected in the sediment record. The possible causes include bioturbation, selective diffusion, or smearing during core manipulation. Highly chlorinated biphenyls in the pre 1950 layers of the sediment core were present at very low levels (Fig. 3), therefore favoring diffusive penetration as the most likely explanation.

With reference to PCBs consumption estimates for South Korea (1930–2000; Breivik et al., 2007), three periods can be distinguished (Fig. 2): (i) the initial period of PCBs use from mid 1940s to the 1960s is characterized by increasing consumption up to 60 t yr^{-1} and low PCBs fluxes in the range of $0.1\text{--}0.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$, (ii) the peak use phase from the 1960s to the 1970s shows a sharp 4 fold increase of PCBs consumption up to $\sim 300 \text{ t a}^{-1}$, which is reflected in our sedimentary record by a maximum value of $0.6 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in the early 1960s and 1970s, and (iii) the restriction period from the 1980s, which is characterized by decreasing consumption and fluxes of PCBs in the sediment record followed by a sharp increase of PCBs fluxes up to $1.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in the period 1990–2010.

Essentially, the bimodal trend of individual and total PCBs concentrations and fluxes in the sediment record results from the superposition of chronologically different maxima of PCBs. PCBs concentrations peaked in the 1970s, pointing toward the first input

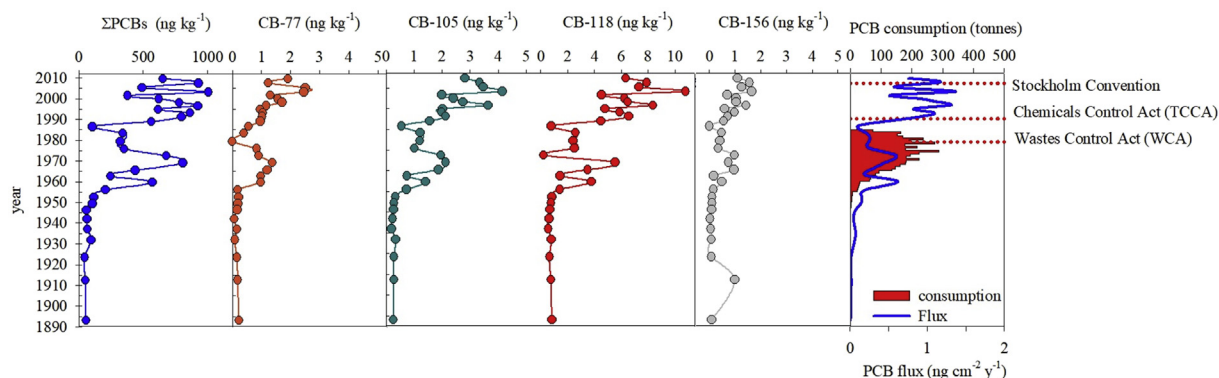


Fig. 2. PCB Individual and total PCB concentration profiles compared to the history of legal regulation for PCBs control, and temporal trends of PCBs consumption and flux in South Korea. Consumption data of PCBs from Breivik et al., 2007.

Table 1
Comparison with PCBs levels in continental shelf sediments from sea basins in the World.

Sea basin	Sampling year	range (ng g ⁻¹)	Reference
North Atlantic and European Seas	2008 2009	0.20 4.50	Robinson et al. (2017)
Barents Sea	2000	<bdl 3.54	Zaborska et al. (2011)
Baltic Sea	2010	0.710 28	(Sobek et al., 2015)
Adriatic Sea	2014	<bdl 4.3	Combi et al. (2016)
NW Mediterranean Sea	2005, 2006, 2008	1.32 37.67	Salvadó et al. (2019)
Gulf of Lion, NW Mediterranean Sea	2005 2006	1.3 38	Salvadó et al. (2013)
SE Mediterranean Sea	2004, 2009 2010	<bdl - 33	Astrahan et al. (2017)
Eastern Mediterranean Sea		0.04 1.18	Mandalakis et al. (2014) Kucuksezgin and Tolga Gonul (2012) Giuliani et al. (2017)
Easter Aegean Sea	2008	< bdl -26.07	
Marmara Sea	2005	5.4 29	
Arctic Ocean	1998 2000, 2006 2007	0.002 0.80	Brown et al. (2009)
Strait of Georgia (Pacific Ocean)	2003 2004	0.484 2.91	Johannessen et al. (2008) Venkatesan et al. (1999)
San Francisco Bay (Pacific Ocean)	1990 1992	0.8 34	
Palos Verdes Shelf (Pacific Ocean)	2007	7.01 2,600	Taylor et al. (2019)
Indian Ocean	2011	0.1204 0.5143	Cheng et al. (2015)
Bohai Sea	2012 2013	0.157 1.699	Wang et al. (2015)
Yellow Sea	2011	0.099 3.13	Duan et al. (2013)
East China Sea	2009	0.1 2.5	Cai et al. (2016)
South China Sea	2015	0 0.12	Kaiser et al. (2018)
Offshore Central Vietnam	2012	61.4 126	Tri et al. (2016)
Taiwan Strait	2009	1 8.1	Wu et al. (2016)
Gulf of Thailand	2009	0.127 2.24	Kwan et al. (2014)
Korea Strait	2010	0.045 1.01	this work

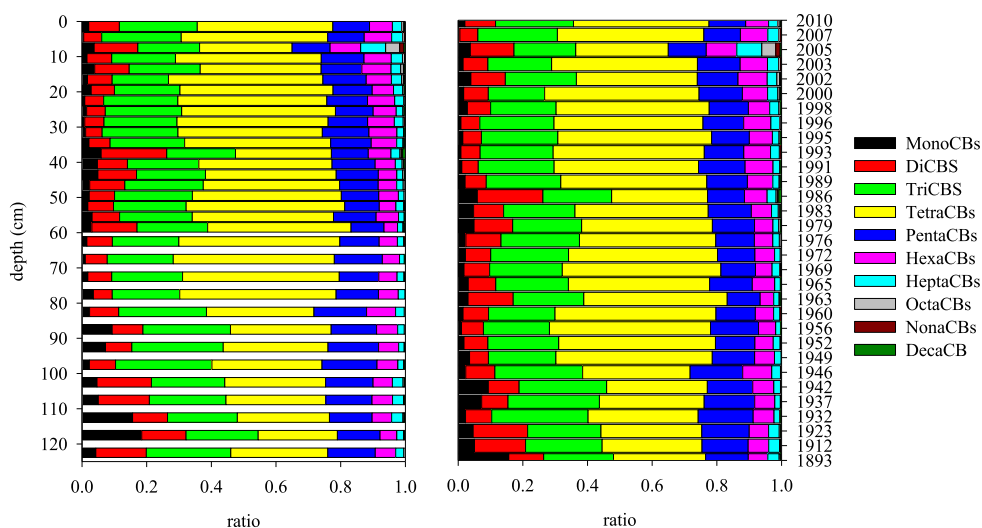


Fig. 3. Depth and year of deposition versus PCB homologue ratios in the sediment record from the continental shelf of the Korea Strait. See the different y-axis scale for each plot.

of PCBs into the continental shelf area of the Korea Strait during the maximum PCBs consumption globally and in South Korea, with a second major delayed input from the 1990s to recent years probably reflecting ongoing, secondary emissions from regional sources.

Although PCBs were never produced in South Korea, approximately 2900–6400 tons were imported from the USA and Japan between 1940s and 1980s, and had been extensively used as dielectric fluids in electrical equipment, as well as plasticizer in paints and elastic joint sealants, and as coating and paints in harbors until their import and use in electronic equipment was completely banned in 1996 (Breivik et al., 2002; Shin and Kim, 2006). Many of these applications resulted in direct emissions of these chemicals to the coastal and marine environment of the southern Korean peninsula (Hong et al., 2010; Meng et al., 2017; Moon et al., 2009, 2008; Terauchi et al., 2009). The use of electric heaters with PCBs containing dielectric fluids was banned in South Korea for the first time by the national Electric

Utility Act (EUA) in 1979, and the wastes containing PCBs have been regulated by the Chemicals Control Act (TCCA) since 1990s. Governmental actions on unintentional production of dioxin like compounds like PCBs included legal guidelines for emissions reduction from waste incinerators, industrial sources such as metal industry, cement and chemical industry, which are regulated by the “Waste Control Act” issued in 1997, and the “POPs Control Act” enacted in 2008 coinciding with the ratification of the Stockholm Convention on POPs (Kim and Yoon, 2014).

3.3. Compositional profiles of PCBs homologues and congeners

The homologue and congener ratios of PCBs in the sediment record from the continental shelf of the Korea Strait are presented in Fig. S4 and Tables S2 and S3 (Supplementary Materials). The analysis of individual PCBs and homologue profiles provides a useful insight on the potential sources of PCBs, as their physico

chemical properties, and thus their persistence in continental shelf sediments depends on their degree of chlorination (Jonsson et al., 2003). It is evident that the composition of individual PCBs in our sediment record is enriched in low chlorinated PCBs, including trichloro, tetrachloro, and pentachloro homologues (TriCBs, TetraCBs, and PentaCBs) accounting for $76 \pm 7\%$ (60–85%) of mono to deca chlorinated total mass concentration. The PCBs homologue profile is shown in Fig. 3. The homologue ratios are, in decreasing order: tetrachlorinated biphenyls (0.40 ± 0.08) > trichlorinated biphenyls (0.23 ± 0.03) > pentachlorinated biphenyls (0.13 ± 0.02) > dichlorinated biphenyls (0.10 ± 0.04). The predominant homologue groups remain fairly constant with depth, with higher chlorinated biphenyls less represented (i.e. hexachloro and octachlorinated biphenyls, 0.07 ± 0.01 , 0.03 ± 0.01 and 0.005 ± 0.007 , respectively). With reference to individual PCBs (Fig. S4b, Supplementary Materials), the predominant dioxin like congener is PCB 118 accounting for $0.09 \pm 0.03\%$ of the total PCBs present in the entire sediment record from the continental shelf of the Korea Strait, followed by PCB 105, PCB 77 and PCB 156 ($0.04 \pm 0.01\%$, $0.02 \pm 0.01\%$, $0.02 \pm 0.03\%$ respectively).

Principal Components Analysis (PCA) was used to compare the PCB profiles of the sediment layers and several potential sources of contamination. Four distinct analyses were carried out, based on different datasets.

The first analysis was based on the mono to deca chlorinated homologue ratios of the sediment layers corresponding to the year intervals 1956–1983 and 1989–2010, the two time periods when the highest concentrations of total PCBs ($441 \pm 204 \text{ ng kg}^{-1}$ and $719 \pm 195 \text{ ng kg}^{-1}$, respectively) were recorded in our sediment record. The second PCA was based on the ratios of the dioxin like congeners in the same sediment layers considered in the first analysis. The goal of these first two PCAs was to enlighten any difference in the PCB profiles of the two time periods when the highest concentrations of total PCBs were recorded in our sediment record.

The third and fourth PCA were respectively based on the homologue ratios and on the dioxin like congener ratios of the layers of the whole sediment record and of several potential sources of contamination. The aim of these two analyses was to identify the most probable origin of the PCBs detected in the sediment core. Generally, Kanechlor and Aroclor technical mixtures and PCB containing transformer oil (Takasuga et al., 2006), waste incineration (Ikonomou et al., 2002), steel manufacturing processes (Fang et al., 2012), and azopigments and phthalocyanine pigments production and use (Anezaki and Nakano, 2014) are considered to be the main regional sources of PCB in South Korea nowadays. Hence, the PCB homologue and congener ratios of those sources were included in the third and fourth PCA.

The results of the first PCA are shown in Fig. 4a and Table S4. The first principal component (PC1) accounted for 70.9% of total variation and was positively correlated with the ratio of tetrachlorobiphenyls. The range of the PC1 scores for the 1956–1983 time period are largely overlapped with those for the 1989–2010, however year 2005 was separated from all other years, having the lowest PC1 score and tetrachlorobiphenyl ratio (see also Fig. 3). The second principal component (PC2) accounted for 13.5% of total variation and was correlated positively with dichlorobiphenyls and negatively with hexachlorobiphenyls. The time period 1956–1983 had higher PC2 scores, corresponding to an higher ratio of dichlorobiphenyls and lower ratio of hexachlorobiphenyls, in comparison to years 1989–2010 (see also Fig. S4a) and the two time periods were clearly separated on this axis. Discriminant analysis, performed on the same data, confirmed the separation between the two time periods. The ratios of hexa, di and tetrachlorobiphenyls had the highest loadings on the discriminant axis and the two time

periods were completely separated on the axis as highlighted in the confusion matrix (Tables S5 and S6).

In the second PCA (Fig. 4b, Table S7), PC1 accounted for 82.4% of total variation and had a strong positive correlation with PCB 118. PC2 accounted for 9.0% of total variation and had a strong positive correlation with PCB 77, and a weaker correlation with PCB 105 (positive) and PCB 118 (negative). The two time periods were fairly separated on the PCA plot, even if the two groups were slightly overlapped, with higher ratios of PCB 77, PCB 105 and PCB 118 in the years 1989–2010 (0.002 ± 0.001 , 0.004 ± 0.001 , and 0.009 ± 0.002 , respectively) (Fig. S4b). Again discriminant analysis, performed on the same data, confirmed the indications of PCA: PCB 118, PCB 105 and PCB 77 had the highest loadings on the discriminant axis and the two periods were slightly overlapped, since years 1991 and 2010 would be assigned to the 1956–1983 time period, based on their scores on the discriminant axis (Tables S8 and S9).

In the third PCA (Fig. 5a, Table S10), PC1 accounted for 42.5% of total variation and had a strong positive correlation with tetrachlorobiphenyls; PC2 accounted for 21.6% of total variation and had a positive correlation with dichlorobiphenyls and a negative correlation with penta, hexa and heptachlorobiphenyls. The points representing the sediment layers were close on the PCA plot, indicating that their composition in terms of PCB homologues was similar, when compared with that of PCB technical mixtures and regional combustion sources. Still, most sediment layers deposited before 1956 formed a separate cluster and were characterized by higher ratios of dichlorobiphenyls (0.11 ± 0.04) and trichlorobiphenyls (0.25 ± 0.03) and lower ratios of tetrachlorobiphenyls (0.34 ± 0.08) in comparison to more recent deposited sediment layers. None of the potential sources included in the analysis clustered with the sediment record from the continental shelf of the Korea Strait; however, Kanechlor 300 and 400, Aroclor 1242 and 1248, atmospheric bulk depositions from the steel manufacturing complex and stack gas emissions from two waste incinerators were the closest to the cluster of the sediment layers deposited both in 1956–1983 and 1989–2010.

In the fourth PCA (Fig. 5b, Table S11), PC1 accounted for 56.8% of total variation and had a strong positive correlation with PCB 118; PC2 accounted for 21.4% of total variation and had a positive correlation with PCB 126 and PCB 77.

Several potential sources clustered with the sediment layers, notably Kanechlor 300 and 400, Aroclor 1242 and atmospheric bulk depositions from the steel manufacturing complex, which were close also in terms of homologue composition, as indicated by the third PCA.

Kanechlor 300, Kanechlor 400, and Aroclor 1242 were located near most sediment layers, suggesting that PCBs in the two time periods were mainly influenced by these three potential primary sources, and the abovementioned three commercial mixtures are mainly composed of tri and tetradichlorobiphenyls PCBs (52% and 20%, 22% and 59%, 37% and 37%, respectively; Takasuga et al., 2006).

The fact that sediments deposited between 1989 and 2010 display a higher abundance of heavier hexachlorobiphenyls in tandem with a lower abundance of lighter dichlorobiphenyls is maybe indicative of a shift in PCBs inputs into the continental shelf of the Korea Strait with respect to earlier interval years (1956–1983) (Fig. 3). However, we cannot exclude other mechanisms, based on the different properties of these two homologue-classes.

The composition of Kanechlor 300 and Aroclor 1242 technical mixtures in terms of dichlorobiphenyl ratios (0.12 and 0.18, respectively; Takasuga et al., 2006) is quite similar to that of sediments deposited in the two time periods; however, Kanechlor 400 trichlorobiphenyls ratio matches that of our sediments. Aroclor and Kanechlor technical products fingerprinting have been found in

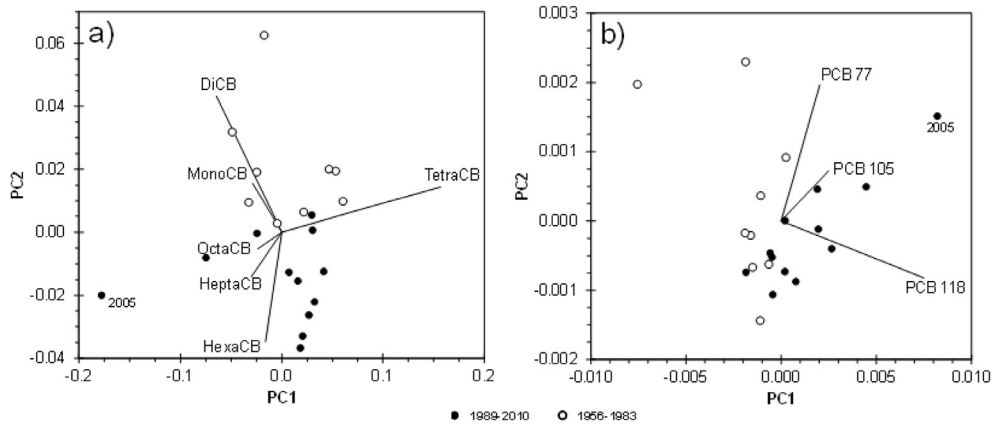


Fig. 4. Principal component analysis (PCA) score and loading plots for a) PCBs homologue ratios, and b) PCBs dioxin-like congener ratios in dated core sections from the continental shelf of the Korea Strait corresponding to the interval years 1956–1983 and 1989–2010. For clarity, variables with low loadings on both PC1 and PC2 were not represented.

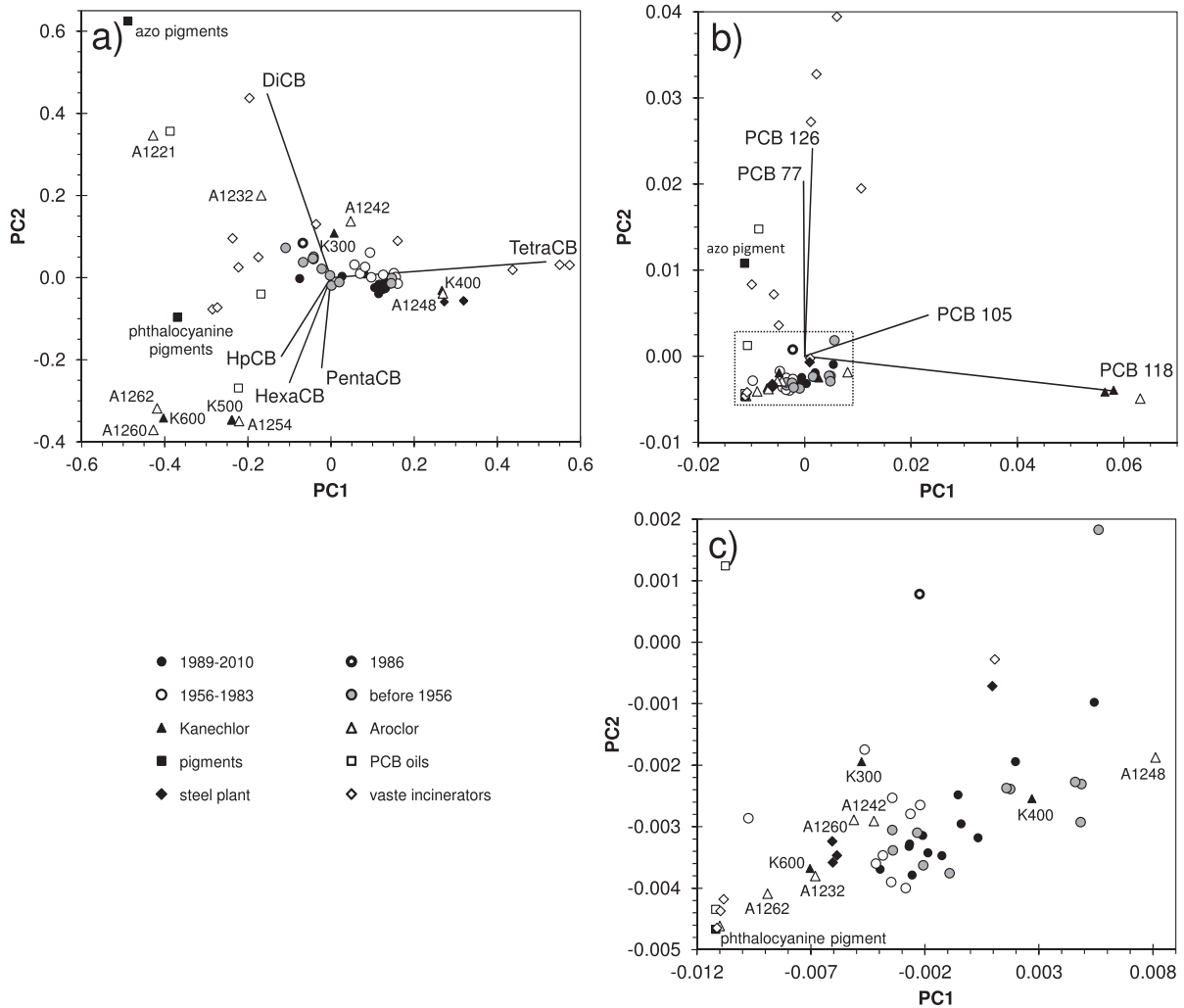


Fig. 5. Principal Components Analysis (PCA) score and loading for a) PCBs homologue ratios, b) PCBs congener ratios, c) PCBs congener ratios (enlargement of the area around the origin of the axes, within the dotted frame in panel b). Markers ratios for PCBs technical products (Aroclor and Kanechlor) and PCB-containing transformer oil are from the work of Takasuga et al. (2006); for atmospheric bulk depositions from a Korean steel complex are from Fang et al. (2012); stack gas emissions from Korean waste incinerators are from and Ikonomou et al. (2002); and azo and phthalocyanine pigments from (Anezaki and Nakano, 2014). For clarity, variables with low loadings on both PC1 and PC2 were not represented.

sediments and soils from heavily industrialized coastal areas of the Korean peninsula (Hong et al., 2005; Kim et al., 2008; Nguyen et al., 2016). This composition with a higher percentage of heavier homologues is also suggestive that the PCBs are residues of a not very recent release into the ocean or, that these PCBs have traveled long before settling down in the continental shelf of the Korea Strait. Both conditions would result in loss of the lighter PCBs in recent years (1989–2010).

Iron and steel making processes are known to be hot spots of unintentional sources of polychlorinated biphenyls (PCBs) to the environment. Among them, PCB 118 has been identified as a marker congener for atmospheric emissions from multiple industrial thermal processes including iron ore sintering (IOS) and electric arc furnace for steel making in China (Li et al., 2011; Cui et al., 2013; Liu et al., 2013).

PCB 118 was also found to be the predominant di PCBs congener in ambient air and in sediments from industrialized bays in South Korea (Moon et al., 2008; Shin and Kim, 2006).

The increasing levels of total PCBs recorded over time, the predominance of lighter tri and tetrachlorobiphenyls and PCB 118, along with a shift in di and hexachlorobiphenyls could be indicative of unintentional sources resembling regional emissions from steel manufacturing processes probably overlapping historical primary sources as Kanechlor and Aroclors in the continental shelf of the Korea Strait across the turn of the 1980s.

4. Conclusions

Our sediment core provides a well resolved historical record for individual and total PCBs accumulation in the continental shelf of the Korea Strait over the last century. The synchronized increase of concentrations and fluxes occurring around the time of the intensive PCBs consumption in South Korea suggests that our sediment record provides a picture of regional consumption trends of these contaminants. Source analysis suggests Kanechlor 300, Kanechlor 400 and Aroclor 1242 commercial products as dominant primary contributors of PCBs in the continental shelf of the Korea Strait between the mid 1950s and mid 1980s. However, unlike some sedimentary records from Europe and North America, modern sediments indicate no decline in PCBs concentrations and fluxes following the global ban on PCBs use, and restrictions on their emissions endorsed in late 1989s and 2000s in South Korea. The increased trend recorded in the last decades and the shifts in lighter and heavier homologues may reflect inputs from regional secondary PCBs sources from steel manufacturing processes. We emphasize that our findings provide a well defined record of contemporary levels and fluxes of PCBs into the continental shelf of the Korea Strait. We believe that these findings make a supplementary contribution to data sets on historical and contemporary trends of PCBs in continental shelf areas. Such data are needed in order to better assess and constrain the regional contemporary trends of these contaminants in the continental shelves of the Asian seas.

Author contributions

RG and GO designed the research. RG processed and interpreted chemical data and carried out Pb 210 date model, SR managed γ ray spectrometric measurements, and AP carried out and interpreted the multivariate statistical analysis of the results. All authors discussed the results and implications, and commented on the manuscript at all stages. RG wrote the paper with comments provided by all authors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.124438>.

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