Occurrences, distribution and sources of Pharmaceuticals and Personal Care Products (PPCPs) in the mangrove dominated estuaries in the central part of the Indian Sundarbans, a world heritage site.

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Abstract

This study aimed to provide the baseline report on the occurrence of five emerging contaminants namely Phenols, Triclosan, NSAIDs, Phthalate and Parabens under pharmaceuticals and personal care products (PPCPs) in the surface water of Indian Sundarbans estuarine system. The emerging contaminants of PPCPs were investigated from the two estuaries in the central of Indian Sundarbans namely Thakuran and Matla covering entire stretch during post monsoon season using gas chromatography mass spectrometry (GC-MS). Among the different groups of PPCPs the most abundant found to be Phenolics with mean concentration ranging from 230 to 4586 ng/L following Triclosan with mean concentration for both Thakuran and Matla ranging from 96 to 1885 ng/L. The surface water concentration of remaining PPCPs ranged widely; like for NSAIDs (290 to 791 ng/L), Phthalates (39-302 ng/L) and Parabens (21-263 ng/L). Among the different Phenolics derivatives the highest concentration was found for octyl phenol ranging 282.2 to 17590.1 ng/L followed by Ketoprofen ranging 614.6 to 2333.7 ng/L and both derivatives observed to be high in the seafront side of Matla estuary. For the Phthalates derivatives high concentration witnessed in upstream of Thakuran and Matla i.e., for Di-2-ethylhexylphthalate ranging from 60.5 to 494.8 ng/L while for Parabens derivatives high concentration observed in downstream of Thakuran i.e., Ethyl paraben ranging from 23.7 to 598.7 ng/L. The correlation of water quality parameters with different PPCPs helps to elucidate the source as Phthalates are positively correlated with DIN and DIP which clarifies its typical anthropogenic source from catchment areas, run off

from domestic sewage and effluents. Significant spatial variation observed for PPCPs indicating persistence and long residence of these xenobiotics in the mangrove dominated estuaries of Indian Sundarbans.

Keywords: Emerging contaminants, GC-MS, distribution, estuaries, mangroves, environmental parameters

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are rapidly been observed in aquatic environments all over the World due to its wide applicability as daily usage and their growing concern as these compounds showed potentially adverse effects on humans and biota (Mimeault et al 2005; Shanmugam et al 2010; Ebele 2017; Ramaswamy et al 2011; 2018).This diverse group of compounds are observed in the antibiotics, analgesics, steroids, antidepressants, antipyretics, stimulants, antimicrobials, disinfectants, fragrances, cosmetics, toothpastes, soaps, shampoos, detergents, lotions, sunscreens and many other chemicals (Wang et al 2013; Liu et al., 2013., Sui et al 2015., Cui et al 2019., Zhang et al., 2020). PPCPs are widely distributed in different compartments of the aquatic systems such as sediment, water and ground water as they persist for longer time period, can be replenished easily, have chemical properties which prevent them from rapid degradation and readily adsorbs to the particle and accumulates in sediment (Wilson et al 2008; Sun et al 2016, Pinckney et al 2017; Zhao et al 2019; Liao et al 2019). In recent years these emerging contaminants (PPCPs) in marine estuaries, rivers and lakes have gained attention across the globe as they are Endocrine-disrupting compounds (EDCs) that interfere with hormonal system, physiology of humans and reproductive systems (Diamanti-Kandarakis, 2009; Schug et al.,2011; WHO/UNEP, 2013; Zhao et al 2019) and due to the scarcity of study on the PPCPs distribution across the aquatic ecosystem.

Transitional environments such as rivers, lagoons and estuaries are unique habitat for study as are situated between land and sea harbouring many aquatic and marine organisms. There are plenty of studies based on pollutants such as metals, dissolved nutrients, greenhouse gases, pesticides, pathogens and biomonitoring using biological organisms as tracers and proxies (Mukhopadhyay et al 2002., Na et al 2018., Dutta et al 2019., Mukherjee et al., 2020). The class of emerging contaminants which have recently gained attention are Parabens (alkyl esters of *p*-hydroxybenzoic acid) ranging from methyl to butyl or benzyl groups; Triclosan (5-chloro-

2 (2,4-dichlorophenoxy) phenol-TCS) are biphenyl ether; Phthalates (plasticizers) ranging from dimethyl to di-n-butyl, benzyl, ethylhexyl and di-n-octyl phthalate; Phenols (phenolics of nonyl, octyl, cumyl and bisphenol A,S,F); NSAIDs (non-steroidal anti-inflammatory drugs) such as Ibuprofen, Ketoprofen, Diclofenac, Naproxen and etc. These emerging contaminants are understudied in transitional environments such as estuaries which links the source to fate of these pollutants. The factors influencing the distribution of PPCPs in highly dynamic environments such as marginal marine habitats are understudied as this could provide the understanding to the insights of potential risk associated to flora and fauna of the ecosystem. The study of spatial or seasonal distribution of PPCPs profile at local sites to gain their local specificities can help to enhance future environmental management programs concerning the health of the ecosystem. This study of PPCP in Indian Sundarbans will be first-hand report providing the baseline information to understand the contamination level and anthropogenic impacts in these environments. The objectives of the present study to determine the occurrences of different groups of compounds under PPCPs such as parabens, phenolics, phthalates, NSAIDs and Triclosan which are polluting the pristine mangrove dominated estuarine environment of Indian Sundarbans with an emphasis to identify their sources relating with the environmental factors influencing their distribution in spatial scale.

2. Materials and Methods

2.1. Study area

The world's largest contiguous mangrove forest the Sundarbans stretches along the coasts of Bangladesh (6017 km^2) and India (4000 km^2) which extends in the southern part of the state of West Bengal in India. The Sundarbans declared as Ramsar site under Ramsar convention in 1992 (https://rsis.ramsar.org/ris) and World heritage site by UNESCO in 1997(https://www.sundarbanaffairswb.in/home/page/sundarban_biosphere) due to its unique ecosystem services by providing the breeding and nursing habitats for diverse marine organisms, houses endangered species such as Royal Bengal Tiger (*Panthera tigiris*) and Ganges river dolphins (*Platanista gangetica*), hotspot of flora and fauna diversity, mangroves are the coastal foundations providing barriers against erosions and severe disaster such as tsunamis and cyclones and lastly provides economy to 3.5 million of livelihoods which sustains on resources and tourists attractions (Ellison 2000; Giri et al 2008; Cavanaugh et al 2015; Kathiresan 2018) .

The Sundarbans ecosystems due to its huge biodiversity and ecological services are severely affected due to pressures by humans as increasing the anthropogenic activities such as over-exploitations of resources by practising pisciculture, aquaculture and salt farming, exploitation of marine organism by fishing, cattle grazing, building dams, bridges and roads for various purposes for example tourism, siltation, introducing mining and refineries, coastal pollutions due to regular oil spills from huge ships and boats, constant change in hydrological regimes, climate change and loss of biodiversity by human intrusions. Apart from anthropogenic activities the ecosystem suffers due to natural stressors such as an increase in sediment salinity, increase level of sulphide in sediment, anaerobic condition due to sea level rise, nutrient limitations and continuous erosion by tides and total forest destruction by tsunamis and cyclones. Sundarbans is highly irregular and is crisscrossed by numerous rivers and waterways forming channels and creeks throughout the intertidal zone. The estuary having the main connective of fresh water from Hooghly river which is called the artery of Sundarbans forming swampy terrace characterized by fluvial marine deposits. The Indian Sundarbans are situated at the land ocean boundary of the world's largest Ganga-Brahmaputra delta and the estuarine phase is crisscrossed by several small and large rivers starting from west to east part of Indian Sundarbans namely Mooriganga, Saptamukhi, Thakuran, Matla, Bidya, Gosaba and Haribhanga to the extreme east side of the mangrove forest towards the boundary of India and Bangladesh. In the Indian part of Sundarbans, the two major and extensive rivers are Matla and Thakuran which are situated in mid of the ecosystem covering the latitudinal part from head to sea mouth.

2.2. Sampling

Water samples for measuring levels PPCPs and other environmental parameters were collected using *Niskin* water sampler (5L, General Oceanics) from stations located from head to sea end of the two major estuaries of Indian Sundarbans namely, Matla and Thakuran. The stations were located in transect wise to get the salinity variation from upper, middle and lower part of the two estuaries (Fig. 1). The total number of stations in the Matla estuary were six and in the Thakuran estuary were three covering their upper, middle and lower part. The samples were collected during post monsoon months (December 2018 and February 2019) to avoid any dilution with rainwater during monsoon and stable condition of estuaries during post monsoon season as compared to pre-monsoon and monsoon.

The samples for PPCP were collected in pre-cleaned amber colored glass bottles and stored in ice box for transporting to laboratory. The *in-situ* environmental parameters from each sampling sites were measured on board like water temperature using mercury thermometer; 0-50ºC graduation, Zeal 76 MM immersion and pH using portable pH meter; Orion Star A211, fitted with a Ross combination electrode calibrated on the US National Bureau of Standards (NBS) scale with reproducibility of ± 0.005 pH units. Dissolved oxygen (DO) samples were fixed in glass bottle of 125 ml using Winkler A (manganous sulphate 60%) and B (alkaline iodide) reagents and analysed onboard following standard protocol (Grasshoff 1983). For dissolved nutrients, water samples were collected in HDPE bottles after filtering through GF/F filter paper (0.45 µm) and were stored in ice box for transporting to laboratory. Among the dissolved nutrients nitrate, ammonia and phosphate were analysed. Moreover, salinity was measured following Grasshoff (1983).

2.3. Sample preparation and analysis

All the reference standards of Phenolics, Triclosan, NSAIDs, Phthalates and Parabens and the derivatizing reagent N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) were purchased from Sigma-Aldrich (USA). Phenanthrene-d10 was procured from Cambridge Isotope Laboratories Inc. (USA). Acetone, n-hexane and ethyl acetate of HPLC grade were procured from Qualigens Fine Chemicals (Mumbai, India). Sodium sulfate (anhydrous) obtained from Hi Media Laboratory Pvt. Ltd. (Mumbai, India). Solid Phase Extraction (SPE) cartridges (Strata C18-E, 1000 mg/6 mL) were from Phenomenex (Torrance, CA, USA). Glass vials of a capacity of 2mL were purchased from Agilent Technologies (Waldbronn, Germany). The Milli-Q water was obtained from Direct Q3-UV (Millipore, India). All glassware used for sample analysis were precleaned with 10% Labolene solution, acid washed rinsed with ultrapure water & acetone and dried in hot air oven. The individual standards stock solutions of 100 µg/ml or ppm of Phthalates, NSAIDs, Phenolics, Triclosan and Parabens were prepared by dissolving 10 mg in 100mL of an acetone: ethyl acetate (1:1, v/v) solvent which were serially further diluted to prepare the working standards in the range 10, 50, 100 ng/L. The working standard solutions for calibration and recovery spike were stored at -20 ◦C.

Five different PPCPs with different derivatives were analyzed in the present study. The different class of PPCPs analyzed in present study were **Phenolics** (octyl phenol (OP), nonyl phenol (NP), bisphenol A (BPA), BPS, BPF), **Triclosan**, **NSAIDS** (non-steroidal anti-inflammatory drugs) (Ibuprofen, Naproxen, Ketoprofen, Diclofenac), **Phthalates** (Dimethyl

phthalate (DMP), Diethyl phthalate (DEP), Di-n-butyl phthalate (DBP); Butyl benzyl phthalate (BBP) and Di-2-ethylhexylphthalate) (DEHP) and **Parabens** (methyl, ethyl, propyl and butyl parabens). For the analysis of different PPCP different extraction procedure have been followed. Triclosan extraction was done by liquid phase extraction following standard protocol (Nishi et al 2008 and Ramaswamy et al 2011a). 1000 ml of water samples was taken in pre-cleaned separating funnel of 2L and added with 10 g of NaOH and 50 ml of n-hexane. The mixture was shaken well for 10 mins and allowed to stand for 30 minutes for separation of layers. The n-hexane impurity layer was discarded and water phase was collected. The pH of the water phase was adjusted to -2 by adding 6M HCL, following which 50 ml of n-hexane was added and shaken again for 10 minutes. After the separation of n-hexane layer was collected and pooled with the previous hexane extract. To the n-hexane extract 3g of Na_2SO_4 (anhydrous baked at 200℃ overnight) was added for dehydration and left undisturbed for 30 minutes to remove moisture from the extract. The n-hexane layer was then transferred to condensation flask and the extract was concentrated to 5ml by rotary evaporate 35 ◦C (BUCHI R-210, Switzerland) and further dried to 1ml. The final extract is collected in sterilized glass vials of 2ml capacity and stored in refrigerator at 4˚C prior analysis in Gas Chromatography - Mass Spectrophotometer (GC-MS)

For other PPCPs like phenolic, NSAIDs, Phthalates and parabens were analyzed following solid phase extraction using selective cartridges like (OASIS HLB) and C1 8E. For phenolic, Phthalates and parabens extraction cartridges were pre-conditioned passing 5ml ethyl acetate, 5ml methanol, 5ml ultra-pure water at a constant rate of 3ml/min. While for NSAIDs preconditioning was done using 3ml 1:1 (v/v) ethyl acetate and acetone; 3 ml methanol; 3 ml ultra-pure water. 1000 ml of water samples was adjusted for pH to acidic range (2 to 3) for phenolics and NSAIDs and to neutral for phthalates and parabens. Sample were passed through the cartridges following which they were left for drying. for Cartridges were eluted with 20ml of ethyl acetate and eluent was dehydrated with Na_2SO_4 (anhydrous baked at 200℃ overnight) The eluent was concentrated using rotavapor and transferred into sterilized glass vials for derivatization. To the concentrated extract 25 µl of MSTFA (N-methyl-N-(trimethylsilyl) trifluoroacetamide) (Ramaswamy et al.2011; Shanmugam et al. 2014, 2010; Chakraborty et al 2018) was added and kept at 70˚C for 30 minutes (for phenolics & phthalates), 35 minutes (for NSAIDs) and 15 minutes (for Parabens). Derivatization is done to

make the compounds more suitable for GC-MS analysis as most compounds require transformation into more volatile and thermally stable and achieved to sensitivity once derivatized. The derivatized extract -injected into GC-MS using auto injector for qualitative and quantitative analysis.

The identification of PPCPs was performed by gas chromatograph (GC-2010) interfaced with a quadrupole mass spectrometer (QP-2010) (Shimadzu Corporation, Japan) where the chromatographic separation of different PPCPs was achieved with DB-1 fused silica capillary column (30m×0.32mm i.d., 0.25μm film thickness, J&W Scientific, Folsom, CA, USA). Helium with a purity of 99.999% was used as the carrier gas at a flow rate of 2.25 mL min^{-1}. An instrumental blank, procedural blank, blank spike, sample duplicate, and sample spike were applied for each sampling. 1μL of derivatized extract was injected in split less mode using an auto sampler. The injector port, interface, ion source and GC-MS temperature program are mentioned in Ramaswamy et al 2011; Shanmugam et al 2010, 2013 and Selvaraj et al 2014. In electron ionization (EI) mode at70 eV the mass spectrometer was operated and at an emission current of 60 μA, full scan data was obtained in a mass range of m/z 35–500. Scanning interval and SIM (selected ion monitoring) sampling rate were 0.5 and 0.2 s with the mass selective detector operated in SIM mode. The calibration of all the mentioned PPCPs such as Triclosan, Phenols, Phthalates, NSAIDs and Parabens were done for three-point concentration such as 10,50 and 100 ng/L. The calibration for all the compounds standards were achieved $r^2>0.99$ with recovery percentage (R%) greater than 99% for mass ion fragments of PPCPs derivatives. The detailed of the mass ion fragments with limit of detection (LOD) for each derivative of PPCP standards are summarized in TS1 (supplementary material).

2.5 Statistical analysis

The box and whisker plot indicates the median and 25% to 75% of data variations. It gives the overall range with minimum and maximum values indicated by whiskers of the five different categories of PPCPs studied during post monsoon months for all sampling locations. To find the relationship between PPCPs and the studied environmental parameters during the sampling period Principal Component Analysis (PCA) was performed (Fig 4). In the PCA plot the first axis itself explains 53.74% of data variability and the second axis i.e., Factor 2 represents 34.52 % of variability, thus the two axes together explain 88.26 % of total data variability. All statistical analyses were performed using Statistica v. 7.0 platforms (StatSoft. Inc., 2004).

3. Results

3.1. Spatial variation of PPCPs

The different concentration of PPCPs for Thakuran and Matla estuaries are shown in box and whisker plot (Fig 2) with median concentration and variations of different PPCP compounds. Among the different PPCPs the most abundant was phenolics in the study area with mean concentration ranging from 230 to 4586 ng/L following Triclosan with mean concentration for both Thakuran and Matla ranging from 96 to 1885 ng/L. The remaining PPCPs in descending range of concentrations are NSAIDs (290 to 791 ng/L), Phthalates (39-302 ng/L) and Parabens (21-263 ng/L) (Fig 2). In the spatial distribution from head (i.e., upper) to mouth (i.e., lower) of estuaries, Phenolics, Triclosan, NSAIDs and Parabens showed higher concentration in the lower stretch of both Matla and Thakuran while only Phthalates showed high concentration in upper part of both estuaries (Table-1). Among the five different PPCPs studied comparatively higher concentration of Phenolics, Triclosan, NSAIDs and Phthalates are found in Matla as compared to Thakuran while Parabens are higher in Thakuran estuary (Table-1 & 2). Phenolics concentration for Matla lower (4586.26 ± 6607.29 ng/L) showed values four times higher than upper and middle of Matla and Thakuran. Phenolics concentration for Thakuran showed narrow variation in middle (1469.59 ± 1756.90 ng/L) and lower (1379.15 ± 1437.99 ng/L) part of the estuary whereas the upper part showed very low concentration (169.81 ± 168.63 ng/L) as compared other parts of both estuaries (Table-1). For Triclosan quite higher values are observed in Matla lower (1885.22 ±0 ng/L) and upper (1613.33 ± 354.92 ng/L) while lowest value observed in Thakuran middle (95.65 ± 0 ng/L) and almost no variation in Thakuran upper (356.52 ± 0 ng/L) and lower (395.65 ± 0 ng/L). For NASIDs higher values are found in Matla lower (790.48 ± 902.80 ng/L) and Thakuran lower (617.33 ± 364.74 ng/L) with narrow variation in concentration for upper and middle for both estuaries (Tbale-1). High concentration of Phthalates is observed in Matla upper (233.59 ± 194.58 ng/L) and middle (237.10 ± 231.69 ng/L) with least value in Thakuran middle (39.10 ± 34.28 ng/L) and low value in Matla lower (87.80 ± 70.45 ng/L). Parabens concentration in Matla showed low and narrow variation as compared to Thakuran where highest values are observed in Thakuran lower (263.31 ± 294.15 ng/L) following Thakuran middle (215.44 ± 232.91 ng/L) and least in Thakuran upper (21.92 ± 9.28 ng/L) presented in Table-1.

Among the different derivatives of PPCPs the highest concentration was found for octyl phenol ranging 282.2 to 17590.1 ng/L with highest values observed in Matla lower (17590.08 ng/L) and least in Thakuran upper (282.19 ng/L) (Fig 3a). The next following derivative was Ketoprofen ranging 614.6 to 2333.7 ng/L which showed narrow variations between Matla and

Thakuran upper and middle while the lower part of Matla (2333.75 ng/L) was almost double in concentration to Thauran lower (1073.29 ng/L) (Fig 3b). Other derivatives of NASIDs did not show huge variations between the two estuaries or in their spatial distributions from head to mouth (Fig 3b). Among the Phthalates derivatives high concentration of Di-2-ethylhexylphthalate (DEHP) was observed in Thakuran upper (691.79 ng/L) and Matla upper (494.75 ng/L) while lowest concentration (3.77 ng/L) was found to be for benzyl butyl phthalate (BBP) in Thakuran upper. High variations among all the Phthalate derivatives are observed for Matla and Thaukuran middle with Matla middle Phthalate derivatives concentration almost six times higher than Thakuran middle (Fig 3c). Among the Parabens derivatives high concentration was observed for ethyl parabens (Eth-paraben) with marked spatial variation in Thakuran estuaries ranging from upper (23.72 ng/L) to lower (598.75 n/L) stations. For Matla and Thakuran upper stations did not show huge variation and the values were low as compared to Thakuran middle and lower (Fig 3d). Though low concentration among the Parabens derivatives were for methyl and propyl Parabens.

The average variation of five different PPCP compounds between two estuaries were compared and it was observed that all the PPCPs except Parabens range was high in Matla as compared to Thakuran estuary (Table-2). The marked variation between the two estuaries were mainly in Triclosan and Parabens (Table-2). Very high concentration of Triclosan observed in Matla (1237.83±747.46) compared to Thakuran (282.61±163.09) while opposite trend was observed for Parabens where high the concentration found in Thakuran (166.89±127.81) than Matla (44.54±24.63).

3.2. Water quality parameters

The environmental parameters of the two major estuaries of India Sundarbans i.e., Matla and Thakuran show minor differences (Table-2). The surface water temperature ranged from 22 to 24 ^{o}C during post-monsoon period. The variations between two estuaries for pH, DO, SPM and DIP are not evident. However, dissolved inorganic nitrogen (DIN) for Matla (10.03±5.27) observed to be high as compared to Thakuran (7.44±5.14) estuary while the Salinity found to be high for Thakuran (25.01±2.67) as compared to Matla (22.38±3.43).

The PCA plot reveals Salinity, pH, DIN and DIP as the predominant elements of the components for first axis while temperature mainly relates to the second axis. It has been observed from the PCA plot that the Phthalates levels in the study period is mainly related to DIN and DIP of water samples while parabens are positively related to salinity and pH of

estuarine water. The remaining PPCP i.e., Phenols, Triclosan and NASIDs are related to temperature but not with other environmental parameters (Fig 4).

4. Discussion

4.1. Spatial distributions of Physico-chemical parameters and PPCPs: -

Surface water temperature was typical for subtropical climate and salinity range is narrow indicating polyhaline condition in these estuaries (Dutta et al., 2019). The oxygen level and its saturation represent well oxygenated condition indicating lower waste water discharge into these systems than urban estuaries. These estuaries within mangrove habitats exhibiting representative pH values of seawater and nutrients level much lesser than fluvial estuaries in the proximity like Hooghly estuary (Mukhopadhyay et al., 2006) indicating marine dominated condition. Minor inter-estuarine variation of physico-chemical parameters represent their similar and homogenous aquatic environmental settings, however lower salinity and higher DIN values in Matla indicating higher amount of fresh water discharge into the system primarily in the form of sewage and waste water.

By comparing the present data with national and international studies it has been observed that the studied PPCPs such as Phenolics, Triclosan and NSAIDs are found to be moderate to high concentration in Matla-Thakuran estuarine. Parabens and Phthalates in the present study observed to be comparative lower ranges with national and international estuarine and river systems (Table-3). Higher levels of Phenolics, Triclosan, NSAIDs and Parabens are at lower stretch of the Matla-Thakuran estuarine system while Phthalates shows higher levels toward the upper stretch of the estuary. High concentrations of these micro contaminants in the lower stretch of estuary could be due to agricultural runoff, through natural processes such as decomposition of organic matter and their high persistence level that these are transported easily and are accumulated over time in such natural habitats (Bayen 2012; Bartons and Peneulas 2017; Kinney and Heuvel 2020; Gan et al 2023)

4.1.1. Phenolics

Phenolics are Endocrine disrupting compounds primarily consists of 4-nonylphenol (4-NP), 4-tert-octylphenol (4-t-OP) and bisphenol A (BPA), which are widely used as non-ionic surfactants in industrial, agricultural and household applications (Diao et al 2017). Phenolics levels in the present mangroves dominated estuaries is comparable to the other estuarine, lake and river samples (Zhao et al 2009., Diao et al 2017 and Selvarja et al 2014) (Table-3). Few

other studies are also observed with 3-4 folds higher values of phenolics than the present study such as the study of Wang et al (2013) who reported the total mean concentration of phenolics ranging from 248-4650 ng/L with average concentration of 1384 ng/L in 22 river estuaries around Dianchi lake, China. High concentration compared to the present study was also reported from Pearl river estuaries China where the mean concentration of Phenolics in water samples ranged from 233.04 to 3352.86 ng/L (Diao et al 2017). There are many other reported values of phenolics much higher than the present studies from river for e.g., the study from Spain where mean concentration reported 37300 ng/L (Cespedes et al 2005) and from Pearl river estuaries, China with concentration of phenolics observed to be 11300 ng/L (Zhao et al 2009). There are few national studies which also reported higher concentration of phenols in Indian rivers namely Kaveri, Vellar and Tamiraparani rivers where the most abundant phenolics observed were NP ranged from ND to 2200 ng/L and OP ranging from ND to 16.3 ng/L (Selvaraj et al 2014). Previous national studies from Hooghly river-estuarine regions reported higher values of BPA which showed 15 times higher values than the present BPA concentration in Malta-Thakuran estuaries (Tabl-3). Among the different derivatives in the present study high levels of OP is been observed following BPF compared to the global reports. The overall trend of phenolics showed high concentration in Matla than Thakuran estuary which might be associated with discharge of waste water as point sources and canal effluents to Baidydhari river. There is always a huge difference between available treatment facilities of the cities and generated waste water. By the reports of 2013 from Central Pollution Control Board, 49% of waste water from four major districts namely Kolkata, North 24 Parganas, Hooghly and Howrah are been directly discharged without treatment to rivers and estuaries. Apart from the direct discharge of sewage and waste water effluents to estuaries and rivers the recreational sites, tourists' boats, fishing trawlers and commercial fishing activities are also adding to the pollution loads to such rural ecosystems (Mansson et al 2008 and Selvaraj et al 2014). In the present study the average concentration of phenolics derivatives in the estuarine water samples ranged in order of OP > BPA > BPF > NP > BPS (Fig. 3a and Table 3). The high concentration of OP in the water is also observed in river water of China (Wang et al 2013). There was no significant variation ($p = 0.33$) found in phenolics across the sampling location from upper to lower stretch of estuaries as tested by Kruskal-Wallis test of analysis of variance (Fig. 3) which might indicate the persistence nature in the system for the compound. Many other studies state the higher concentration of Phenolics in estuarine water samples are not only by general anthropogenic discharges such as sewage treatment plants, urban city wastes or industrial effluents but might be due to some other factors such as sorption/desorption

by sediment, long time for biotransformation of phenolics (Wang et al 2013., Diao et al 2017) and other the natural sources such as plant litter leaching as source of Phenolics (Sanyal et al 2020). Other studies reported that the half-life period of transformed phenolics group such as nonyl phenol are more than months so are easily transported and persistent a long way by river flow which might also results observing high concentration of phenolics in the present estuarine water (Ying et al., 2002; L and Li, 2003, Xu et al 2006). The highest and abundant compound observed in the present study is phenolics among other PPCPs indicates its long-term biodegradation and persistent nature along with some natural sources as the decomposition of organic materials of dead plants apart from only anthropogenic. In the present study the natural sources can be from huge mangrove litter leaching in the present study as evident from optical proxies ($S_{275-295}$ and $SUVA_{254}$) of more terrigenous type chromophoric dissolved organic matter (CDOM) in Indian Sundarbans (Sanyal et al 2020), due to the paucity of the studies regarding the mangrove litter leaching or the natural sources of phenolics into estuarine systems it is difficult to conclude the dominant or exact natural source of phenolics in Indian Sundarbans.

4.1.2 Triclosan

Triclosan are used as antimicrobial agents and are also used by many textiles industries as additive to prevent odour, used in plastics as antimicrobial additive to protect from deterioration, decolourisation and odour, used to eliminate house dust mites and by many other industries to prevent the growth of bacteria and fungi (Sabaliunas et al 2003; Ramaswamy et al 2011; Pintado-herrera et al 2014). The next highly abundant PPCP observed in the present study is Triclosan (Fig. 2). Hence Triclosan has no natural sources and are added to the rivers or estuaries by sewage, hospitals and waste water effluents (Wilson et al 2008; Ramaswamy et al 2011; Wijnen et al 2018). The present study of Triclosan concentrations observed to be high (up to1885 ng/L) as compared to many global studies from estuaries and river (Bester 2005; Hua et al 2005; Wu et al 2007; Pintado-herrera et al 2014) which reported concentration between<1-300 ng/L. Among the different international studies till date highest reported levels of Triclosan is 2300 ng/L from 139 sites of streams surface waters in United States (Kolpin et al 2002). In comparison with the national studies the highest known concentration in natural water bodies reported from Tamiraparani in South Indian state of Tamil Nadu where concentration reported up to 51600 ng/L at Cheranmahadevi following 3800 ng/L at Tirunelveli surface river water (Ramaswamy et al 2011). The reason for high concentration of Triclosan in the study of Ramaswamy et al (2011) was from household or sewage effluents,

STP effluents, hospitals discharge and industrial activities. Triclosan levels are also higher in Matla than Thakuran estuary alike with the phenolics trend across the estaury which clarifies the fact that more sewage and urban wastes are directly added through canals and point sources such as direct addition of untreated sewage waste water, tourists' activities and recreational sites without treatment to the Bidyadhari river and furthermore it gets mixed with Matla estuary. In the present study the Triclosan sources might be significantly from STP effluents and from community sewers rather than direct outputs from large industries as the upper stretch of the estuary do not show spike in concentration. Matla-Thakuran estuaries is surrounded by densely populated districts with total population of Kolkata and North 24 parganas sum up to 25.5 million and 86 lakhs population of south 24 parganas which uses the ferry connections along the river, supports fisherman livelihood and this estuarine region is a unique breeding and nursery ground for fishes (Mandal et al 2019). The domestic and small-scale industries effluents along with the southern Kolkata sewage waste water from treatment plants directly gets dumped to the estuarine rivers and ultimately drains to Bay of Bengal. The higher vales of Triclosan in lower stretch of both the estuaries shows its high residence time with persistence nature which gets accumulated and gets transported to longer distance.

4.1.3 Non-steroidal anti-inflammatory drugs (NSAIDs)

NSAIDs belongs to the mostly used pharmaceuticals in the humans and veterinary medicine. The four types of NSAIDs in the present study are analgesics commonly known as pain killers and are widely used as over the counter drugs (Hudec et al 2011). Each group of compounds have varying degree of analgesics and anti-inflammatory properties depending upon their high over the counter sales. The present study mean concentration of NSAIDs ranged up to 791 ng/L (Fig. 2) which is comparable to most of the rivers and estuarine such as Togola and Budzinski (2007); Silva et al (2011); Daneshvar et al (2012) and Shanmugam et al (2013), reported concentrations from ND to highest 1060 ng /L. There were studies from rivers of Canada and Taiwan which reported concentration higher up to 6400 ng/L (Brun et al. 2006; Selke et al. 2010; Lin et al 2010; Aydin and Talinli 2013; Marsik et al 2017) (Table-3). Highest recorded NSAIDs concentration in natural water bodies is from Nairobi river basin Kenya which reported Ibuprofen concentration varying from 10000 to 30000 ng/L (Koreje et al 2012). In the present study the most abundant NSAIDs is Ketoprofen following ibuprofen, diclofenac and naproxen (Fig 4), similar high concentration of Ketoprofen and Ibuprofen concentrations are reported in Ebro river basin, Spain (Silva et al 2011) and from national study from Kaveri, Vellare and Tamiraparani, India (Shanmugam et al 2013). In many previous studies the high

concentration of these drugs is not only due to higher usage but lack of efficiency or functional unit of STP in urban areas near the estuaries or rivers and difficult in removal of ketoprofen and ibuprofen during sewage treatments. The mean concentration of NSAIDs from head to mouth of the estuaries of both Matla and Thakuran also did not show wide variation. Though slightly higher values are observed at the lower stretch of both the estuaries likely due to the high residence time of these compounds and is readily not removed by physical factors such as oxidation or irradiation.

4.1.4 Phthalates

Esters of phthalic acid are of environmental relevance due to their ecotoxicological potential and high production rates as they are used in many chemical industries and representatives of high production volume chemicals (Clara et al 2010; ESIS, 2019). Phthalates are plasticizers which are mainly used as polymers in production of plastic products like polyvinyl chloride (PVC), vinyl flooring, adhesives, lubricants, varnishes and paints, gelling agents, dispersants, packing materials of toys, textiles, detergents, medical devices, stabilizers, binders, lubricating and emulsifying agents, etc. (Latini 2005; EU-RAR 2008; USEPA 2012, Selvaraja et al 2014). The results of phthalate mean concentration in Indian Sundarbans mangrove ecosystem ranges from 39 to 302 ng/L (Fig. 2) while the upper part of both the estuaries i.e., Matla and Thakuran showed high concentration of phthalates than the lower part of estuaries (Table- 1 and 2). The range of phthalate in the present study is found to be low as compared to the national study by Selvaraja et al (2014), reported phthalates from Kaveri river, India ranging from ND to 822 ng/L while the present range of phthalate concentration are found to be low for certain derivatives as compared with the other international studies such as Dargnat et al. 2009, from Seine river, France; He et al (2011) from Yangtze, China; Santhi and Mustafa (2013) from Selangor river, Malaysia (Table-3). Though many global riverine concentrations of phthalates are reported high up to 5000 ng/L (Vethaak et al 2005) in Dommel river, Netherlands, from Spain rivers namely Muga, Fluvia, Ter, Besos,Llobregat, Ebro concentration reported as high as 4980 ng/L (Sanchez-Avila et al. 2012) and from Eleven point white river, USA reported concentration up to 4140 ng/L (Solı´s et al. 2007). Few studies have reported low concentration of phthalates ranging from 10 to 60 ng/L in Hoje Sweden by Bendz et al. (2005) (Table-3). High concentrations of phthalate in the present study are DEHP following DBP, DEP and least observed was DMP (Fig 3c and Table-3) which is comparable with the study of Hooghly river estuary where highest levels was reported for DEHP followed by DEP and DBP (Mukhopadhyay and Chakraborty 2021). The most abundant and ubiquitous phthalate in the

present study is DEHP, DEP and DBP showed comparable range of concentrations reported from other national and international studies such as from Yangtze river, China (He et al. 2011); Rhine, Elbe, Ruhr, Mosel, Havel, Spree, Oder rivers, Germany (Fromme et al. 2002) and Kaveri river, India (Selvaraja et al. 2014). The stations which are located in the upper part of the estuaries of Matla and Thakuran showed higher levels of phthalates than the stations situated close to the sea mouth (Fig 3) which indicates that the main sources of Phthalates are from sewage effluents of urban, household, stormwater runoff and agricultural runoff rather than any point or local sewer sources with low chance of getting diluted with marine water.

4.1.5 Parabens

Parabens are ubiquitously found in estuarine and river waters as these are present in daily usage products such as shampoos, shower gels, toothpastes, creams, lotions, soaps, fragrances, UV-filters, preservative chemicals in food and beverages due to their antifungal and antibacterial potentials (Darbre et al 2004; Zhang et al 2011; Ye et al 2008; Alan 2008; Blanco et al 2009; Liao et al., 2013; Zhao et al 2019). Since the low cost and wide applicability of Parabens containing products on nails, skin, scalp, lips, mucosae and in food preservations lead to continuous exposure of human and are directly or indirectly are discharged to natural water bodies such as rivers, lakes, estuaries and ultimately to sea. In the present study amongst the different groups of PPCPs the lowest concentration observed is for Parabens. In the present study parabens ranges from 22 to 263 ng/L from upper to lower stretch of both the estuaries of Indian Sundarbans (Table 1 and Table 2). The concentration of Parabens towards the lower stretch of the estuary was found to be more and the range of the present study is slightly higher as comparable to the national study of Ramaswamy et al (2011) from Kaveri, Vellare, Tamiraparani rivers and Pichavaram mangrove, south eastern part of India and in comparable range with international study of Hasegawa et al. (2016) Japan and from Urban streams in Tokushima and Osaka, Japan (Yamamoto et al, 2011). Highest concentration (up to 52100 ng/L) of parabens till date is reported from Mogi Guaçu River, Brazil which is almost 20 folds higher than the present study following the study of Peng et al. (2007) from Pearl river delta, South China reported concentration up to 3142 ng/L. Lower concentration of Parabens i.e. < 50 ng/L are also reported from the rivers of South Wales, UK (Kasprzyk-Hordern et al. 2008); North-eastern Switzerland (Jonkers et al.2010); Galicia, Spain (Gonzalez-Mari˜no et al., 2009); Greater Pittsburgh area, USA (Renz et al., 2013); Pearl river estuary (Zhao et al 2019). Many similar studies with high and low levels of Parabens with their different derivatives are given in Table-3 and in comparison, Parabens levels in Matla-Thakuran estuary is found to be high

for its some derivates. (Fig 3d). The most abundant Parabens found in many studies is ethyl parabens which is also observed in all sampling locations of the present study (Fig 3d). The level of Parabens concentration shows higher values in the lower stretch of both the estuaries and changes sharply for Thakuran estuary lower (21.91 to 263.30 ng/L) than Matla (37.98 to 48.14 ng/L) in Table-1 which might be due to point source of effluents to Thakuran lower. The high values of Parabens in Thakuran can be due to the dumping of untreated wastes of household sewage from nearby villages or any local point source which results in huge variation and higher concentration. Though higher values are witnessed in the lower stretch which might indicate the persistence nature with longer residence time and not easily biodegraded but transported without removal to longer stretch of the estuary.

4.2. PPCP relationship with environmental parameters

Very few studies have analyzed the relationship of PPCPs with water quality parameters such as temperature, salinity, pH, dissolved oxygen, dissolved nutrients, suspended particulate matters and etc. (Glassmeyer 2005; Yang et al 2013; Lv et al 2014; Sun et al 2016). The relationship of these PPCPs with physic-chemical parameters of estuarine water helps to understand the source and nature of these compounds and can be used as sewage markers for the ecosystem (Sun et al 2016). From the present analysis it has been observed that Phenols, Triclosan and NSAIDs are positive and significantly correlated with temperature while phthalates are positively correlated with dissolved inorganic nitrogen and phosphate. The relationship with PPCPs with temperature has previously been reported as key factors in degradation of these long chain organic compounds (Xu et al. 2006; Cailleaud et al. 2007). The positive relationship of Phthalates with DIN and DIP may clearly show the source as allochthonous such as effluents, domestics and run off from catchment areas. As in case of Phthalates high levels are observed at the upper stretch of the estuaries which indicates its total anthropogenic inputs and readily does not mix or transported to longer stretch of estuaries. The relationship of Parabens with pH and salinity might indicate the mixing and dilution with sea water and their persistence capacity in the system for longer period. Studies have reported about the biodegradation process as primary mechanisms for removal of such derivatives depending upon the pH and dissolved oxygen concentration of water sample which accelerates the metabolic breakdown of these compounds. Water samples with low pH could make difficulties in the hydrolytic transformation of PPCPs while aerobic conditions facilitate easier biotransformation than anaerobic condition (Joss et al. 2005; Lonappan et al. 2016; Marsik et al 2017. The positive relation of Parabens with salinity and pH in the present study might

indicate its longer residence time which do not get easily degraded and persists in the environments. Salinity shows positive significant correlation with Phenolics and NSAIDs which might be due to the change in solubility of these compounds in higher salinity and alkaline nature of seawater. Triclosan shows negative significant correlation with salinity which might be due to "the salting out" effect where the aqueous solubility of neutral non polar compounds decreases in presence of major sea water ions such as Na^+, K^+, Cl^- and SO_4^{2-} (Zhou and Liu, 2000).

5. Conclusion

The study presents the first-time report on the occurrences, distribution and sources of pharmaceuticals and personal care products (PPCPs) from the estuarine water of Indian Sundarbans. Results showed comparative ranges with some of the international river and estuarine systems along with national studies. The most abundant PPCP found in the present study is phenolics which showed persistent nature with longer residence time and high accumulation in the natural habitat as higher values observed in lower stretch of estuaries and few stations located at the upper stretch of estuary. The spatial distribution of PPCPs along the major estuaries of Indian Sundarbans showed significant variation for parabens while other PPCPs such as phenolics, triclosan and NSAIDs did not show marked variation or trend from head to mouth of the estuary. Though decreasing trend in concentration for phthalates were observed from upper to lower stretch of the estuary. Phthalates shows positive relation with DIN and DIP which elucidates its typical anthropogenic sources from catchment areas, direct runoffs of plastic wastes from domestic and small industrial effluents along with storm runoff to the estuaries. The positive relationship of parabens with pH and salinity might states that this compound is difficult to remove by physical or biological processes or sea water dilution and can be transported to long way which persists in the environment due to its longer residence and higher accumulation nature. Thus, these compounds can be used as specific markers for sewage and effluents as these markers can help to monitor the ecological status of the ecosystem and could delineate the fact of improper function of STPs of the cities. Further studies are needed to understand the specific discharge of these contaminants from urban pool mainly from sewage treatment plants to test their efficiency in successful removal of these micropollutants which gets diluted to the estuaries and rives or are adsorbed to sediments during transportation.

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Fig. 1 Map of sampling location in Indian Sundarbans mangrove ecosystem.

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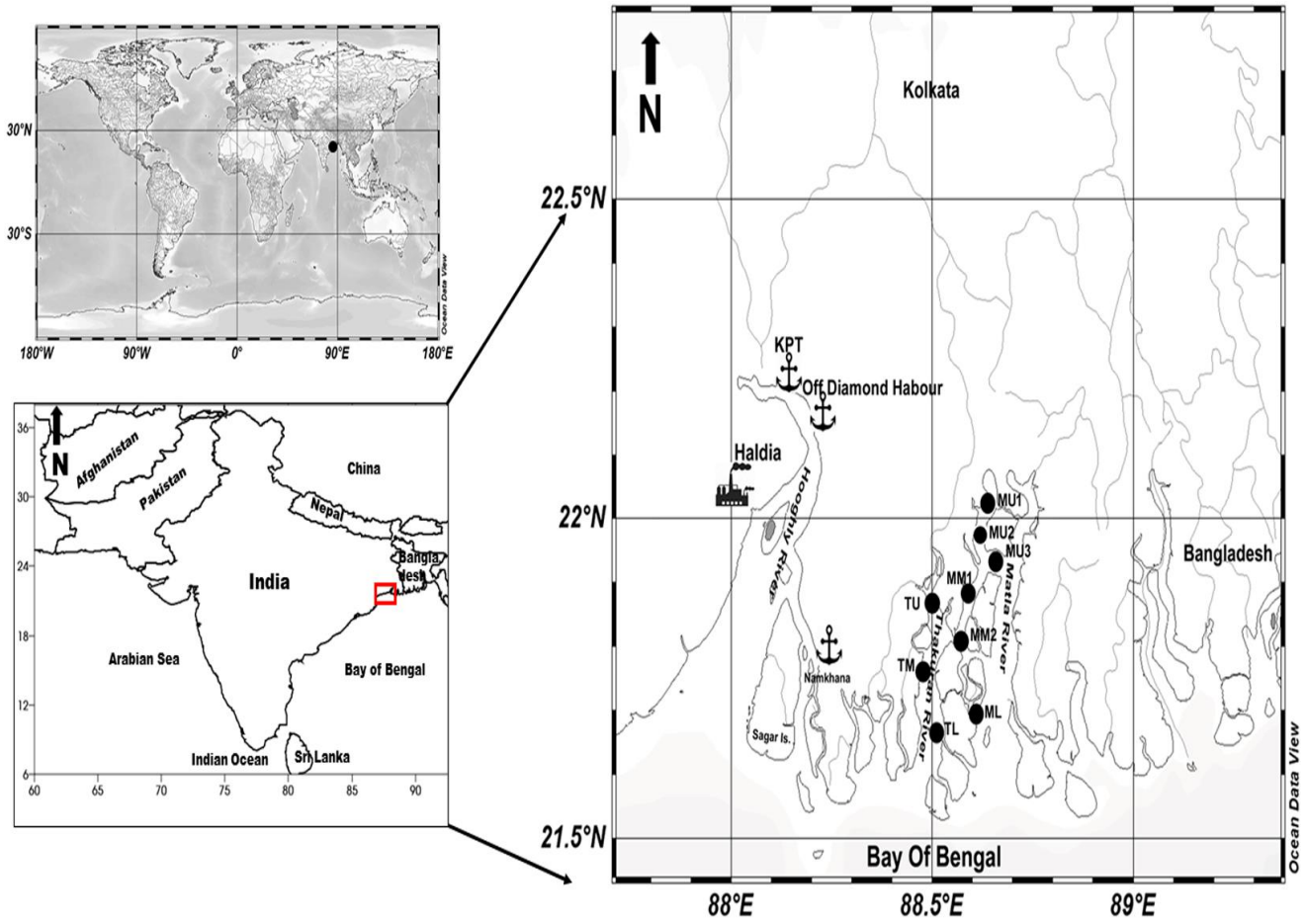
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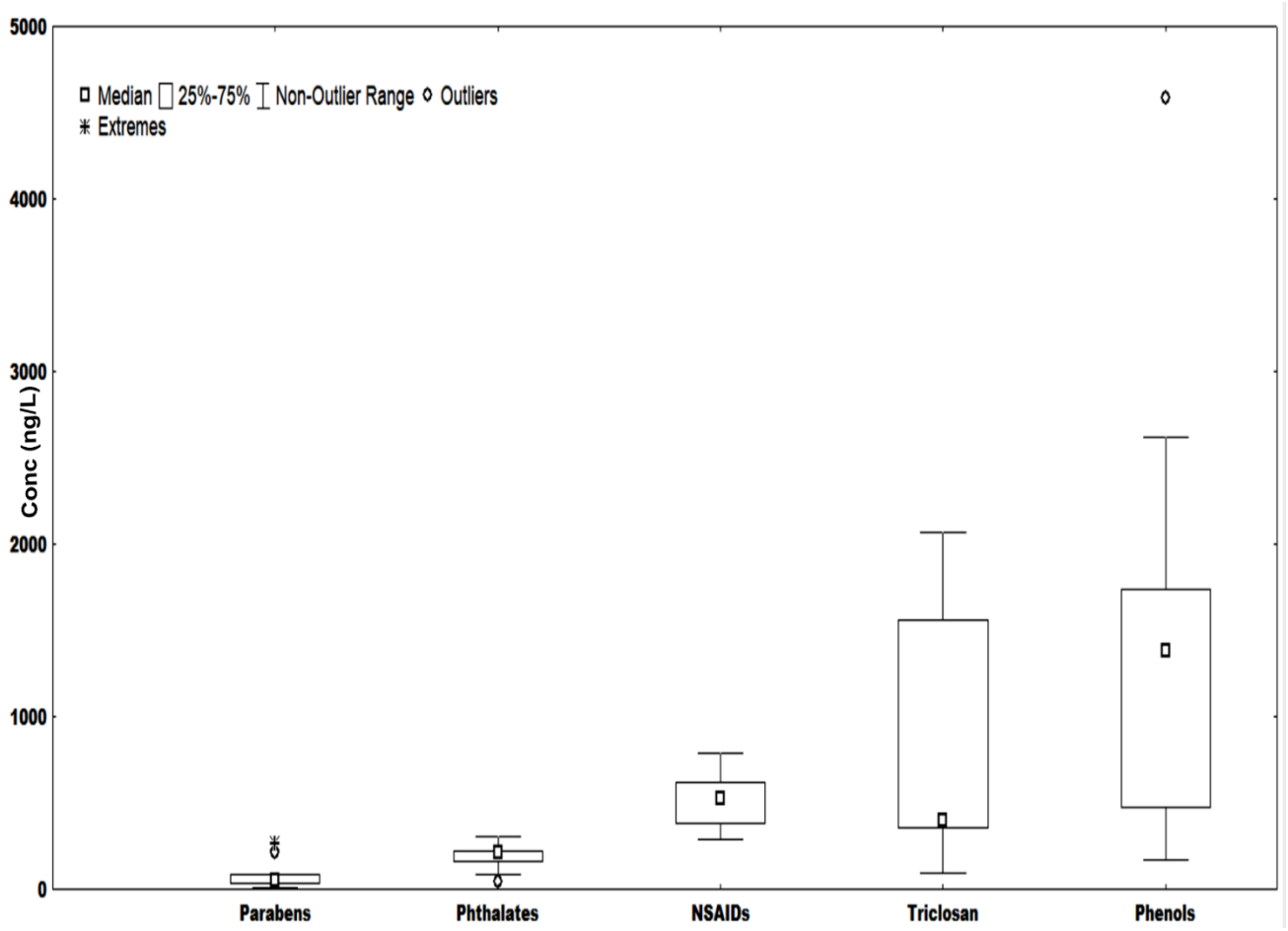
Fig 2. Box and whisker plot of five different studied PPCPs. The point inside the box denotes the median concentration of PPCP of each group, the box denotes the 25 and 75 percentiles of data.



582 **Fig 3.** Concentration levels of four different derivatives of PPCPs: a) Phenols; b) NASIDs; c)
583 Phthalates and d) Parabens in Indian Sundarbans

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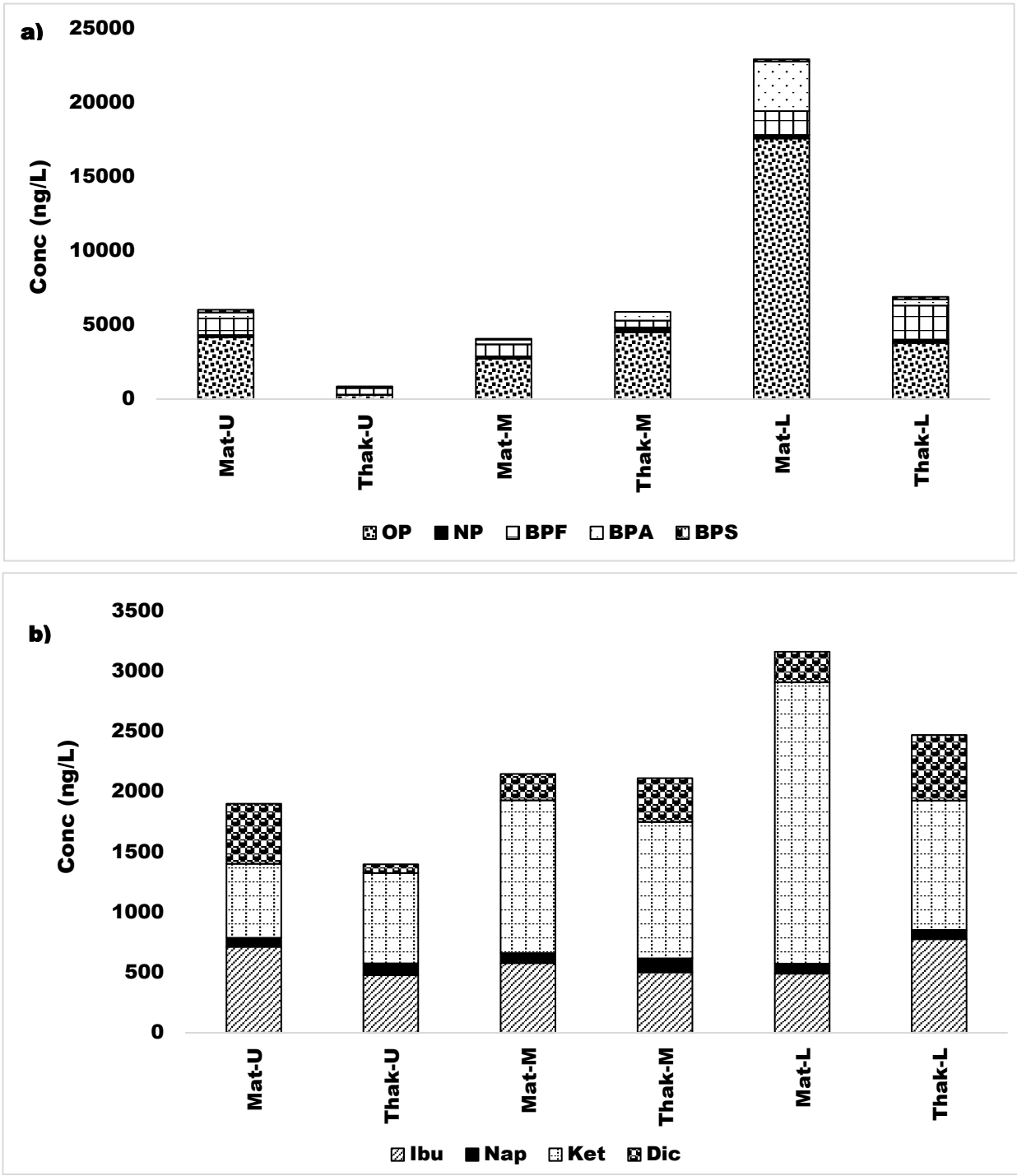

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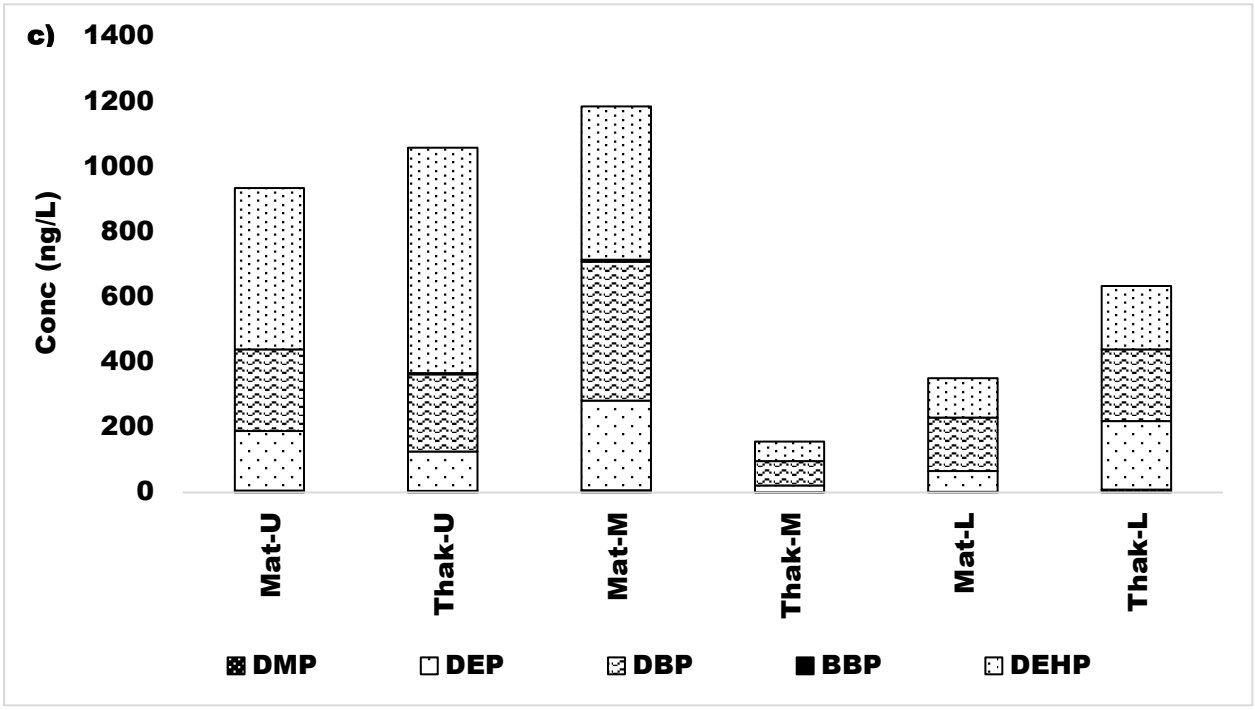
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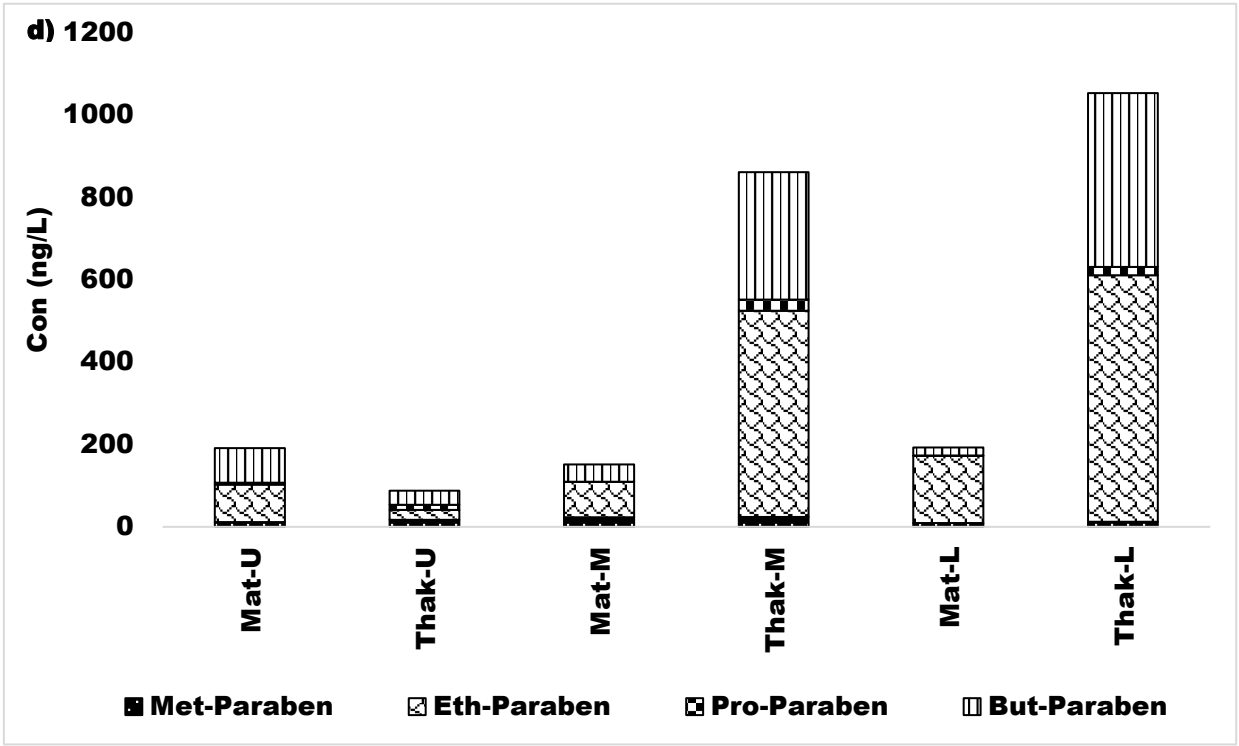
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Eth-Paraben
Pro-Paraben
But-Paraben

Fig 4. Principal component analysis based on environmental parameters as supplementary variables and PPCPs as active variables

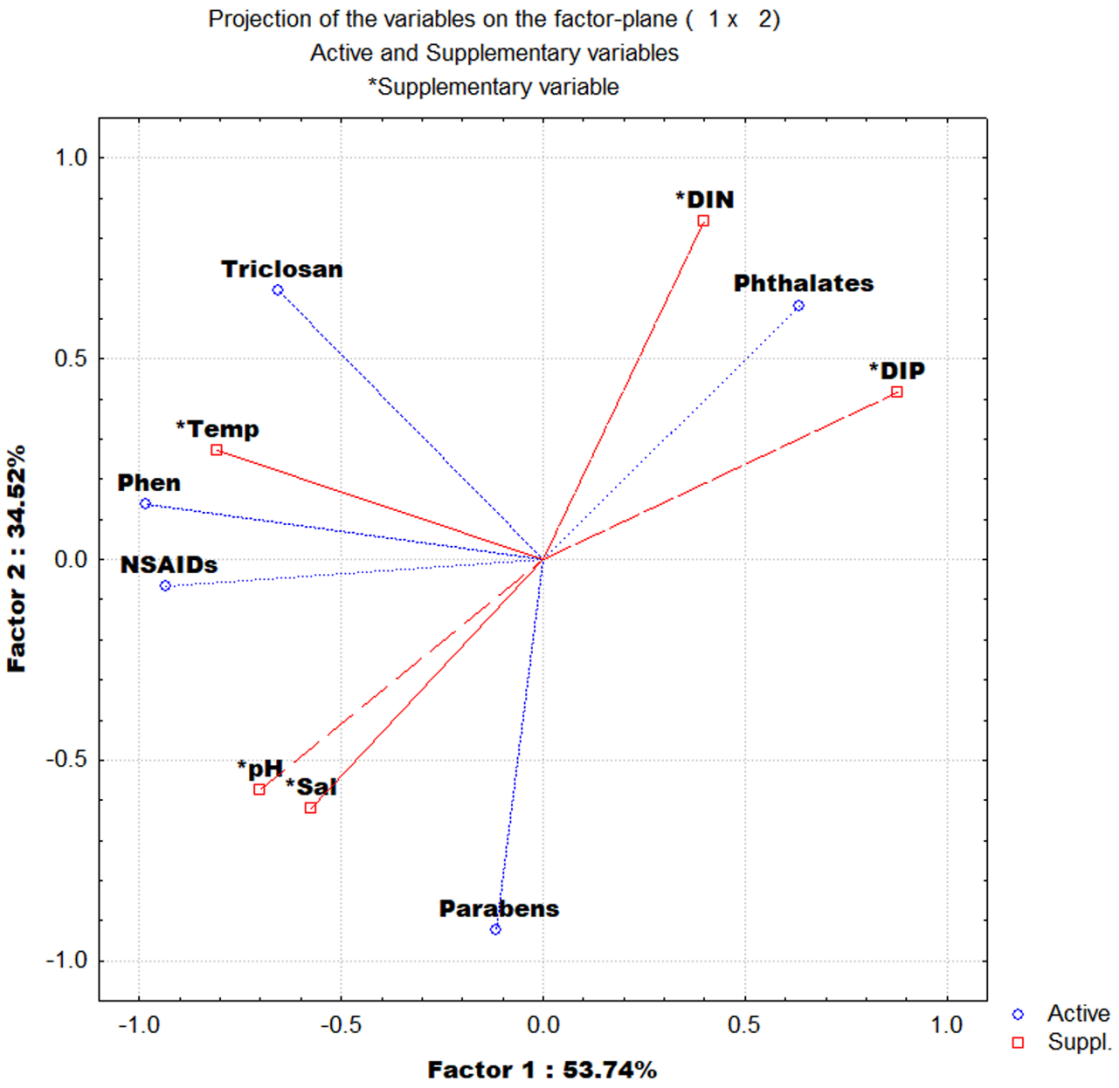

Table 1-Average values with standard deviation of PPCP concentration transect wise in Matla and Thakuran estuaries

PPCPs	Estuary transects	Matla	Thakuran
Phenolics (ng/L)	Upper	1206.86 ± 1514.69	169.81 ± 168.63
	Middle	814.11 ± 985.48	1469.59 ± 1756.90
	Lower	4586.26 ± 6607.29	1379.15 ± 1437.99
Triclosan (ng/L)	Upper	1613.33 ± 354.92	356.52 ± 0
	Middle	780.87 ± 7.99	95.65 ± 0
	Lower	1885.22 ±0	395.65 ± 0
NSAIDs (ng/L)	Upper	475.15 ± 243.66	349.36 ± 281.93
	Middle	536.58 ± 459.87	528.02 ± 376.24
	Lower	790.48 ± 902.80	617.33 ± 364.74
Phthalates (ng/L)	Upper	233.59 ± 194.58	211.63 ± 285.23
	Middle	237.10 ± 231.69	39.10 ± 34.28
	Lower	87.80 ± 70.45	158.4 ± 99.94
Parabens (ng/L)	Upper	47.70 ± 61.63	21.92 ± 9.28
	Middle	37.98 ± 48.55	215.44 ± 232.91
	Lower	48.14 ± 77.26	263.31 ± 294.15

Table 2-Average values with standard deviation of environmental parameters and PPCP concentration of Matla and Thakuran estuaries of post monsoon month.

Parameters	Matla	Thakuran
Water T°C	23.13±1.04	22.77±0.29
Sal	22.38±3.43	25.01±2.67
pH	8.13±0.21	8.21±0.13
DO (mg/L)	7.57±0.60	7.72±0.65
SPM (mg/L)	52.23±21.84	54.44±4.02
DIN (µM)	10.03±5.27	7.44±5.14
DIP (µM)	0.89±0.29	0.80±0.28
Phenolics (ng/L)	1704.85±1677.80	1006.18±725.73
Triclosan (ng/L)	1237.83±747.46	282.61±163.09
NSAIDs (ng/L)	548.18±198.89	498.24±136.44
Phthalates (ng/L)	217.64±79.05	136.38±88.34
Parabens (ng/L)	44.54±24.63	166.89±127.81

Table 3-Comparision of different derivatives of PPCP with other estuaries and rivers of the world

Study location	Emerging contaminants in water samples					Reference
Phenolics	OP	NP	BPA	BPS	BPF	
Pearl river estuary, South China	3.3-259	92-3950	24.9-811	NP	NP	Zhao et al (2009)
Dianchi lake, China	2.7-21.3	12.5-45.2	50.6-530.3	NP	NP	Wang et al (2012)
Kaveri, Vellar and Tamiraparani rivers, South India	ND-16.3	ND-2200	6.6-136	NP	NP	Selvaraj et al (2014)
Pearl river estuary, China	1.2-3.9	233-3352.8	12.4-62.7	NP	NP	Diao et al (2017)
Matla and Thakuran, Indian Sundarbans	282.2-17590.1	16.6-330.9	61.2-585.1	40.7-187.3	448.4-2288.5	Our study
Triclosan						
139 streams in US	140-2300					Kolpin et al (2002)
Hong Kong, China	15-110					Wu et al (2007)
Mississippi River, U.S.	8.8-34.9					Zhang et al 2007
Pearl river estuary, South China	8.1-247					Zhao et al (2009)
Guadalete river estuary, South-West Spain	27-310					Pintado-herrera et al (2014)
Tamiraparani, Cheranmahadevi and Tirunelveli, Tamil Nadu, South India	3800-5160					Ramaswamy et al (2011)
Matla and Thakuran, Indian Sundarbans	95.6-1885.2					Our study
NSAIDs	Naproxen	Diclofenac	Ibuprofen	Ketoprofen		
Pearl river estuaries, China	ND-328	8.3-114	ND-113	NP		Peng et al (2008) and Zhao et al (2010)
Sindian river, Taiwan	35.2-270	ND-56.5	ND-4350	ND-45		Lin et al (2010)
Rivers, Canada	ND-4500	ND-89	ND-6400	ND-79		Brun et al (2006)
Seine river estuary, France	<2.6-275	71-172	<2-610	<2.4-33.2		Togola and Budzinski (2007)
River, Poland	ND-753	ND-429	ND	ND-258		Baranowska and Kowalski (2011)

Ebro river basin, Spain	ND-109	ND-148	ND-541	ND-1060		Silva et al (2011)
Fyris river, Sweden	447	286	818	364		Daneshvar et al. (2012)
Tiber river, Italy	200-264	Nd-120	95-210	Nd-150		Patrolecco et al. (2013)
Vellar, Kaveri and Tamiraparani river, India	ND-28	ND-103	ND-200	ND-100		Shanmugam et al (2003)
Matla and Thakuran, Indian Sundarbans	73.9-114.4	71.2-543.4	476.2-776.8	614.6-2333.7		Our study
Phthalates	DMP	DEP	DBP	BBP	DEHP	
Dommel river, Netherlands	10-190	70-2300	70-3100	10-1800	900-5000	Vethaak et al (2005)
Eleven point, White, USA	NP	NP	140-4140	40-350	NP	Solı´s et al. (2007)
Muga, Fluvia, Ter, Besos, Llobregat, Ebro, Spain	NP	50-280	NP	<LOQ-20	120-4980	Sanchez-Avila et al. (2012)
Yangtze, China	<10–25	<10-211	105-286	10-21	<10-836	He et al (2011)
Seine, France	26-184	71-181	67-319	ND	160-314	Dargnat et al. (2009)
Kaveri river, India	ND-94	36-520	ND-372	5.4-145	ND-822	Selvaraj et al 2014
Matla and Thakuran, Indian Sundarbans	1.2-9.3	20-275.1	74.7-425.9	ND-6.1	60.5-494.8	Our study
Parabens	MeP	EtP	PrP	BuP		
South Wales, United Kingdom	0.3-400	0.5-15	0.2-24	0.3-52		Kasprzyk-Hordern et al (2008)
Pearl River Delta, South China	0-1062	NP	0-3142	ND		Peng et al (2008)
Sea near outfalls, Ria de Aveiro, Portugal	5.1-62	0.3-15	0.5-6.1	0.2-7.1		Jonkers et al (2010)
Beijing area, China	0.8-920	ND-294	ND-565	ND-41.5		Li et al (2016)
Jiulong River estuary,China	1.6-68.8	NP	0.4-69.9	ND		Sun et al (2016)
Kenting National Park, Hengchun Peninsula, Taiwan.	6.7-104	ND-2.8	0.7-56.2	ND-1.8		Kung et al (2018)

Pearl river Estuary, China	0.2-4.8	0.5-1.2	0.6-1.9	0.1-0.5	Zhao et al (2019)
Matla and Thakuran, Indian Sundarbans	9.5-23.8	23.7-501.1	0.1-27	19.6-421.7	Our study

NP not performed, **ND** not detected, **BDL** below detection limit, **LOQ** limit of quantification

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