



GC–MS analysis and ecotoxicological risk assessment of triclosan, carbamazepine and parabens in Indian rivers

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ABSTRACT

Pharmaceutical and personal care products are used extensively worldwide and their residues are frequently reported in aquatic environments. In this study, antiepileptic, antimicrobial and preservative compounds were analyzed in surface water and sediment from the Kaveri, Vellar and Tamiraparani rivers, and in the Pichavaram mangrove in India by gas chromatography–mass spectrometry (GC–MS). The mean concentration of carbamazepine recorded in the Kaveri River water (28.3 ng/L) was higher than in the other rivers and the mangrove. Because carbamazepine is used only in human drugs, this may reflect the relative contributions of human excretions/sewage in these rivers. The mean triclosan level in the Tamiraparani River (944 ng/L) was an order of magnitude greater than in the other water systems, and the concentrations at two of the sites reported here (3800–5160 ng/L) are, to our best knowledge, among the highest detected in surface waters. Sediment levels were, however, comparable with other sites. We conclude that industrial releases are likely major contributors of triclosan into this river system. Among parabens, ethyl paraben was predominantly observed. Hazard Quotients suggest greater environmental risks for triclosan than for carbamazepine and parabens. This is the first study on antiepileptic, antimicrobial and preservatives in rivers and mangroves from India.

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1. Introduction

The presence of Pharmaceutical and Personal Care Products (PPCPs) in the environment and their possible effects on non-target organisms are of concern worldwide [1–4]. A large variety of PPCPs and metabolites thereof are continually introduced into the environment through human wastes by excretion, washings, manufacturing, etc. and are thus widely detected in aquatic ecosystems [4–11]. For example, carbamazepine (CBZ), a common antiepileptic drug, is usually poorly removed (~10% removal) by sewage treatment plants (STPs), and it therefore ends up in surface waters [8,9,12]. As CBZ is exclusively used by humans, its presence in natural waters can be used as an indicator of human urine and fecal contamination. Triclosan (5-chloro-2 (2,4-dichlorophenoxy) phenol-TCS) is an antimicrobial agent used in shampoos, soaps and medicated cosmetics, and other commercial products including textiles and plastics, to prevent microbial growth. As a result

of its ubiquitous use, TCS is widespread in aquatic environments [1,5,11,13]. Parabens are a group of *p*-hydroxybenzoic acid esters, with alkyl substituents ranging from methyl to butyl or benzyl groups. They are extensively used as preservatives and bactericides in many personal care products, as well as in food and pharmaceutical products, textile dyes and paints [14]. Several studies have confirmed the presence of parabens in river water [10,15,16], and there are ample reports available on the toxicity of CBZ, TCS and parabens to aquatic organisms [17].

The Kaveri (Cauvery) River, which is about 800 km long, is one of the major rivers in India. It originates at Talakaveri (11°9'N, 79°52'E) and flows southeast through the three provinces of India (Karnataka, Kerala and Tamil Nadu), and finally empties into the Bay of Bengal. The river basin is about 72,000 km² in area, has many tributaries and is densely inhabited (350 people/km²) [18]. The Vellar River originates in the Chitteri hills (11°25'N, 79°31'E) in Tamil Nadu state, flows along the southeast coast and forms an estuarine system with the Bay of Bengal at Parangipettai (formerly known as Porto Novo). The Pichavaram mangrove is a typical swamp, extending between the estuaries of Vellar and Coleroon, a distributary of the Kaveri River. The Tamiraparani River is a perennial river, originating from the Western Ghats in Tamil Nadu state. Its river delta is one of the most developed and populated regions in southern India. The river flows roughly east and debouches in the Gulf of Mannar,

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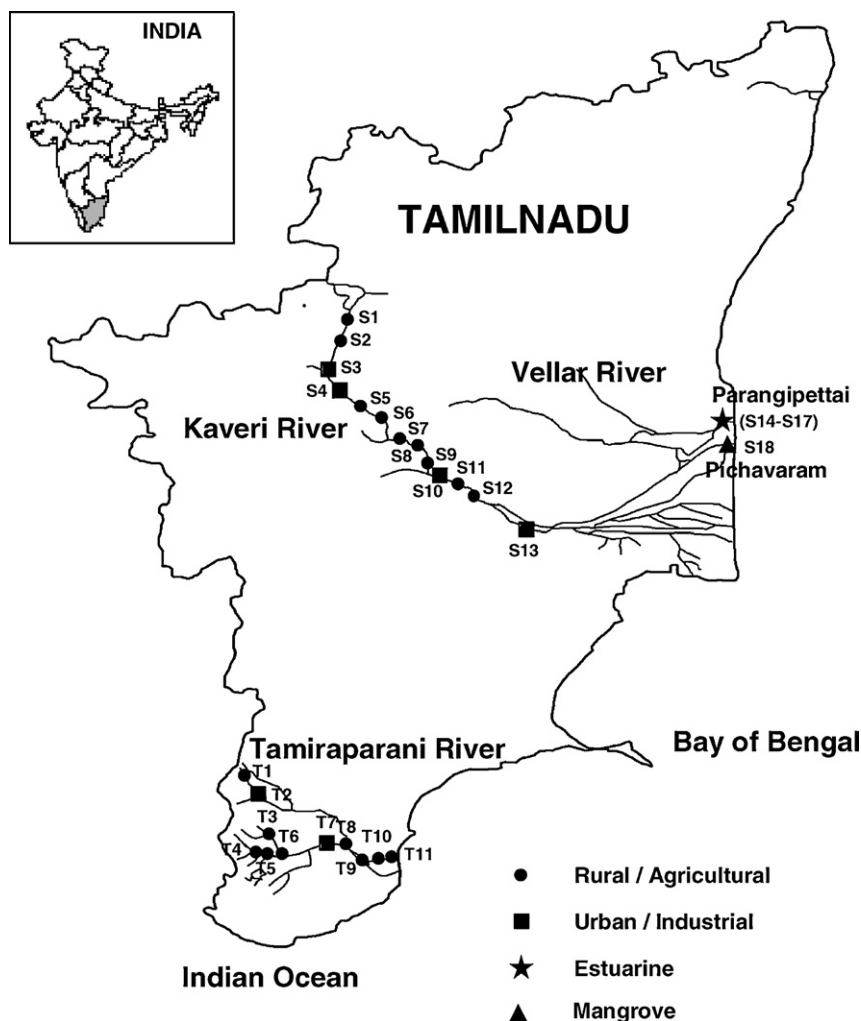


Fig. 1. Sampling sites of the Kaveri, Vellar and Tamiraparani rivers, India.

a Marine Bioserve, of the Bay of Bengal near Thoothukudi. These rivers have been supporting irrigated agriculture for centuries and serve as lifelines of southern India.

The water quality of these rivers has been affected due to the discharge of treated and untreated industrial wastes and agricultural runoff in addition to untreated domestic wastewaters throughout their stretch. Moreover, most of the Indian cities/towns are struggling to treat sewage as per the Central Pollution Control Board (Government of India) standard before disposing of it into the environment (natural streams, etc.). About 75% of the sewage, however, is still discharged in to local waterways without any treatment. If drinking water supplies are contaminated to a significant extent, human health effects cannot be excluded. Recently, the National River Conservation Plan (NRCP) of the Ministry of Environment and Forests, India, took up the task of installing sewage treatment plants (STPs) in most of the cities/towns close to major rivers. Furthermore, urbanization and industrial activities in the river basins have been on the rise for the past few decades. Although studies on pesticide [19–21], heavy metal [22–24] and radionuclide [25] pollution in these river systems are available, emerging contaminants like PPCPs have so far received no or little attention in India. Furthermore, hardly any published data can be found on the presence of these substances and/or the risks associated with their occurrence in the aquatic environment. An exception from this trend is the finding of antibiotics and other pharmaceutical residues in treated wastewaters from pharmaceutical industries located in the state of Andhra Pradesh, India [6,7]. Industrial activities have also contam-

inated ground, surface and drinking water in nearby villages [7]. In the present study, we attempted to determine the occurrence of CBZ, TCS and parabens (methyl-, ethyl-, propyl- and butyl-) in water and sediment from the Kaveri, Vellar and Tamiraparani rivers, and the Pichavaram mangrove in India using GC–MS, to understand the anthropogenic load and also to begin assessing the associated ecotoxicological risks.

2. Materials and methods

2.1. Study area and sample collection

Sampling sites and location details are shown in Fig. 1 and Table S1 (Supporting Information). Water and sediment samples were collected from 29 sites along the Kaveri (13), Vellar (4) and Tamiraparani rivers (11) as well as at the Pichavaram mangrove (1) after the northeast monsoon during January and February 2009. Sites were selected to represent both rural and urban environments, avoiding sampling in the immediate effluent plume from any local discharges, thus allowing discharges to mix with river water. Composite grab samples of water ($n=2$ per site) and sediment ($n=3$ per site) were collected in 2 L precleaned amber glass bottles and clean polyethylene bags, respectively, and transported on ice to the laboratory for chemical analysis (stored at 4 and -20°C for water and sediment samples, respectively). The details of glassware preparation were given in our recent paper [26].

2.2. Chemicals and standards

The reference standards of CBZ, TCS, methyl paraben-MeP, ethyl paraben-EtP, propyl paraben-PrP and butyl paraben-BuP, and the derivatizing reagent *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) were purchased from Sigma–Aldrich (USA). Phenanthrene-*d*₁₀ 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) and glass wool were obtained from HiMedia Laboratory Pvt. Ltd. (Mumbai, India). Silica gel (60–120 mesh) was procured from Merck Specialties Private Limited (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 2 mL were purchased from Agilent Technologies (Waldbronn, Germany). The Milli-Q water was obtained from Direct Q3-UV (Millipore, India).

2.3. Standard solutions

The individual standards of CBZ, TCS and all the parabens were prepared by dissolving 10 mg in 100 mL of an acetone:ethyl acetate (1:1, v/v) stock solutions. The working standard solutions for calibration and recovery spike were prepared from the stock standard solutions and stored at –20 °C.

2.4. Chemical extraction

2.4.1. Triclosan from water

Water samples were extracted according to the method of Nishi et al. [27] with minor modifications. Briefly, a 1000 mL sample was put into a 2 L separating funnel together with 10 g of NaOH and was shaken well. The solution was then washed with 50 mL of *n*-hexane with shaking for 10 min, after which the phases were allowed to separate. The aqueous phase was transferred into a separating funnel, after which the pH was adjusted to ~2. The aqueous phase was then extracted twice with 50 mL of *n*-hexane. Five grams of Na₂SO₄ (baked at 200 °C for 12 h) were added to remove moisture from the combined hexane extracts. The resultant solution was condensed to 1 mL using a rotary evaporator at 35 °C (BUCHI R-210, Switzerland) for silica gel cleanup.

2.4.2. Carbamazepine and parabens from water by solid phase extraction (SPE)

The SPE was performed as per the method of Peng et al. [16] with minor modifications. Briefly, the pH of each water sample (1000 mL) was adjusted to 7.0, and the solution was passed through preconditioned (each 6 mL of ethyl acetate, methanol and Milli-Q water in sequence) SPE cartridges at the rate of 5 mL/min. Then, the cartridges were washed with 5 mL of 5% methanol in Milli-Q water and were dried completely. Finally, analytes were eluted

with 15 mL of methanol:ethyl acetate mixture (1:1, v/v). The eluate was condensed using a rotary evaporator, dried by purging with N₂, reconstituted in ethyl acetate and subjected to silica gel clean up.

2.4.3. Triclosan from sediment

Sediment extraction was performed based on the method described by Okumura and Nishikawa [13] with some modifications. Briefly, the sediment was air-dried and precautions were taken to avoid contamination. After removing any plant debris and large particles, 10 g of air-dried homogenized sediment was mixed with 50 mL of acetone in an Erlenmeyer flask and was extracted for 12 h in an orbital shaker (Orbitek, India). The supernatant was then filtered through Whatman paper, and the residue on the filter paper was extracted twice with 25 mL of acetone. The combined extracts were taken in a 1 L separating funnel along with 500 mL Milli-Q water and 5 g of NaOH and were washed with 50 mL of *n*-hexane. The aqueous layer was processed as mentioned in the earlier section for the water sample (Section 2.4.1). Sediment TCS concentration was expressed on a dry weight basis.

2.4.4. Silica gel clean-up

2.4.4.1. Triclosan. Three grams of silica gel (baked at 200 °C, 12 h) was stirred with ~10 mL of *n*-hexane:acetone (1:1, v/v) to make a slurry and packed in a glass column (16 cm × 1.5 cm), after which Na₂SO₄ was layered (~1 cm) on the top and conditioned with 15 mL of the *n*-hexane and acetone mixture. The condensed extract was then eluted with 15 mL of the *n*-hexane and acetone mixture. The eluate was concentrated to 1 mL and stored in a vial at 4 °C until GC–MS analysis.

2.4.4.2. Carbamazepine and parabens. The silica gel clean up column was prepared as mentioned for TCS, but ethyl acetate was used for column conditioning and eluting the analytes instead of the *n*-hexane and acetone mixture. The eluate was condensed (0.5 mL) and subjected for derivatization.

2.4.5. MSTFA derivatization of CBZ and parabens

The advantages of derivatizing polar compounds for GC–MS analysis were elaborately described in our previous paper [26]. Briefly, the extracts (0.5 mL) were derivatized under the optimized conditions of 20 μL MSTFA at 70 °C for 30 min.

2.5. Instrumental analysis

Chemical analyses were performed using a gas chromatograph (GC-2010) interfaced with a quadrupole mass spectrometer (QP-2010) (Shimadzu Corporation, Japan). Detailed instrumental conditions have been described elsewhere [26]. The mass ions monitored for each compound are given in Table 1.

Table 1
Overview of physico-chemical characteristics and the GC–MS method showing correlation coefficient (R^2), precision ($n = 5$), LODs and recovery of PPCPs in surface waters.

Analyte	CAS number	Molecular weight	Log K_{ow} ^a	Water solu. ^b	Mass ions	R^2 ^c	Precision (% RSD)	LOD (ng/L)	Recovery (%) ($n = 3$)
Carbamazepine (CBZ)	298-46-4	236.3	2.45	112	193, 149, 165	0.999	0.58	1.6	102 ± 0.59
Triclosan (TCS)	3380-34-5	289.55	4.8	1.97–4.6	218, 288, 290	0.999	7.03	3.0	100.4 ± 7.3
Methyl paraben (MeP)	99-76-3	152.15	1.93	2.45	209, 224, 135	0.983	6.8	1.5	84.6 ± 5.7 ^d
Ethyl paraben (EtP)	120-47-8	166.18	2.19	0.96	223, 193, 238	0.997	4.05	0.5	81.1 ± 3.28
Propyl paraben (PrP)	94-13-3	180.2	2.71	0.39	193, 210, 195	0.999	3.89	0.6	90.9 ± 3.54
Butyl paraben (BuP)	94-26-8	194.23	3.57	<0.4	210, 195, 193	0.997	3.6	0.5	91.2 ± 3.28
							3.25	0.6	97.6 ± 3.17

^a At 25 °C and pH 7.

^b Water solubility in mg/L at 25 °C.

^c Linear range 50–250 ng/mL.

^d Sediment-ng/g dw.

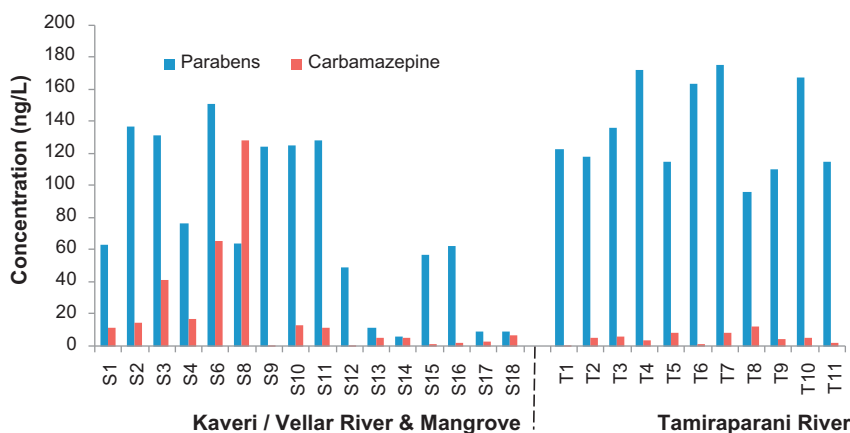


Fig. 2. Total parabens and carbamazepine in water (ng/L) from the Kaveri, Vellar and Tamiraparani rivers.

2.6. Quality control

Milli-Q water (1000 mL) and sediment (10 g) were spiked with 100 ng/mL of the TCS standard, and they were extracted and quantified as mentioned in earlier sections. The recovery, precision and limit of detection (LOD) for water and sediment samples are summarized in Table 1. Similarly, a 1000-mL sample of Milli-Q water spiked with CBZ and parabens (MeP, EtP, PrP and BuP) was analyzed as described for river water. The mean recoveries, precision and LOD with coefficients (R^2) of CBZ, MeP, EtP, PrP and BuP are given in Table 1. Duplicate analysis of samples was made at random to check the accuracy and precision of the data. Phenanthrene- d_{10} (100 ng/mL) was spiked into the final extract before analysis to check the GC-MS sensitivity. Blanks were run for each batch of five samples to find any contamination from chemicals and/or glassware.

2.7. Hazard quotients and ecotoxicological risk assessment

Environmental occurrence data of PPCPs in India and estimated risks for the local aquatic environments are scarce. The Hazard Quotient (HQ) is one way to express the ecological risk of a stressor [8,9,28,29]. In most risk assessment approaches; for example, those based on EMA (European Medicines Agency) guidelines, the HQ is calculated as the ratio between the Predicted Environmental Concentration (PEC) and the predicted no effect concentration (PNEC) [30,31]. Usually, the PEC in surface water will be calculated based on estimated or actual sales figures of pharmaceuticals [30]. Nevertheless, this exercise is very difficult for countries like India, where such data is difficult to retrieve and/or has a high degree of uncertainty. Using Measured Environmental Concentrations (MEC) instead of the PEC is an attractive option that we have adopted here which also reduces some of the uncertainties.

Hazard quotients of CBZ, TCS and four paraben compounds were therefore derived for the rivers and mangrove using the highest measured environmental concentration (MEC_{wat}) in the respective water systems, divided by the predicted no effect concentrations ($PNEC_{\text{wat}}$). The PNEC values were calculated based on chronic toxicity values and, if not available, the EC_{50} or LC_{50} values of acute toxicity tests obtained from the literature (Table S2 supporting information). If more than one value was available, then the lowest value was used. Safety factors of 1000 and 10 were used to divide the median effect or lethal concentration (EC_{50} or LC_{50}) and the chronic data, respectively, to arrive at the $PNEC_{\text{wat}}$ [SI 3].

3. Results and discussion

3.1. Carbamazepine in surface water

Carbamazepine levels in water from the rivers and the mangrove are shown in Fig. 2. The detection frequency is 100%, which shows that carbamazepine is prevalent in surface waters in India. Based on the consumption of CBZ, India occupies second place (115.5 ton in 2007) behind the USA, but is first place in Asia [32]. Carbamazepine is highly persistent and its removal efficiencies by STPs are usually below 10% [33]. The highest median concentration was found in the Kaveri River (13.0 ng/L), followed by the Tamiraparani River (5.14 ng/L) and the Vellar River (2.67 ng/L) (Fig. 3d); the maximum concentrations were 128, 12.2 and 5.72 ng/L, respectively. The higher concentration recorded in the Kaveri River is in accordance with a high population density in this river basin (350 people/km² [18]). The presence of CBZ in the Pichavaram mangrove water (6.65 ng/L) indicates the anthropogenic chemical input to this coastal mangrove environment, which is an important tourist attraction. CBZ has been detected in surface waters all over the world. For example, Gonzalez Alonso et al. [34] reported concentrations of up to 184 ng/L from rivers near Madrid in Spain, and Ginebreda et al. [8] found CBZ in 90% of samples with levels ranging from 80 to 3090 ng/L in the Llobregat River, Spain. Gros et al. [9] also observed 100% detection frequency in Ebro River, Spain, whereas Zhao et al. [12] reported 81% detection frequency with a maximum concentration of 43.1 ng/L in the Pearl River system in China. Carbamazepine levels in the Indian rivers are comparable with those found in the Pearl River in China, but lower than in the European rivers.

3.2. Triclosan in surface water and sediment

The triclosan concentration in water and sediment samples from the Kaveri River, Vellar River (estuary) and Pichavaram mangrove are shown in Fig. 4. Fig. 5 shows the concentrations in the Tamiraparani River. The TCS distribution pattern observed in water was (in decreasing order) the Tamiraparani River > Kaveri River > Pichavaram mangrove > Vellar River (estuary). This TCS distribution is quite different from the distribution of CBZ, which suggests an additional input of TCS other than human sewage. Generally, the TCS concentration in the surface water is greatly influenced by the input of wastewaters discharged from households, hospitals, industries and STP effluents. The TCS concentration (139 ng/L) in a water sample at Bhavani (S3) was higher than those in other locations. River Bhavani, a major tributary, might have

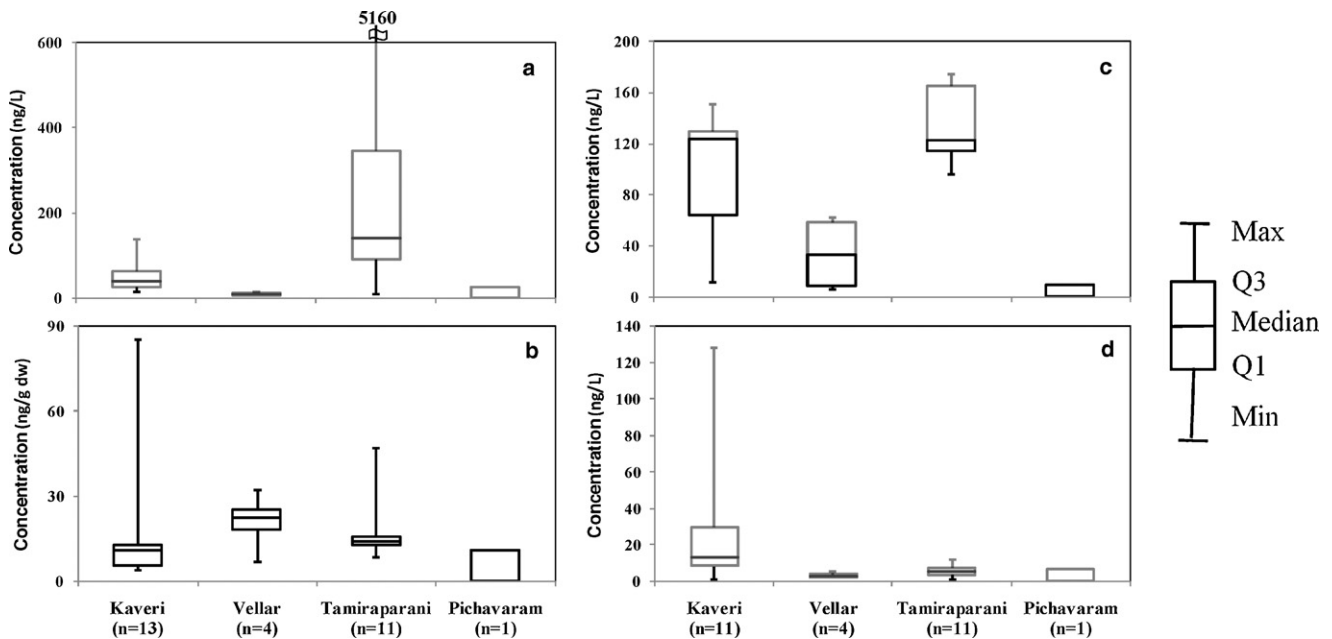


Fig. 3. Comparison of PPCPs levels in surface water (ng/L) and sediment among rivers in southern India (a. TCS in water; b. TCS in sediment; c. total paraben in water; d. carbamazepine in water).

been contaminated with industrial (textile, tanning and dyeing industries) effluents and community sewers, which joins the Kaveri River upstream just before Bhavani town. Furthermore, mixing of untreated household, textile, hospital and laundry unit wastewaters from the twin towns (Bhavani and Komarapalayam) with a total population of about 100,000 might also be a reason for the somewhat higher observed levels. The second highest concentration (102 ng/L) was obtained at Vangal (S9), and it cannot be explained easily by household sewage, as this is a small village which only has a population of a few thousands.

In the Tamiraparani River, the highest concentrations were found at Cheranmahadevi (T6) (5160 ng/L) followed by Tirunelveli (T7) (3800 ng/L), about 20 km downstream from T6. The median concentration of 142 ng/L is considerably higher than the median concentrations observed for the Kaveri (40.7 ng/L) and Vellar (8.95 ng/L) rivers, respectively. These findings suggest that, in addition to domestic sewage, industrial activities contribute significantly to the TCS load in the Tamiraparani River system. The TCS concentration at Cheranmahadevi (population: ~16,000) is probably attributed to the influence of industrial (including textile mill

effluents) activities upstream of this site, leading to contamination of the river as far down as Tirunelveli. Indeed, TCS is used extensively in textiles to impart odor-protection properties, by inhibiting the growth of bacteria and fungi, and to eliminate house dust mites. It is also used in the manufacturing of plastics as an antimicrobial additive to protect articles from deterioration, odors and discoloration. Pothitou and Voutsas [35] reported TCS concentrations of 85 and 188 ng/L in influents and 82 and 25 ng/L in effluents of the textile and tannery industries, respectively, in northern Greece. The levels of TCS found in the Tamiraparani River are, to the best of our knowledge, among the highest found in surface waters. Kolpin et al. [5] found concentrations of up to 2200 ng/L in US surface water.

Unlike water concentrations, the TCS distribution in sediments of the four water systems are similar. The mean concentrations are 21 ± 10.5 ng/g for the Vellar estuary, 16.8 ± 22 ng/g for the Kaveri River, 16.6 ± 10 ng/g for the Tamiraparani River and 11 ng/g for the Pichavaram mangrove. The median concentration of TCS in sediments from all the three rivers (Kaveri, Tamiraparani and Vellar) was 11.0, 14.0 and 22.5 ng/g, and the maximum concentration was 85.3, 46.87 and 32.1 ng/g, respectively. Exceptionally elevated TCS

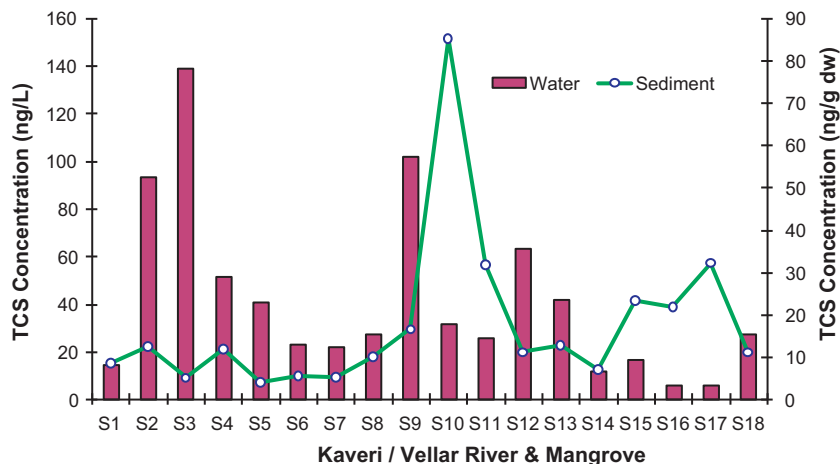


Fig. 4. Triclosan in water (ng/L) and sediment (ng/g dry wt.) from the Kaveri and Vellar rivers, India.

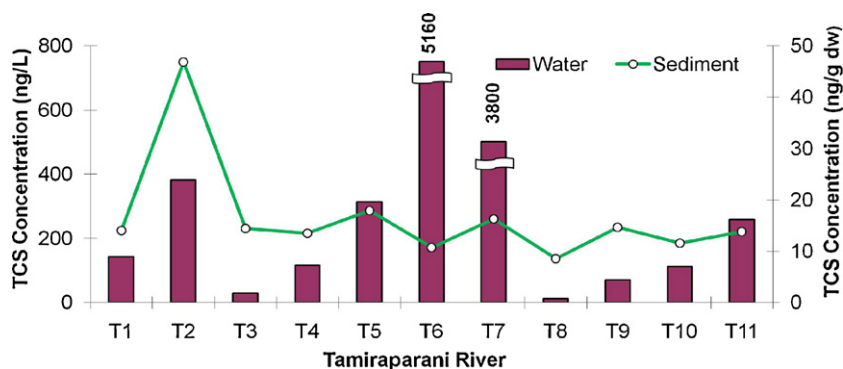


Fig. 5. Triclosan in water (ng/L) and sediment (ng/g dry wt.) from the Tamiraparani River, India.

concentrations in surface water from two (T6 and T7) out of 11 sites in Tamiraparani are, however, not reflected by increased levels in the respective sediments (Fig. 5). This difference may be explained by a non-continuous release of TCS near Cheranamahadevi. It is also possible that the sediment here does not act as an important sink for TCS. As a comparison, the water (mean) concentration of TCS in the Vellar estuary is, on average, about five and two times lower than in the Kaveri River and Pichavaram mangrove, respectively, and an order of magnitude lower than the Tamiraparani River. As TCS is highly lipophilic, the sinking and/or settling rates of particulates, as well as the degradation rates, may differ between environments, making the interpretation somewhat difficult. We did not analyze the total organic content of the sediments, which could have further aided the interpretation. Studies on the influence of salinity on TCS distribution will also help to understand the fate of personal care products in estuarine or marine ecosystem. The concentrations found in this study are somewhat higher than reported sediment levels from the Tama River, Japan (1.7–4.6 ng/g) [13] and Swiss lakes (<2 ng/g) [36], but are comparable with the Hudson River estuary, USA (9–37 ng/g) [37] and lower than in the Pearl River, China (<LOQ to 1329 ng/g) [11].

3.3. Parabens in surface water

The main sources of parabens for the aquatic environment are STP effluents, and wastewaters from hospitals and industries (like textile manufactures, tanneries, etc.). The concentrations of total parabens are shown in Fig. 2 for each of the sampling sites. The percentile concentrations of total parabens from the rivers are shown in Fig. 3c. The median concentration of total parabens in the Kaveri and Tamiraparani rivers was almost identical (124 and 123 ng/L, respectively), but was one order of magnitude lower in the Vellar River (33.2 ng/L). The concentration of methyl paraben ranged from ND to 22.8 ng/L, ND to 14.8 ng/L and ND to 3.43 ng/L in the Kaveri, Tamiraparani and Vellar rivers, respectively. The highest concentration of MeP was found in the Kaveri River (22.8 ng/L) at Bhavani (S3) where an elevated TCS level was also found. Ethyl paraben was quantified in all of the water samples, and ranged from 5.93 to 142 ng/L, 88.9 to 147 ng/L and 2.47 to 58.7 ng/L in the Kaveri, Tamiraparani and Vellar rivers, respectively. The highest concentration (147 ng/L) of the Tamiraparani River was obtained at Tirunelveli (T7). The elevated levels here may reflect the anthropogenic input of treated and/or untreated sewage, and wastewaters from industries and hospitals from the city, which has about 410,000 inhabitants. Propyl paraben was quantified at only three sites from the Kaveri River (ND to 57.0 ng/L) and five sites from the Tamiraparani River (ND to 38.6 ng/L), but not at all in the Vellar River (estuary). In mangrove waters, neither MeP nor BuP was quantified. Compared to other parabens, BuP was quantified at very low concentration with low detection frequency (14%) in this study.

Similarly, Kasprzyk-Hordern et al. [38] did not detect BuP in water from the River Taff, UK, but found MeP (10–48 ng/L) as the most abundant paraben followed by EtP (4–8 ng/L). Although MeP and PrP are the predominantly used preservatives in PPCP formulations, their concentrations were lower than those of EtP. Based on the median concentrations of total paraben, the following distribution trend was observed: Kaveri River (124 ng/L) = Tamiraparani River (123 ng/L) > Vellar River (33.23 ng/L) > Pichavaram mangrove (9.19 ng/L). Many studies have reported the presence of parabens in aquatic environments. Peng et al. [16] found only MeP (ND to 1062 ng/L) and BuP (ND to 2142 ng/L) from the Pearl River, China. Jonkers et al. [15] reported median concentrations of 5, 0.1, 0.6 and 0.3 ng/L for MeP, EtP, PrP and BuP, respectively, from the Glatt River, Switzerland. The same authors also detected all four parabens in surface water from the rivers of Ria de Aveiro, Portugal [10]. In this study, the concentrations of parabens were low when compared to the Pearl River, China, but comparable or higher than in the Glatt River, Switzerland and the rivers of Ria de Aveiro, Portugal. Furthermore, comparable levels of MeP but elevated levels of EtP were observed in this study by comparison to a study from the River Taff, UK [38]. This difference shows that natural waters in developing countries may have comparable/elevated levels of selected PPCP residues to those found in many more developed countries. For PPCPs that are more effectively removed by STPs, one could speculate that somewhat higher levels could be expected in countries like India due to the relative lack of advanced effluent treatment facilities.

3.4. Ecotoxicological risk assessment

The HQs of CBZ, TCS and parabens derived for fish, amphibian, crustaceans, mussel, ciliate, microalgae and plankton are summarized in Table S3 (Supporting Information) and Fig. 6. PNECs derived mainly from chronic, EC₅₀ and/or LC₅₀ values are listed in Table S2 (Supporting Information). The outcome of such analyses is of course dependent on the nature of the bioassays used to derive PNECs; i.e., what organisms are used, whether the tests are acute or chronic and whether they include sensitive and relevant endpoints. Nonetheless, given the available toxicity data, TCS is suggested to pose a higher risk for aquatic life at all sites than CBZ and parabens. Particularly high HQs for TCS (Fig. 6b) were found in the Tamiraparani River. In contrast to most drugs with human targets, TCS exhibits a high toxicity to many lower trophic organisms, such as microalgae [39]. For example, Wilson et al. [40] reported significant changes in phytoplankton community composition in stream communities exposed to TCS concentrations as low as 15 ng/L and ~33% reduction in algal genus richness at 150 ng/L. Most studies show very low toxicity of TCS to vertebrates, however, Veldhoen et al. [3] reported effects of TCS on thyroxin-induced metamorphosis in frog tadpoles at a concentration as low as 150 ng/L. Peak levels

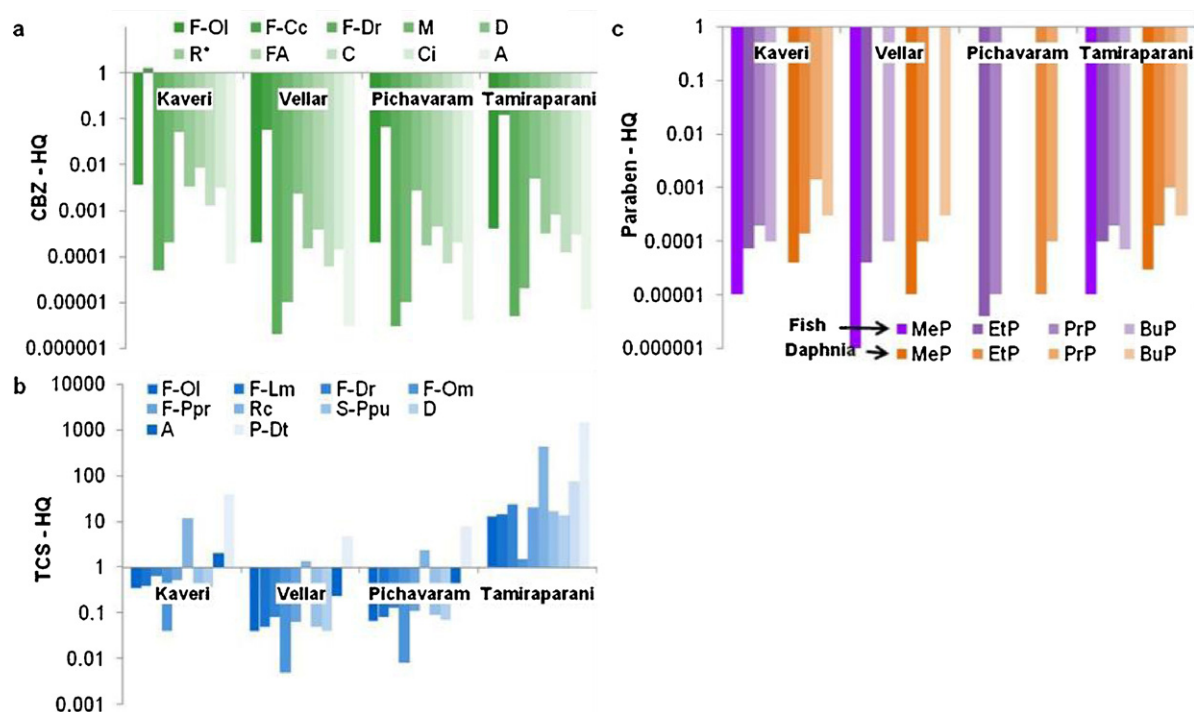


Fig. 6. PPCPs Hazard Quotients (HQ) derived for the rivers in India (a. Carbamazepine, b. Triclosan, c. Parabens) (F – Fish; OI – *Oryzias latipes*; Dr – *Danio rerio*; Lm – *Lepomis macrochirus*; Cc – *Cyprinus carpio*; Om – *Oncorhynchus mykiss*; M – Mussel; Ppr – *Pimephales promelas*; R – Rotifer; Rc – *Rana catesbeiana*; S – Shrimp; Ppu – *Palaemonetes pugio*; D – *Daphnia magna*; FA – Freshwater Amphipod; C – Cnidarian; Ci – Ciliate; A – Algae; P – Phytoplankton; Dt – *Dunaliella tertiolecta*).

of 3800 and 5160 ng/L at two of the sites in the Tamiraparani River indicate a high risk of impact on local algal communities, with possible effects extending to other trophic levels of the ecological web. Although assessing risks for inducing microbial resistance mechanisms in microbes by extensive TCS exposure is outside the scope of this paper, this possibility should not be ignored [41].

Carbamazepine did not seem to cause any health risks for any of the organism groups, based on available chronic toxicity data and the highest MEC of each water system (Fig. 6a). The effects on fish, however, may be an exception, as Triebkorn et al. [42] reported effects of CBZ on the ultrastructure of the kidney, liver and gills at a concentration of 1000 ng/L. The highest level that we found in this study was 128 ng/L (S8-Velur, Kaveri River). More targeted tests, for example, on the behavior of aquatic vertebrates, will likely contribute further to our understanding of the potential ecological effects of CBZ.

Even lower HQs (Fig. 6c) were found for the parabens from all river systems, based on toxicity data for fathead minnow, *Pimephales promelas* and the water flea, *Daphnia magna*. There are, however, considerably fewer toxicity studies of parabens in aquatic organisms on which to base the assessments [43].

4. Conclusions

Measurable levels of CBZ, TCS and parabens observed in the Kaveri River, Vellar River/estuary, Pichavaram mangrove and Tamiraparani River demonstrate the contamination of natural (surface) waters in India by PPCPs. To our knowledge, this is the first report of these PPCPs in Indian rivers. The surface water levels of TCS at two sites in the Tamiraparani River were very high. The elevated levels of TCS at these sites can probably not be fully explained by contamination from household sewage alone, and considerable contributions from industrial effluents are likely. The Hazard Quotients indicate a plausible environmental impact of TCS on microalgae and possibly on other organisms, particularly in the Tamiraparani and Kaveri River ecosystems. Managing the pollu-

tion of surface waters from wastewater generation due to rapid urbanization and industrialization is a great challenge for developing countries like India. Rivers are the most important drinking water sources in India and almost no STPs have been equipped to completely treat the wastewaters generated from the cities/towns situated along the entire river stretches till today. In this context, the present report will provide vital information on what the expected levels of contamination are for different PPCPs in surface waters, thus providing input to future wastewater management in India.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.12.037.

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