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Plasticizers and bisphenol A in Adyar and Cooum riverine sediments, India: occurrences, sources and risk assessment

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Abstract Adyar and Cooum, the two rivers intersecting Chennai city, are exposed to serious pollution due to the release of large quantities of dumped waste, untreated wastewater and sewage. Sediments can act as repository for emerging organic contaminants. Hence, we have monitored the occurrence and risk associated with plasticizers [six phthalic acid esters (PAEs), bis(2-ethyl hexyl adipate) (DEHA)] and bisphenol A (BPA) in surface riverine sediments of Adyar and Cooum rivers from residential/commercial, industrial and electronic waste recycling sites. $\Sigma_7$plasticizers (PAEs + DEHA) in the Adyar riverine sediment (ARS) and Cooum riverine sediment (CRS)

varied between 51.82–1796 and 28.13–856 ng/g, respectively. More than three-fourth of $\Sigma_7$plasticizers came from bis(2-ethylhexyl) phthalate (DEHP), in accordance with the high production and usage of this compound. BPA varied between 10.70–2026 and 7.58–1398 ng/g in ARS and CRS, respectively. Average concentrations of plasticizers and BPA were four times higher in electronic waste (e-waste) recycling sites when compared with industrial and residential/commercial sites. BPA and DEHP showed a strong and significant correlation ($R^2 = 0.7; p < 0.01$) in the e-waste sites thereby indicating common source types. Sites present at close proximity to raw sewage pumping stations contributed to 70% of the total BPA observed in this study. For the derived pore water concentration of plasticizers and BPA, the ecotoxicological risk has been found to be higher in ARS over CRS. However, sediment concentrations in all the sites of ARS and CRS were much below the recommended serious risk concentration for human (SRC_{human}) and serious risk concentration for ecotoxicological (SRC_{eco}).

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Introduction

Plastics have become the material of choice, driving the global plasticizer market to reach an enormous amount of 15 billion US dollars in 2015. Approximately, two-third of the world's market share for plasticizers belong to Asia with a compound annual growth rate (CAGR) of 13% (Chemical Weekly 2009). Plasticizers like phthalic acid esters (PAEs) range between 10 and 60% by weight predominantly in polyvinyl chloride (PVC) materials (Hahladakis et al. 2018). In 2015, the global use of plasticizers was 8.4 million tons (MT), and bis(2-ethylhexyl) phthalate (DEHP) represented 37% of the global plasticizer market. Additives like bisphenol A (BPA) is used up to 3% by weight mostly in polycarbonate (71%) and epoxy resins (29%) (Huang et al. 2012). In 2010, worldwide BPA capacity was 5MT, and Asia was the largest producer contributing to 45% of the total capacity (Huang et al. 2012).

PAEs and BPA are potential endocrine-disrupting chemicals (EDCs) with the ability to impair the function of hormones at trace levels (He et al. 2009). Transcriptional changes induced by plasticizers and BPA through peroxisome proliferator-activated receptors (PPARs) have been found to induce cellular stress, developmental or growth impairments and reproduction alterations (Mathieu-Denoncourt et al. 2015). Only in certain countries in the European Union, few PAEs are banned from their use in toys and few cosmetic and personal care products (Ramirez et al. 2019). Six PAEs, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DnOP), are included as priority pollutants by the United States Environmental Protection Agency (USEPA) (USEPA 2014), the European Union (EU) (SCHEER 2019) and the Chinese water lists (Zhang et al. 2015). DEHP and BBP are classified by the USEPA as probable (group2B) and possible carcinogen (class C), respectively. Consequently, the usage of certain PAEs and BPA has been restricted to certain products especially those that come in contact with food (Centre for Food Safety 2012; European Commission 2011).

As PAEs do not share a chemical bond with the polymeric material, they are prone to leach out majorly during manufacturing and disposal, eventually becoming bioavailable to human beings and the environment (Cadogan et al. 1994). Unlike PAEs, BPA is chemically bound to the polycarbonate material; hence, leaching of BPA is facilitated only at elevated temperatures or under alkaline conditions (pH > 8) (Biedermann-Brem and Grob 2009). Typically, in developing countries, open burning of dumped waste (Chakraborty et al. 2019a), untreated wastewater and storm-water (Zhang et al. 2012) are reported to be the main sources of both BPA and PAEs in sediments.

Wastewater discharge from industries and domestic outlets coupled with flow dynamics of rivers were found to be the primary sources of both PAEs and BPA in surface riverine sediments in the lower stretch of River Ganga in India (Chakraborty et al. 2019a). Similarly, PAEs have been reported in surface sediments from Kaveri River (Selvaraj et al. 2015) and Cochin Estuary (Ramzi et al. 2018) in the south and Gomti River (Srivastava et al. 2010) in the northern part of India. PAEs were found up to 80.4 mg/kg in Chinese riverine sediments and were several orders higher in magnitude when compared with other organic pollutants (Zhang et al. 2018). High sediment concentrations of BPA were observed in Taiwan (up to 10.5 mg/kg) due to the discharge of wastewater from industries involved in the manufacturing and processing of BPA-based products (Huang et al. 2012). BPA concentration in riverine sediments from North America showed a drastic increase between 1996–2014 [39 ng/g dry weight (dw)] when compared with the concentration between 1996–2006 (3.4 ng/g dw) (Staples et al. 2018). However, in Europe, riverine sediments concentration of BPA remained approximately the same between 1996–2006 (259 ng/g dw) and 1996–2014 (177 ng/g dw) (Staples et al. 2018).

Sediments not only act as a sink but also play an intermediate role in pollutant conversion from environmental matrices to biological organisms (Mackintosh et al. 2004). In India, a major problem associated with the contamination of sediments is the discharge of wastewater directly into rivers where approximately 64% of the produced wastewater goes untreated (ENVIS Centre on Hygiene 2018). In Chennai city, due to the influence of electronic waste (e-waste) recycling activities, open burning of dumped waste, wastewater discharge and industrial emission, PAEs and BPA have been evidenced in the soil (Chakraborty et al. 2019b), surface water (Yamazaki et al. 2015) and air (Fu and Kawamura 2010; Sampath

et al. 2017). Although sediments can act as a sink as well as a secondary emission source for plasticizers and BPA, there is a paucity of data concerning the sediment pollution from Chennai city. Hence, we have monitored plasticizers (six PAEs and DEHA) and BPA in the Adyar riverine sediment (ARS) and Cooum riverine sediment (CRS) with the following objectives: (1) to study the spatial distribution along the residential/commercial, industrial and e-waste recycling sites of ARS and CRS, (2) to identify the sources using compositional profiling and site-wise variability and (3) to assess the risk to ambient organisms using predicted no-effect concentrations (PNEC) by converting sediment concentrations to equivalent pore water concentrations.

Materials and methods

Sample collection

Chennai is the third largest port city in India with a population of 4.6 million (2011 census) crisscrossed by two main rivers: Adyar and Cooum. Nearly 98% of the land area in Chennai is used for industrial, residential and commercial purposes (Guruge et al. 2017) due to the exponential increase in anthropogenic activities such as urbanization, industrialization, intertidal land reclamation, harbor activities and aquaculture. Altogether 36 surface sediment (0–10 cm) samples were collected using a stainless steel scoop from three different site types, viz. e-waste ($n = 3$), residential/commercial ($n = 23$) and industrial ($n = 10$) sites from Adyar and Cooum rivers (Fig. 1). Details of the sampling procedure are given elsewhere (Chakraborty et al. 2019a). Representative samples for each site were collected and wrapped in aluminum foil, stored at -20 °C until extraction. Sampling site details are given in Table S1 of the Supporting Information (SI).

Chemicals and reagents

A mixture of seven plasticizers including six PAEs, namely DMP, DEP, DnBP, BBP, DnOP, DEHP and one adipate (bis(2ethylhexyl) adipate (DEHA)) was purchased from Supelco Analytical (Philadelphia, PA, USA). BPA standard (99.99% purity) was purchased from Sigma-Aldrich. Isotope labeled standards of

$^{13}C_{12}$-DEHP, $^{13}C_{12}$-BPA were procured from Cambridge Isotope laboratories. Neutral silica gel (80–100 mesh) and alumina (100–200 mesh) were cleaned with dichloromethane using soxhlet apparatus for 24 h, and kept in an oven at 180 °C and 250 °C for 12 h, respectively. Anhydrous sodium sulfate was heated at 450 °C for 4 h. The filter paper was pre-cleaned with *n*-hexane using ultrasonication prior to use. All solvents including dichloromethane, *n*-hexane, methanol, acetone and other chemicals were of HPLC grade.

Extraction and clean-up

Plasticizers

Briefly, 20 g of homogenized air-dried sediment samples were taken and extracted using dichloromethane for 24 h at a rate of 4–6 cycles per h using a soxhlet extractor. For method blanks, empty thimbles were extracted. Concentrated extracts were cleaned and fractionated on a glass column packed with glass wool, silica gel, alumina and anhydrous sodium sulfate. Concentrated eluates of 1 mL were stored at 4°C until instrumental analysis.

BPA

Five grams of homogenized air-dried sediment samples were taken and extracted in microwave-assisted extraction vessels for 2 h with 25 mL of methanol using a CEM MARS 6 reaction system as explained elsewhere (Chakraborty et al. 2019a). Pooled extracts were concentrated to 1 mL and subjected to a clean-up procedure in a silica gel and anhydrous sodium sulfate glass column. Detailed description regarding the extraction and clean-up procedure is given in the SI. The final solution was reduced to 1 mL using nitrogen blow-down and derivatized by *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) prior to instrumental analysis.

Instrumental conditions

Plasticizers and BPA were detected and quantified using an Agilent 7890B gas chromatography coupled to a 5977A mass spectrometer equipped with an HP-5MS column (30 m × 0.25mmi.d. × 0.25 μm film thickness). The flow rate of the carrier gas (He, 99.99% purity) was kept constant at 1.5 mL/min.
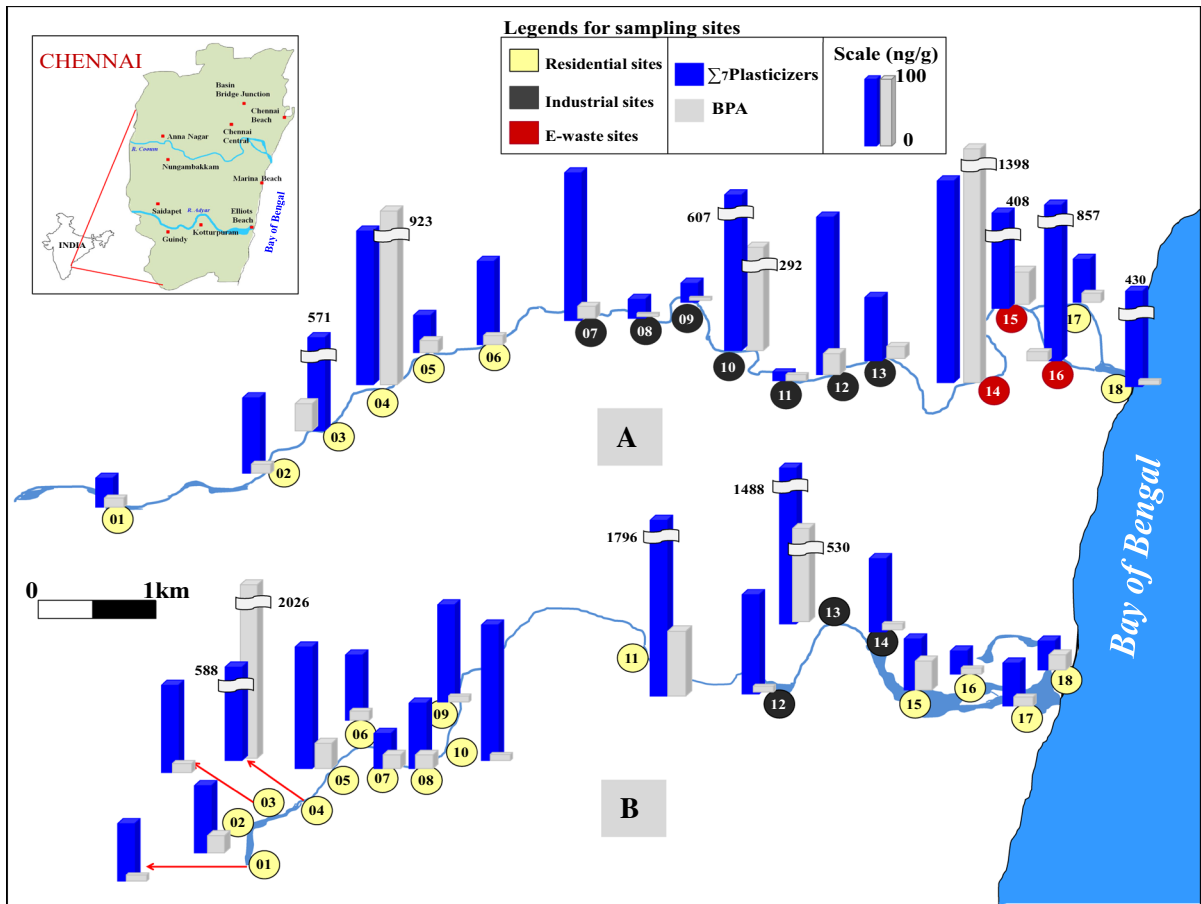
Fig. 1 Spatial distribution of $\sum_7$plasticizers (6PAEs + DEHA) and bisphenol A in riverine sediments of Cooum (**a**) and Adyar rivers (**b**)

Further details about the instrumental procedure are given elsewhere (Chakraborty et al. 2019a).

Quality assurance and quality control

Strict quality assurance and quality control procedures were followed during the analytical process in order to ensure accuracy in the results obtained. Limits of detection (LOD), limits of quantification (LOQ), mass fragments and precision values are given in Table S2. For every set of four samples, one blank sample was extracted and analyzed. Along with procedural blanks, instrumental blanks and spiked procedural blanks were run with a set of every ten samples. Surrogate recoveries for $^{13}C_{12}$-DEHP and $^{13}C_{12}$-BPA were 81–113% and 82–109%, respectively. Plasticizers and BPA were found in negligible levels in instrumental blank samples. Only minor concentrations of

DEHP and DBP were found in the procedural blanks and they were subtracted accordingly.

Determination of sediment organic carbon (SOC)

Sediment organic carbon (SOC) was calculated by the loss on ignition method given elsewhere (Chakraborty et al. 2019a). Briefly, oven-dried samples were weighed before and after combustion at 360 °C for 2 h in a muffle furnace.

Screening-level risk assessment

Risk quotient (RQ) was obtained using the method explained elsewhere (Chakraborty et al. 2019a). Briefly, Eqs. (1) and (2) were used to calculate the risk:

$$\text{Cporewater (ng/L)} = \frac{1000 \times \text{Cs (ng/g)}}{\text{Koc}} \times \%\text{ total organic carbon}$$

(1)

$$RQ = \frac{MEC}{PNEC}$$

(2)

where, Cs is the analyte concentration in sediments and Koc is the organic carbon partition coefficient. MEC is the measured environmental concentration and PNEC is the predicted no-effect concentration. RQ was calculated for each site and compound. Criteria for interpreting the RQ are given as follows: RQ < 0.1, "low risk"; RQ ranging from 0.1 to 1, "medium risk"; and RQ > 1, "high risk."

Human health risk assessment was compared to serious risk concentrations (SRC$_{human}$) available for DEP, DMP, DBP and DEHP based on the SEDISOIL model (Lijzen et al. 2001). The SRC$_{human}$ derived for aquatic sediments differs from that of soil due to differences in exposure routes. Further, an ecotoxicological risk assessment was carried out by comparing the concentration in sediment to the available ecotoxicological serious risk concentration (SRC$_{eco}$) for PAEs.

Data analysis

GraphPad Prism 8 software was used for graphical representation of PAEs and BPA concentration comparison with other studies. Statistical analysis including linear regression analysis and one-way ANOVA at 95% confidence intervals were used to understand the variability in the obtained dataset using SPSS version 22. The dataset was not normally distributed.

Results and discussion

Spatial distribution of seven plasticizers (6PAEs and DEHA) and BPA along the Cooum riverine sediment (CRS) and the Adyar riverine sediment (ARS) is shown in Fig. 1a, b. Overall concentration of six PAEs, DEHA and BPA in this study varied between 21.8–1792 (282 ± 386 ng/g; Avg ± SD), 0.28–29.96 (8.18 ± 5.63 ng/g; Avg ± SD) and 7.58–2026 (166 ± 425 ng/g; Avg ± SD), respectively (Table 1). DEHP and DBP contributed to more than 80% of the total PAEs in the present study. Similarly, a high percentage of these PAEs were observed in the riverine sediments from the local industrial zone of Kaohsiung Harbor, Taiwan (Chen et al. 2013), Pearl River in China (Liu et al. 2014), Jiangshu Province in China (Wang et al. 2014) and Indian rivers such as Kaveri in south India (Selvaraj et al. 2015), lower stretch of Ganga in the eastern part of India (Wang et al. 2014) and Gomti river in northern India (Srivastava et al. 2010). DMP, DEP and DBP varied between 6.81–369 ng/g (71.4 ± 92.9 ng/g; Avg ± SD) and 7.18–431 ng/g (57.7 ± 97.9 ng/g; Avg ± SD) in CRS and ARS, respectively. PAEs with relatively higher molecular weight (HMW; C_7–C_{13}), viz. BBP, DEHP and DnOP varied between 7.94–835 ng/g (182 ± 229 ng/g; Avg ± SD) and 18.5–1391 ng/g (252 ± 424 ng/g; Avg ± SD) in CRS and ARS, respectively. The low flow velocity of Adyar and Cooum rivers could facilitate the deposition of hydrophobic and particle-bound PAEs such as DEHP into the sediments as observed elsewhere (Yang et al. 2015). Both PAEs and BPA were found to have high accumulation probability toward carbon-rich substances and have low transport potential in sediments (Adeogun et al. 2015; Jiang et al. 2018).

SOC varied between 0.24 and 37.4% with the maximum level at a residential site in CRS (CM 03, Nerkundram, Table S1). It is noteworthy that no PAEs, DEHA or BPA showed any correlation with SOC. The absence of correlation between SOC and organic contaminants was previously reasoned due to the continuous influx of contaminants indicating a fresh source (Chakraborty et al. 2019a; Huang et al. 2018). Close to 216 discharge outfalls are present along the bank of both the rivers catering to a continuous fresh source of contaminants throughout the year. In addition, binding mechanisms of PAEs and BPA with sediment other than hydrophobic interactions with organic matter could be effective and responsible for the lack of correlation between each analyte and SOC. It is to be noted that the concentration of plasticizers and BPA did not show any statistical differences between ARS and CRS, thereby, implying similar source types. It is to be noted that these two rivers are within 20 km range and flow through the same city, therefore exposed to similar types of pollution sources.

Table 1 Concentrations of the seven plasticizers (6PAEs + DEHA) and BPA (ng/g) in riverine sediments of Adyar and Cooum rivers

Compounds	Range of concentrations (Avg ± SD) (ng/g)	
	Adyar ($n = 18$)	Cooum ($n = 18$)
Dimethyl phthalate (DMP)	3.55–32.1 (8.06 ± 10.6)	3.54–4.77 (4.05 ± 0.49)
Diethyl phthalate (DEP)	ND–377 (39.8 ± 95.0)	3.30–8.16 (4.33 ± 1.38)
Di-*n*-butyl phthalate (DBP)	0.86–49.4 (20.3 ± 14.2)	5.02–361 (66.5 ± 91.9)
Benzyl butyl phthalate (BBP)	7.57–8.27 (7.77 ± 0.26)	7.57–8.44 (7.78 ± 0.30)
Bis(2 ethylhexyl) phthalate (DEHP)	0.88–1383 (242 ± 424)	4.23–816 (172 ± 226)
Bis(2 ethylhexyl) adipate (DEHA)	0.28–30.0 (8.29 ± 7.16)	3.60–14 (8.08 ± 3.76)
Di-*n*-octyl phthalate (DnOP)	4.54–10.3 (6.08 ± 1.80)	4.36–10.4 (5.54 ± 1.73)
$\sum_7$plasticizers (6PAEs + DEHA)	51.8–1796 (159 ± 348)	28.1–857 (261 ± 234)
Bisphenol A (BPA)	10.70–2026 (167 ± 479)	7.58–1398 (164 ± 377)

Spatial distribution in Adyar and Cooum riverine sediments

Chennai contributes to 11% of the plastic waste produced in India. There are ∼ 84,584 small- and medium-scale industries in Chennai situated mainly in five taluks/subdistricts focusing majorly on electronics, rubber, plastic manufacturing, leather, textile and paper, all of which are potential sources for plasticizers (Chen et al. 2017) and BPA (Huang et al. 2012).

Cooum

The upper stretch of Cooum river (up to 27 km) is used for agricultural purposes; however, the middle and the lower stretch are exposed to serious pollution receiving approximately one-third of the wastewater produced from the Chennai city (Giridharan et al. 2009). Geomean of $\sum_7$plasticizers in CRS was 169 ng/g with more than 90% contribution from DEHP and DBP. The highest level of $\sum_7$plasticizers (with > 90% DEHP) was found at Park Town (CM16, 857 ng/g) located in close proximity to Pudupet, where previously maximum DEHP concentrations were observed in surface soils due to the informal e-waste recycling activities (Chakraborty et al. 2019b). Waste sludge disposal on the banks of the river from such informal e-waste recycling activities is a potential source of DEHP (Chakraborty et al. 2019a). Furthermore, low flow conditions can also facilitate high concentrations of PAEs in riverine sediments as observed in Taiwan (Huang et al. 2008). The high contribution of DBP

might be associated with the release of approximately 80 MLD of domestic wastewater into the Cooum river without any prior treatment as DBP was the dominant PAE in gray water from various household activities (Deshayes et al. 2017). It is noteworthy that the mean concentration of $\sum_7$plasticizers was two fold higher at sites located downstream of the river (CM16–CM18; 458 ng/g) near the mouth of the Bay of Bengal than the mean concentration of other sites (221 ng/g). The width of the Cooum river between sites CM16–CM18 was found to be substantially reduced (∼ 50 m) along with the presence of sand bars near the merging point of the river and the Bay of Bengal. Therefore, low flow conditions coupled with man-made construction, leading to the reduction in the dilution factor, might be the reason for elevated concentrations at the downstream of the river as observed in Qiantang River in east China (Sun et al. 2013). In CRS, BPA was detected in all the sites. The highest concentration of BPA was found at an e-waste site, Chintradipet (CM14, 1398 ng/g) followed by an industrial site AminjiKarai (CM10, 291.96 ng/g). Similar elevated concentrations of BPA were previously observed in the suburban transect of Hooghly riverine sediment in India, due to the presence of electronic scrap recycling industries (Chakraborty et al. 2019a). Crude methods used during pyrolysis of e-waste were found to be an important emission source of BPA in the e-waste sites of Chennai city (Chakraborty et al. 2019b). About two-thirds of the BPA loaded in CRS came from five sites, i.e., CM10–CM14. It is to be noted that this is the most polluted

stretch of Cooum river due to 130 discharge outfalls within a length of 6 km apart from the wastewater released from thousands of encroachments along the river bank. Such conditions in the river might have resulted in increasing the half-life of PAEs by 3–10 times (Sun et al. 2013).

Adyar

Adyar river estuary is one of the economically important and highly productive transition zones connecting Chennai city with the Bay of Bengal. Geomean of $\sum_7$plasticizers in ARS was 167 ng/g with major contributions from DEHP (83%) and DEP (13%), respectively. A large number of industrial effluents, strong sorption and prevalent anaerobic conditions might be responsible for elevated levels of DEHP (Yuan et al. 2002). Higher contribution from DEHP and DEP could be associated with the release of domestic/household waste from storm-water drains as > 60% of the total outfalls are connected to establishments in and around the area. The highest concentration of $\sum_7$plasticizers were observed at a residential site in ARS (AD 11, Thomas Nagar, 1796 ng/g), possibly due to the presence of a large number of plastic industries at close proximity. This belt comprises 2480 micro/small-scale plastic industries involved in molds and dyes, auto-components, electronic, packaging and transport and household items (MSME 2013). In addition, the highest level of DEP (377 ng/g) was also observed at this site, which could be associated with the release of gray water (Deshayes et al. 2017). The dominance of DEP over DBP as observed in ARS is consistent with Epe Lagoon, Nigeria (Adeogun et al. 2015) and Jiang Han Plain in China (Liu et al. 2010), possibly suggesting similarities in usage patterns.

BPA was found in all the ARS samples with a geomean of 34.5 ng/g. The highest concentration of BPA was observed in a residential site, Gowri Nagar (AD-04, 2026 ng/g). High BPA concentration in sediment samples was associated with municipal, industrial and sewage discharges (Mortazavi et al. 2013). The close proximity ($\sim$ 1 km) of AD-04 (Gowri Nagar) to a discharge outlet of a common effluent treatment plant (CETP) might account for the elevated concentration at this particular site. Furthermore, direct discharge of untreated domestic wastewater from the nearby pumping stations of sewage

treatment plants (STPs) might have also impacted such high BPA concentrations. The concentrations of both BPA and PAEs in CRS were slightly lower than those in ARS.

Comparison with other studies

Mean concentrations of 6 PAEs in ARS and CRS were comparable with studies from Kaveri River, India (Selvaraj et al. 2015) and Epe Lagoon, Nigeria (Adeogun et al. 2015), but were three folds higher than the mean concentration from the lower stretch of Ganga River (Chakraborty et al. 2019a) and Gomti River in India (Srivastava et al. 2010) (Fig. 2). Concentrations of PAEs, especially DEHP, were found to be much lower when compared with the Pearl River Delta in China (Hong Liu et al. 2014), False Creek Harbor in Vancouver (Mackintosh et al. 2006) and rivers from Taiwan (Huang et al. 2008) (Fig. 3).

The mean concentration of BPA in the present study was comparable with surface sediment concentrations of Elbe River, Germany (Stachel et al. 2005) and Marecchia River, Italy (Pignotti and Dinelli 2018) (Fig. 3). However, the average concentration in the present study was found to be much higher than Klang estuary in Malaysia (Omar et al. 2018), Hogsmill, Blackwater and Bourne Rivers in southern England (Wilkinson et al. 2018), Hooghly River in India (Chakraborty et al. 2019a) and Okinawa and Ishigaki Islands in Japan (Kawahata et al. 2004) (Fig. 3). Mean concentrations of both BPA and plasticizers in the present study were approximately three folds higher than the lower stretch of the Ganges in India (Chakraborty et al. 2019a), suggesting that low flow rates and lesser dilution might be the reasons for the higher BPA and PAEs levels in the current study. The concentrations of plasticizers and BPA were found to be lower or comparable to Chinese riverine sediments in recent times, especially those that are exposed to discharge of untreated sewage (Li et al. 2019). Apart from urbanization and river dynamics, usage and production patterns of these compounds can also play a vital role in the occurrence of plasticizers and BPA in riverine sediments.
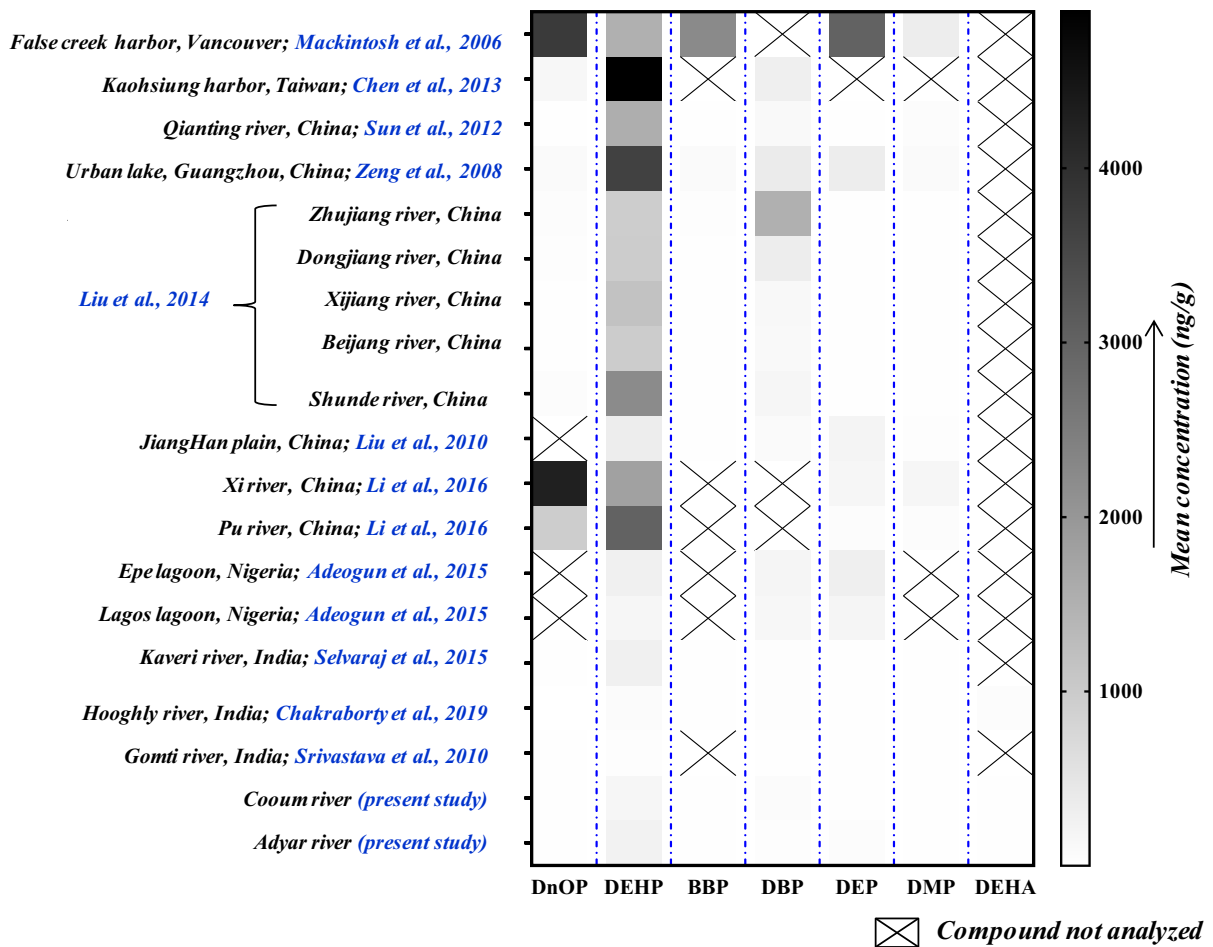
Fig. 2 Comparison between concentrations of seven plasticizers ($\sum_6$PAEs + DEHA) in the present study with other riverine sediment studies using GraphPad Prism

Compositional profiling and site-wise variability

The median concentration of $\sum_7$plasticizers in e-waste sites (407 ng/g) was nearly three times higher than industrial (150 ng/g) and residential sites (125 ng/g). Furthermore, residential and industrial sites were found to be significantly different ($p < 0.05$) from e-waste sites in this study. DEHP and BPA were found maximum in the e-waste zone with a four fold higher median concentration than industrial and residential sites (Fig. 4). Furthermore, a strong and significant correlation ($R^2 = 0.71$; $p < 0.01$) was observed between DEHP and BPA levels from e-waste sites suggesting a common source. In Chennai, DEHP and BPA were the predominant organic pollutants found to be associated with informal e-waste recycling workshops in surface soil

(Chakraborty et al. 2019b). This observation is in line with the concentrations found in the industrial corridor of Hooghly riverine sediment, marked with a plethora of e-waste scrap recycling industries (Chakraborty et al. 2019a). Nearly, half of DEHP and BPA burdens observed in this study stemmed from e-waste sites. A strong correlation between log-transformed concentrations of plasticizers in sediments and log K_{ow} values suggest that compounds with higher partition coefficients have a higher tendency to partition in the sediment phase (Lee et al. 2019). In the present study, a significant correlation was found between log concentrations of all plasticizers and their respective log K_{ow} values for both residential ($R^2 = 0.51$; $p < 0.05$) and industrial sites ($R^2 = 0.68$; $p < 0.05$). However, log-transformed concentrations in e-waste sites did not show any correlation with log K_{ow} values
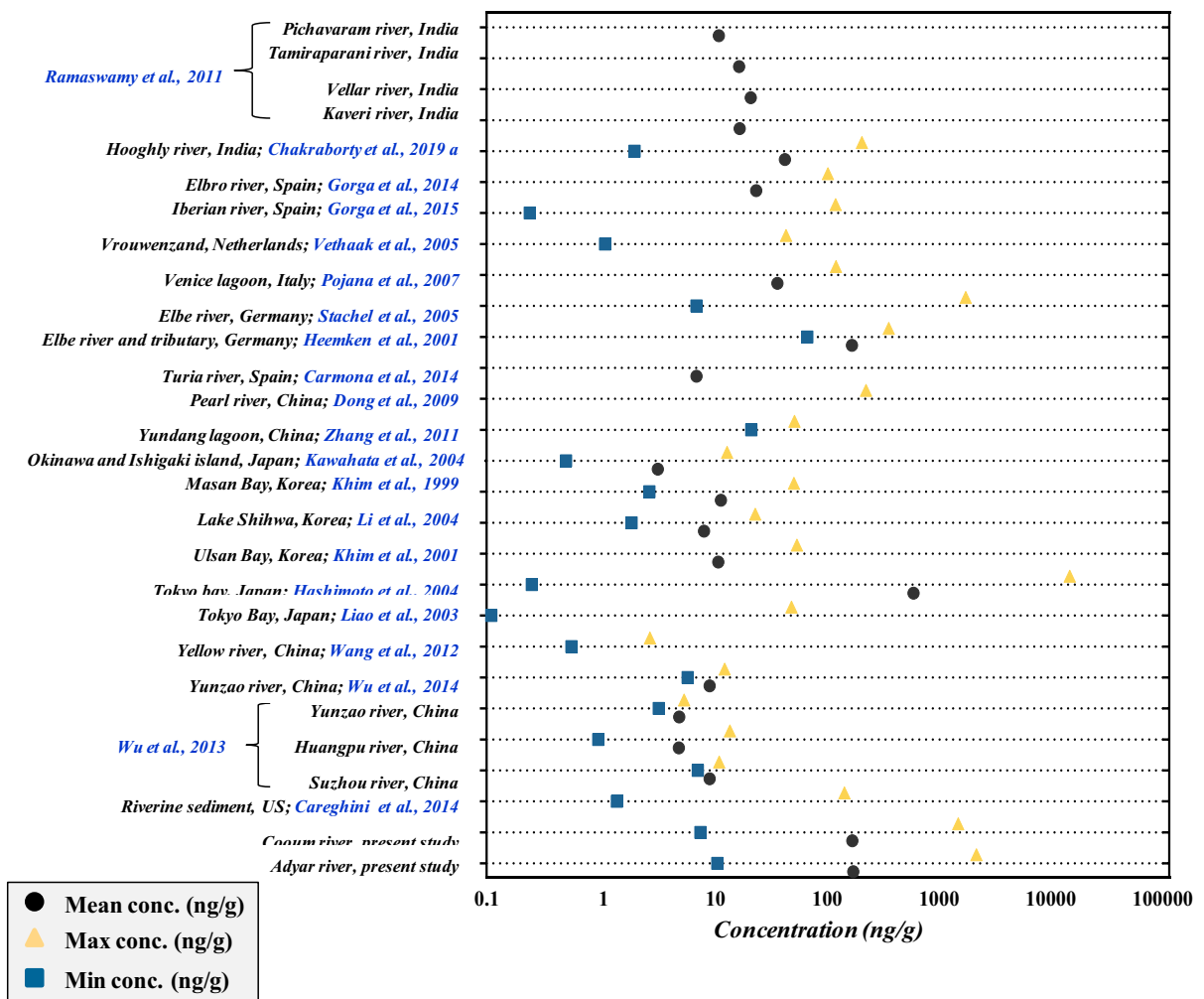
Fig. 3 Comparison between concentrations of bisphenol A in the present study with other riverine sediment studies using GraphPad Prism

suggesting fresh inputs of these compounds. This could be due to the dumping of sludges from e-waste recycling workshops in the river (Chakraborty et al. 2019a).

Industrial sites contributed to one-third of the total plasticizers found in this study with major concentrations of DEHP, BBP, DEHA and DnOP. Industrial emission is an important source of plasticizers and can release up to 114,000 kg/year of DEHP alone (Sidhu et al. 2005). By filling the interstitial spaces in the polymeric material, plasticizers can impart flexibility and enhance the workability of the material (Benjamin et al. 2015). Plasticizers are an important component of the packaging industries with DEHP alone found up to 61,013 µg/kg of the packaging material (Fierens

et al. 2012). The industrial area of Chennai is marked with 2500 small and large-scale packaging industries. Moreover, Chennai is one of the most important economic cities in India with its main focus on the automobile sector. Previously, a high concentration of DEHA and DnOP were observed in soil samples from Chennai city when compared with other metropolitan cities in India associated with automobile shredding residues (ASR) (Chakraborty et al. 2019b). Therefore, improper dumping of waste from various plastic molding and other polymer industries in close proximity in addition to ASR might have resulted in elevated concentrations of HMW-PAEs and DEHA in sediment samples from the industrial sites.
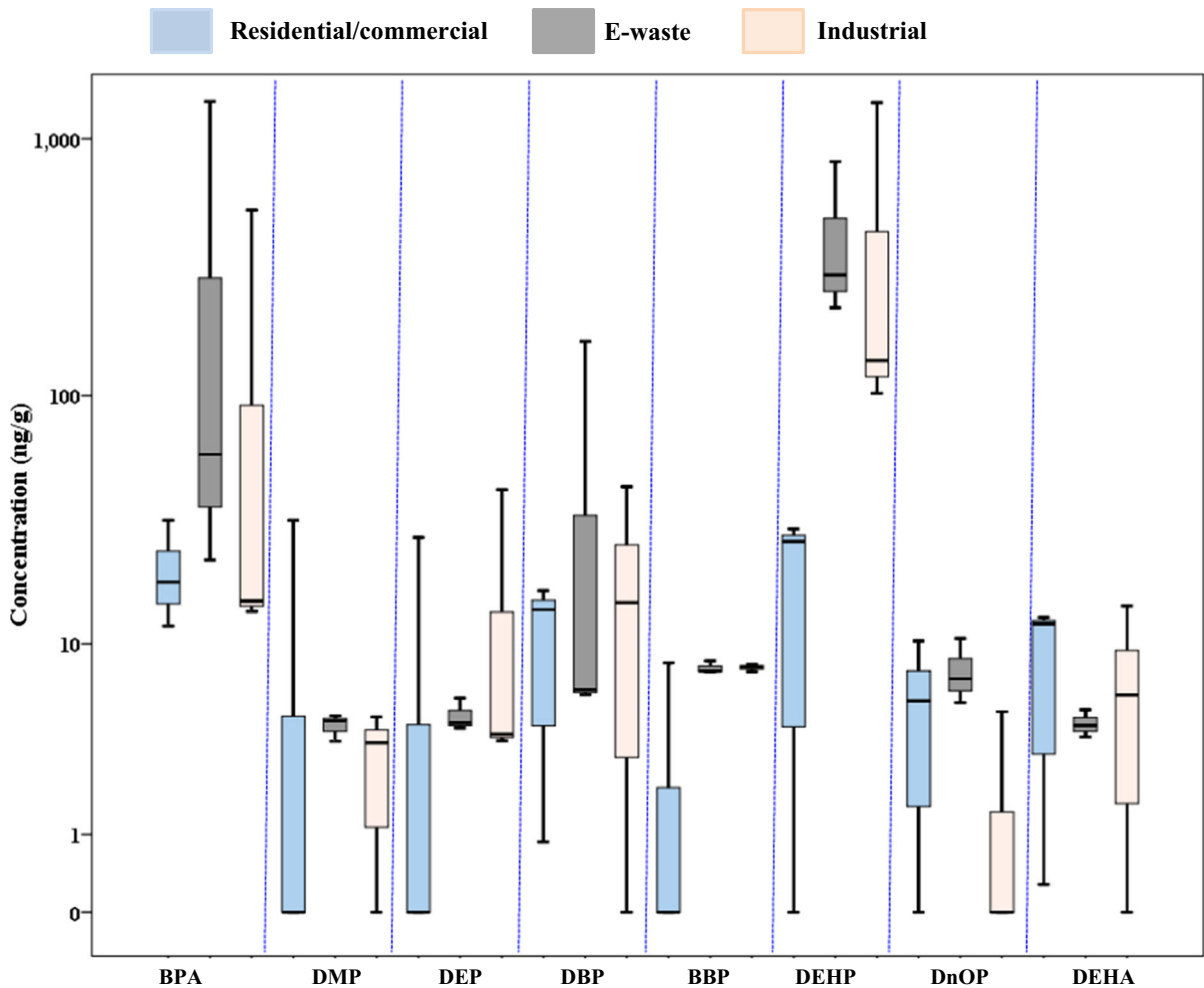
Fig. 4 Box whisker plots representing levels of seven plasticizers ($\sum_6$PAEs + DEHA) and bisphenol A in residential/commercial, industrial and e-waste transects along Adyar and Cooum riverine sediments

About one-third of DEHP and BPA in this study stemmed from residential sites. Uncontrolled open burning of domestic waste was found to emit over 75,000 kg/year of BPA and 2,500,000 kg/year of DEHP (Sidhu et al. 2005). In addition, the burning of waste containing plastics was previously reasoned for high concentrations of DEHP in atmospheric particulate matter from the Adyar residential sites (Fu et al. 2010). Further, high concentrations of both DEHP and BPA have been reported in dumpsite soil of Chennai city (Chakraborty et al. 2019b). Hence, we suspect that a high concentration of DEHP and BPA in residential sites might be due to refuse burning in open fires. In addition, almost 70% of BPA in the present study were from the sites situated nearby raw sewage

outlets from various STPs. BPA is used in various commercial and personal care products, and raw sewage can act as an important source of BPA in sediments. Large amounts of suspended solids might have further facilitated the deposition of BPA in surface riverine sediments (Flint et al. 2012). DEP and DBP are the predominant PAEs found in the domestic waste (Koniecki et al. 2011; Romero-Franco et al. 2011) and can contribute up to 54% of the total PAEs observed in gray water from various household activities (Deshayes et al. 2017). In the present study, the average concentration of DEP and DBP in the residential sites was two folds higher than the industrial sites. Higher concentrations of microplastics were reported in beach sediments along the downstream of

the Adyar and Cooum rivers due to domestic discharge, surface runoff and municipal dumping (Sathish et al. 2019). Leaching of DEP and DBP from microplastics can be a possible source of PAEs in this region (Ramirez et al. 2019). Therefore, apart from the discharge of domestic wastewater, shallow depth of the river might have facilitated the release of PAEs from microplastics in ARS and CRS.

Screening-level risk assessment

A screening-level risk assessment of PAEs and BPA was carried out for organisms from different trophic levels by converting the sediment concentration to equivalent pore water concentration. Fig. S1A and B shows box whisker plots representing the risk associated with PAEs to three trophic levels (Algae: *Pseudokirchneriella subcapitata*; crustacean: *Daphnia magna;* fish: *Lepomis macrochirus*). For both ARS and CRS, DEHP posed the highest risk to all three organisms among other PAEs. E-waste and industrial sites mainly contributed to the risk associated with PAEs in sediments. Among the study organisms, those belonging to a lower trophic level (algae and crustacean) had the highest median value of RQ. Though the PAE concentration was lower in CRS than in ARS, the RQ was found comparatively higher in CRS, mainly due to the DBP content especially at residential site CM18, where the highest concentration of DBP was recorded (360.53 ng/g). The predicted ecotoxicological risk assessment for BPA for a varied number of organisms, viz. porifera, cnidaria, mollusk, crustacean, arthropods, insects and fish is given in Fig. S2 A and B. Median values of RQ revealed that insects, fishes and molluscs were subjected to a higher risk by BPA when compared with other organisms. It is noteworthy that as the average concentrations of plasticizers and BPA were higher in the present study than Hooghly riverine sediments, the RQ of these contaminants for fishes was approximately two folds higher than the former (Chakraborty et al. 2019a). The major exposure routes of pollutants through sediments are dermal exposure and sediment ingestion. However, the concentration of PAEs observed in the present study was found to be much lower than the recommended SRC_{human} and SRC_{eco} for all the sites, thereby, suggesting that neither humans nor aquatic organisms were exposed to serious risks due to the observed concentration of PAEs in sediments.

However, risks posed to different sections of the trophic level due to synergistic effects of plasticizers cannot be ignored.

Conclusion

This study reports the distribution of $\sum_7$plasticizers (6 PAEs and DEHA) and BPA along two major rivers flowing through Chennai city. Elevated levels of BPA and plasticizers were mainly attributed to the high load of industrial and domestic wastewater activities in addition to the burning of plastic waste along both the rivers. E-waste sites showed the highest concentration of both plasticizers and BPA in riverine sediments when compared to both residential and industrial sites. Average concentrations of plasticizers and BPA were found higher in ARS than CRS primarily due to the presence of multifarious plastic related industries in and around the former river. Screening-level risk assessment showed that only a few residential sites were affected by the PAE concentrations, whereas BPA posed a greater threat primarily to the benthic community in the area. Although the concentrations of PAEs were found to be much lower than the given SRC_{human} and SRC_{eco}, further investigation is needed as a synergistic effect on the organisms influenced by a concoction of contaminants cannot be ignored. High average concentrations of BPA and plasticizers in riverine sediments from both the rivers might have resulted from the low water flows thereby reducing the dilution factor. The concentrations of plasticizers and BPA in sediments justify the need to restrict the discharge of wastewater into the two rivers. However, further studies to assess the sediments quality in Chennai city are necessary.

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