Persistent Organic Pollutants in Core Sediments of Indian Sundarban Mangrove Wetland (a UNESCO World Heritage Site)

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Introduction

Persistent organic pollutants (POPs) are xenobiotic lipophilic, bioaccumulative, toxic and highly volatile trans-boundary pollutants, thus acknowledged as a global problem. The paper critically examines the distribution, composition and relative pollution levels of five classes of persistent organic pollutants (POPs) in core sediment samples (<63 μm particle size) in Indian Sundarban mangrove Wetland, north-eastern part of the Bay of Bengal. This environment suffers from environmental degradation due to rapid human settlement, tourism and port activities, and operation of excessive number of mechanized boats, deforestation and increasing agricultural and aquaculture practices. The ongoing degradation is also related to huge siltation, flooding, storm runoff, atmospheric deposition and other stresses resulting changes in water quality, depletion of fishery resources, choking of river mouth and inlets, and overall loss of biodiversity as evident in recent years.

Materials and methods

Cores of 30 cm length were collected using PVC cores (length 40 cm; diameter 5 cm) by gently pushing into the sediment from 7 sampling stations covering eastern and western sides of Sundarban, belonging to distinctive geographic, geomorphic and sedimentological settings with variations of energy domains characterized by wave-tide climate. Core samples were dug out, capped and then frozen on return to the laboratory. Each core was sliced into 4 cm fractions (sub-samples) with a PVC spatula from top (0–4 cm) to bottom layers (20–24 or 24–28 cm) and dried in a ventilated oven at 40^0C. Dried subsamples were then pulverized using an agate mortar and pestle, sieved through 63 μm metallic mesh and individually transferred into pre-cleaned, inert polypropylene bags and stored at -20 ^{0} C until subsequent extraction and chemical analyses. Organic carbon (C_{org}) content of the sediments was determined following a rapid titration method [1] and pH was determined with the help of an ORP meter (model no.HI 98160). Statistical computation of textural parameters was done by using formulae of [2]. An aliquot of sample was injected into a gaschromatograph Trace GC 2000 (Thermo Electron, Austin, TX, USA) equipped with a PTV injector and coupled with a PolarisQ Ion Trap mass spectrometer, using an AS 2000 autosampler (Thermo Electron). A procedural blank was run in parallel with every batch of 4 samples to maintain quality assurance and quality control.

Results and discussion

The pooled mean values of the mass fraction of $\sum_4$HCHs and $\sum_6$DDTs in the sediments were 0.05–12, and 0.05–11.50 ng g^{-1} dry weight, respectively. The vertical distribution of pesticides reveals an erratic pattern. The concentration of four isomers of HCHs reveals a heterogenic distribution where γ-HCH (lindane) and β-HCH shared

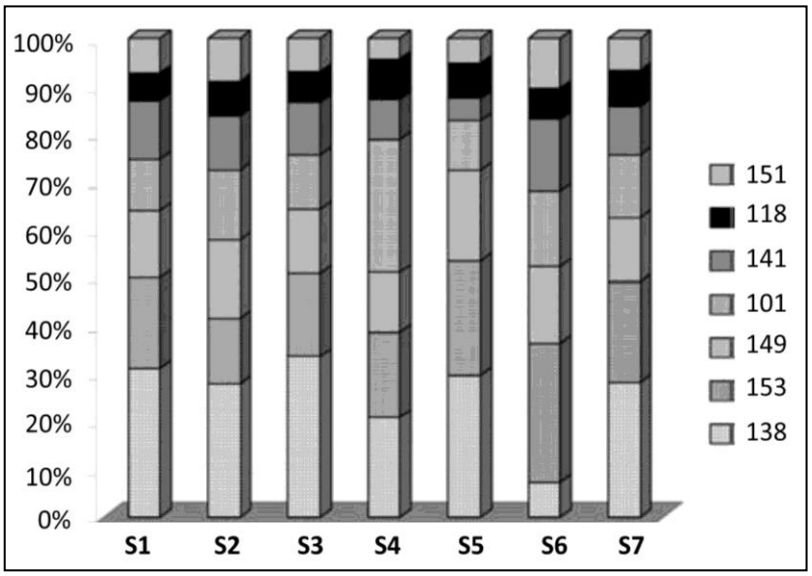
the dominant part. An overall dominance of β-HCH was recorded, which might be explained by the lower vapour pressure and less degradable property of this isomer compared to other HCHs [3]. The transformation of α- and γ-HCH to β-HCH may be the reason for the predominance of β -HCH in sediments [4, 5]**.** The relatively low percentage composition of **α**-HCH in this study is because this congener has a high vapour pressure and Henry's law constant and therefore is readily lost. In this study the ratio of **α**- to **γ** -isomers (**α**/**γ** ratio) ranged from 0.43 to 1.21 (pooled mean values of cores), well below these in the technical mixture (i.e., 4–7). The low a/c ratio in the sediment samples might be due to sources of purified lindane in the area. Generally, a ratio of ≤0.33 is considered an aged mixture, while a relatively high pp'DDT/pp'DDE ratio implies a recent input [6]**.** The observed ratios (0.41–2.70) were well above 0.33 for all the stations, indicating recent pp' DDT influxes in this coastal environment. DDT is still used to eradicate contagious disease (such as malaria and dengue) in tropical countries and is then globally redistributed throughout the atmosphere [7]. Results of correlation matrix reveal positive correlations between ∑DDTs and clay (r=0.75, p=0.05) and silt (r=0.69, p=0.05) and also between ∑HCHs and clay (r=0.66, p=0.01) and silt (r=0.65, p=0.05). Again, positive correlations between ∑HCHs and ∑DDTs suggest similar sources of these two xenobiotics, and similar environmental behavior [8]. The presence of HCH isomers and DDT metabolites can be attributed to the use of these pesticides in agricultural and anti-malaria sanitary activities, used throughout the country due to their cost benefits, bioefficacy potential, and popularity among the farmers. The authors observed the unique phytoremediation efficiency of selective mangrove plants, namely *Avicennia officinalis*, *Avicennia alba* and *Ceriops decandra* inhabiting in Sundarban regions for absorption, accumulation and translocation of DDT metabolites by adopting intricate cohesive mechanisms.

The total concentrations of $\sum_{16}$ PAHs ranged from 132 to 2938 ng g^{-1}, with a mean of 634 ng g^{-1}, and the sum of 10 out of 16 priority PAHs ($\sum_{10}$PAH) varied from 123 to 2441 ng g^{-1}, with a mean of 555 ng g^{-1}, and the 5 carcinogenic PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno [1,2,3-cd]pyrene, and dibenz[a,h]anthracene) accounted for 68–73% of the priority PAHs. Maximum concentrations of the sediment core were obtained at subsoil depth of 12–16 cm. The prevalence of four to six aromatic ring PAHs and cross-plots of specific isomer ratios such as phenanthrene/anthracene, fluoranthene/pyrene,and methyl phenanthrenes/phenanthrene suggested the predominance of wood and coal combustion sources, the atmospheric deposition, and surface runoff to be the major transport pathways. A good correlation existed between the benzo[a]pyrene level and the total PAH concentrations, making this compound a potential molecular marker for PAH pollution and is sufficient for derivation of a carcinogenic potency factor. The toxic equivalency factor (TEQS carc) was used to quantify the carcinogenicity of other PAH relative to benzo[a]pyrene and to estimate benzo[a]pyrene – equivalent doses (BaPeq.dose). Total TEQS carc values calculated for samples values calculated for samples varied from 6.95 ng g^{-1} TEQS carc to 119 ng g^{-1} TEQS carc, with an average of 59 ng/g dry weight TEQS carc. These values were lower than those of other literature-reported sites, such as surface sediments of Imo River, Nigeria [9,10,11]. No uniform temporal trend on DDT, HCH, PAH, PCB and PBDE levels was recorded due to particular hydrological characteristics of the wetland and/or non-homologous inputs from point sources (untreated municipal wastewater and local industries, electronic wastes from the dump sites, etc.) of these compounds. Peak concentrations of HCH isomers and DDT metabolites as well as PCB levels have exceeded in few cases the lower limit of sediment quality guidelines of Environmental Protection Agency and Canadian Council of Ministers of the Environment, inducing ecotoxicological impact as per the sediment quality guidelines. Accumulation of PAHs in individual organs of the benthic bivalve mollusks (*Meretrix meretrix, Sanguilonaria acuminata* and *Anadara granosa)* also exhibited wide differences in the individual body tissues which are mainly due to their different physiological conditions and feeding habits. The carcinogenic compounds (benzo(a)

phenanthrene, benzo(k) fluoranthene and benzo(a) anthracene) were dominant in visceral mass and gill of *S. acuminata* and hence this filter-feeder could be efficiently used as bioindicator of PAH contamination.

A non-homogenous contamination of the sediments with $\sum_{12}$ PBDE and Σ_{23}PCB values ranging from 0.08 to 29.03 ng g^{-1} and 0.50 to 26.90 ng g^{-1} dry weight respectively, reflecting moderate to low contamination closely in conformity to other Asian aquatic environments. The general order of decreasing congener contribution to the total PBDE load was: BDE 47 > 99 > 100 > 154, similar to the distribution pattern worldwide. Although tetrabromodiphenyl ether BDE 47 was found in all samples followed by hexabromodiphenyl ether BDE-154, they were not necessarily the dominant congeners. For PCB, the general decreasing order of the dominant congeners to the total load was: CB138 > 153 > 149 > 101, indicating the predominance of hexa-chlorinated congeners (Fig. 1). The spatial distribution revealed significant differences in concentration related to local urbanization with industrial and land-based sources.

Fig. 1: Profile of seven dominant PCB congeners of the seven sampling sites in Sundarban mangrove wetland



Sundarban, tectonically active and geochemically youngest river basin can be recognized as the most delicate, vulnerable and globally threatened ecosystems residing at the boundary between land and water. These are subjected to driven changes in the structure and functioning of ecosystem most susceptible to the impact of climate change. The possible means by which climate variability affects these wetland ecological processes are many and vary across a broad range of spatiotemporal scales. This tectonically active deltaic region is highly vulnerable to climate change producing alterations in temperature, precipitation, erosion and salinity. These multiple pressures can act synergistically to change ecosystem structure and function. Moreover, increases in the intensity and frequency of

storm events as well as floods linked to climate change as observed in this coastal regions could lead to severe chemical contamination to waters bodies which has also been discussed.

Because of the propensity to accumulate OCPs, especially DDT metabolites in various compartments of wildlife and human food webs in human blood [12], mother's milk [13] and blubber of the endangered gangetic dolphin [14], there is an is an urgent need for reliable monitoring for these xenobiotics present in various parts of India, so that any mass fractions exceeding environmental quality standards can be detected and appropriate action can be taken. The author strongly recommends regular monitoring on enrichment of these micropollutants considering both biotic and abiotic compartments of Sundarban for effective management of this productive and fragile environment.

References

1. Walkey A, Black TA (1934) *Soil Science*, **37** 23–38.
2. Folk RL and Ward WC (1957) Journal of Sediment Petrology, **27** 3–26.
3. Willett KL, Ulrich EM and Hites RA (1998) *Environmental Science and Technology*, **32** 2197–2207.
4. John AK, Dua M, Tuteja D, Saxena R, Saxena DM and Lal R (1998) *Biotechnology Letter*, 885–887
5. Senoo K, Wada H (1989) *Soil Plant Water*, **35** 79–87

6. Stranberg B, Van Bavel B, Bergavist PA, Broman D, Ishq R, Naf C, Pettersen H and Rappe C (1998) *Environmental Science and Technology*, **32** 1754–1759
7. Sharpe RM (1995) Nature, **375** 538–539

8. Iwata H, Tanabe S, Aramoto M, Sakai N, Nishimura A and Tatsukawa R (1994) *Marine Pollution Bulletin*, **28** 746–753
9. Oyo-Ita, Orok E. Oyo-Ita, Samuel U. Ugim, Nnaemeka N. J. Nnaji and Soumaya Elarbaoui (2016) *Polycyclic Aromatic Compounds*, 1-16

10 .Pedro P.O. Pinheiro, PO. Massone CG and Carreira, RS (2017) *Marine Pollution Bulletin*, (in press)
11. Raeisi, A, Arfaeinia,H, Seifi M, Mehdi, SS, Keshtkar, M and Dobaradaran, S (2016) *Water Science & Technology* **74** 12-17
12.. Subramaniam K, and Solomon J (2006) *Indian Journal of Clinical Biochemistry*, **21** 169-72.

13. . Someya M, Ohtake M, Kunisue T, Subramanian A, Takahashi S, Chakraborty P, Ramachandran R and Tanabe S. *Environment international*, (2010) **36** 27-35.
14. Tanabe S, Iwata H and Tatsukawa R (1993) *Science of the Total Environment*, **154** 163–177