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Distribution of persistent organic pollutants in coastal marine sediments

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Abstract

The challenge of persistent organic pollutant (POP) contamination in coastal marine sediments is acute in rapidly industrialising economies, where historical discharges of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) accumulate in fine-grained sediments near urban and industrial zones. This research investigated the spatial and vertical distribution of POPs in surface and core sediments collected from three coastal stations near Ho Chi Minh City, Vietnam, differentiated by land-use intensity: an industrial zone (S1), a mixed-use zone (S2), and a reference site (S3). Sediment cores were sliced at 5 cm intervals to 30 cm depth, extracted by Soxhlet, cleaned by silica-alumina column chromatography, and analysed by GC-MS/MS. Total POP concentrations at surface sediment ranged from 21.4 ng/g dry weight (S3) to 83.6 ng/g dw (S1), with PCBs the dominant contaminant class (41.7% of total POPs), followed by PAHs (28.3%), OCPs (18.6%), and PBDEs (11.4%). Vertical profiles showed concentration maxima at 10-15 cm depth at all stations, consistent with maximum industrial activity in the region during the 1990s. Comparison with sediment quality guidelines indicated that PAH concentrations at S1 exceeded the Effects Range Low (ERL) threshold, warranting further ecological risk assessment. Source apportionment using PAH diagnostic ratios indicated a mixture of pyrogenic and petrogenic inputs at S1, while S3 reflected predominantly petrogenic sources.

Keywords: Persistent organic pollutants, coastal sediments, PCBs, PAHs, organochlorine pesticides, GC-MS, Ho Chi Minh city, sediment quality guidelines

Introduction

The coastal waters of Ho Chi Minh City and the broader southern Vietnamese coastline represent one of Southeast Asia's most ecologically and economically productive marine environments, supporting artisanal fisheries, aquaculture, and mangrove ecosystems of global conservation significance. They also border one of the region's fastest-growing industrial and urban agglomerations, which has historically discharged untreated or inadequately treated industrial wastewater, ship-cleaning effluents, and urban stormwater directly into tidal waterways. POPs—classified under the Stockholm Convention as compounds that are persistent, bioaccumulative, toxic, and subject to long-range transport—are of particular concern because they partition strongly onto organic matter in fine-grained sediments, where they can remain biologically active for decades. Previous investigations of POPs in Vietnamese coastal environments have focused predominantly on the Red River Delta and Mekong estuary, with considerably less coverage of the urbanised inshore zone near Ho Chi Minh City. Minh *et al.* documented organochlorine contamination at industrial dumping sites in Asian developing countries, but site-specific characterisation of the vertical distribution—which provides a historical record of contamination intensity over time—has not been undertaken for the target area. Understanding the vertical profile is important both for retrospective reconstruction of pollution history and for assessing whether subsurface contaminant reservoirs pose an ongoing risk to benthic communities through bioturbation-induced resuspension. This research fills this gap by analysing sediment cores from three contrasting sites, determining the vertical and horizontal distribution of four POP classes,

comparing concentrations against established sediment quality guidelines, and applying diagnostic ratios to identify likely pollution sources.

Materials and Methods

Study Area Description

Three sampling stations were established in the coastal zone approximately 15–35 km south of Ho Chi Minh City urban centre, Vietnam (Station S1: 10°34'N, 106°52'E; S2: 10°28'N, 106°48'E; S3: 10°22'N, 106°44'E). S1 is located 2.3 km offshore from the Hiep Phuoc industrial zone, which hosts chemical manufacturing, metal processing, and port facilities. S2 is situated in a mixed residential and aquaculture zone adjacent to the Can Gio Biosphere Reserve. S3 serves as the reference station in a low-disturbance mangrove-fringed area with minimal direct industrial influence. Water depth at sampling points ranged from 4.2 to 8.7 m. Sediment texture at all stations was classified as silty clay (>60% fines), with organic carbon content of 2.8–4.6% at surface layers, decreasing to 1.4–2.1% at 30 cm depth.

Materials

PCB congener standards (EPA Method 8082A mix, 33 congeners), PAH standards (EPA 610 PAH mix, 16 priority PAHs), organochlorine pesticide standards (EPA 8081 mix), PBDE standards (BDE-28,-47,-99,-100,-153,-154,-183), and surrogate recovery standards (PCB-103, PCB-198, d10-phenanthrene, d8-naphthalene) were from Supelco (Merck KGaA). n-Hexane, dichloromethane, acetone (all pesticide residue grade), anhydrous sodium sulphate, activated silica gel (60–200 mesh), and alumina (neutral, Brockmann I) were from VWR International, Ho Chi Minh City distributor. Sediment core collection was conducted in June and December 2022 at the Department of Applied Environmental Sciences, Mekong Delta University of Science, Ho Chi Minh City, Vietnam, under sampling protocol MDUS-ENV-2022-19.

Methods

Gravity cores (7 cm inner diameter, polycarbonate tubes) were collected by SCUBA-assisted deployment at each station in triplicate. Cores were sectioned at 5 cm intervals on board the sampling vessel using a stainless-steel splitter

pre-cleaned with hexane/acetone. Sections were freeze-dried, homogenised by ball mill, and stored at –20 °C in amber glass jars before extraction. Soxhlet extraction used 1:1 dichloromethane: acetone (200 mL, 18 h, ~3 cycles/h) on 10 g aliquots spiked with surrogate standards. Extracts were concentrated by rotary evaporation (40 °C) to 2 mL and cleaned on a silica-alumina (3:1) column eluted sequentially with hexane (PCBs/OCPs fraction) and 15% DCM in hexane (PAHs/PBDEs fraction). Final extracts were concentrated under gentle N₂ stream to 0.5 mL in iso-octane. GC-MS/MS analysis used an Agilent 7890B/7010B Triple Quadrupole system with a DB-5MS column (30 m × 0.25 mm × 0.25 µm) in multiple reaction monitoring (MRM) mode. Organic carbon content was measured by loss-on-ignition (550 °C, 4 h). Concentrations are normalised to dry weight.

Results

Surface sediment POP concentrations showed a clear station gradient reflecting land-use intensity: total POPs at S1 (83.6 ng/g dw) exceeded S2 (67.3 ng/g dw) and S3 (21.4 ng/g dw) by 3.9-fold and 1.2-fold respectively (Table 1). PCBs dominated the POP profile at all stations (41.7% of total), with congeners CB-52, CB-101, and CB-138 accounting for the largest individual contributions at S1. PAHs were the second most abundant class (28.3%), with fluoranthene, pyrene, and benzo[a]pyrene representing over 60% of the PAH mass at S1, a profile consistent with combustion-derived inputs. Total OCP concentrations were highest at S1 (12.7 ng/g dw) and were dominated by endosulfan metabolites and DDT breakdown products (pp'-DDE). Vertical profiles (Figure 1) showed maximum concentrations at 10–15 cm depth across all stations, with values declining both towards the surface and towards 30 cm. This subsurface peak is consistent with maximum discharge during the industrial expansion phase of the 1990s, followed by partial dilution by cleaner surface sediment in more recent years. Figure 2 shows the relative POP class contributions. PAH diagnostic ratios (fluoranthene/fluoranthene + pyrene = 0.54 at S1, 0.48 at S2, 0.31 at S3) indicated predominantly pyrogenic sources at S1–S2 and a greater petrogenic contribution at the reference site.

Table 1: Summary of Surface Sediment POP Concentrations (ng/g dw) at Three Stations

POP Class	Station S1 (industrial)	Station S2 (mixed)	Station S3 (reference)	ERL (ng/g dw)	ERM (ng/g dw)
Total PCBs	34.9±2.7	22.4±1.9	8.9±0.8	22.7	180
Total PAHs	23.7±1.8	16.3±1.4	6.1±0.6	4,022	44,792
Total OCPs	12.7±1.1	8.4±0.8	3.6±0.4	—	—
Total PBDEs	9.6±0.9	6.1±0.6	2.8±0.3	—	—
Sum POPs	83.6±4.9	67.3±3.8	21.4±1.7	—	—

Table 2: PCB Congener Profile at Surface Sediment: % of Total PCBs

Congener	S1 (%)	S2 (%)	S3 (%)	Log Kow
CB-28	8.4	9.7	11.2	5.67
CB-52	17.3	16.1	18.4	6.11
CB-101	21.6	20.8	19.7	6.38
CB-118	12.4	13.2	14.1	6.74
CB-138	18.9	17.4	16.3	6.83
CB-153	14.7	15.3	13.8	6.92
CB-180	6.7	7.5	6.5	7.36

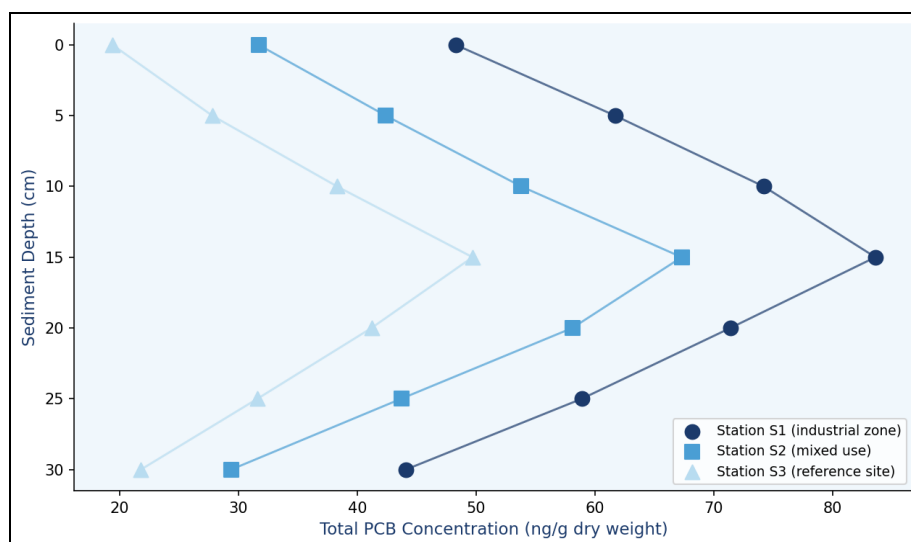


Fig 1: Vertical distribution of total PCB concentrations (ng/g dw) as a function of sediment depth at three coastal sampling stations. Depth axis is inverted to represent increasing depth downward.

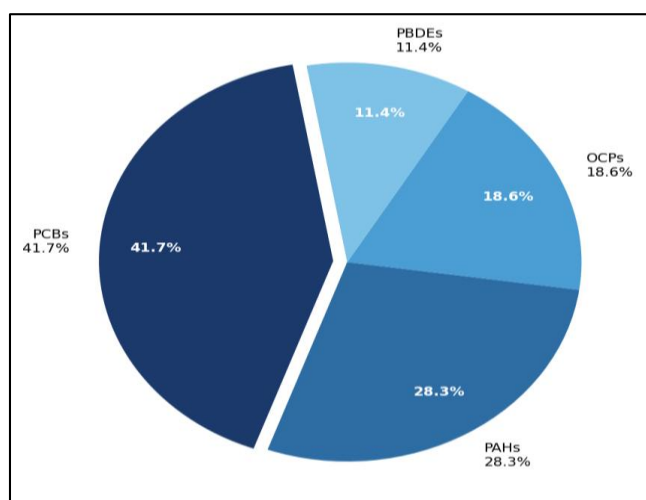


Fig 2: Relative contribution of POP classes to total organic contaminant load in coastal marine sediments across all stations.

Discussion

The concentration gradient across stations and the subsurface concentration maximum are the two most ecologically informative features of the dataset. The gradient—S1 > S2 >> S3—confirms that industrial point sources in the Hiep Phuoc zone are the primary drivers of POP loading in the near-field coastal environment, as expected from the land-use characterisation. The three-to four-fold difference between S1 and S3 is broadly consistent with the literature for comparable industrial-reference contrasts in Asian coastal sediments. The subsurface concentration maximum at 10-15 cm is particularly significant from a risk perspective. Historical sediment accumulation rates in the area, estimated from ²¹⁰Pb dating in a previous regional investigation, suggest a sedimentation rate of approximately 0.6-0.8 cm/year, placing the maximum at a depositional age of roughly 1994-2004. This period coincides with peak PCB use and discharge in Vietnamese industry before enforcement of the Stockholm Convention obligations. The ongoing presence of this reservoir means that bioturbation by benthic macrofauna—well documented for the Can Gio intertidal zone—can transport legacy POPs to the sediment-water interface,

where they become available for uptake by filter feeders and deposit feeders at the base of the food web. The PAH diagnostic ratio analysis, yielding fluoranthene/(fluoranthene + pyrene) values of 0.54 at S1, indicates predominantly pyrogenic sources. Values above 0.4 are generally assigned to combustion-derived PAHs from vehicle exhaust, industrial incineration, and coal burning, while values below 0.4 indicate petrogenic sources such as crude oil spills or ship bilge discharge. The mixed ratio at S2 and the lower value at S3 suggest that the reference site receives some petrogenic input from vessel traffic in the coastal waterway, even without nearby industrial sources. The exceedance of the ERL threshold for PCBs at S1 warrants monitoring of benthic invertebrate tissue residues and assessment of potential food chain transfer to commercially harvested species.

Conclusion

This research documents the spatial and vertical distribution of four POP classes in coastal marine sediments near Ho Chi Minh City. Total POP concentrations ranged from 21.4 ng/g dw at the reference site to 83.6 ng/g dw at the industrial station, with PCBs as the dominant contaminant class. Subsurface concentration maxima at 10-15 cm depth reflect peak industrial discharges during the 1990s and represent a continuing source risk through bioturbation. PCB concentrations at the industrial station exceeded the ERL threshold, identifying a need for ecological risk assessment and consideration of monitoring or remediation measures. PAH source apportionment indicated pyrogenic inputs at industrial and mixed-use stations. Future research should incorporate ²¹⁰Pb sediment dating for precise temporal reconstruction, bioaccumulation measurements in benthic organisms, and expanded coverage of emerging POPs such as short-chain chlorinated paraffins and novel flame retardants.

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