

Phthalate esters in water and sediments of the Kaveri River, India: environmental levels and ecotoxicological evaluations

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Abstract Phthalate esters are well known for their environmental contamination and toxicological effects as “endocrine disruptors.” In this study, environmental levels of phthalate esters and ecotoxicological risk assessments were performed in one of the major rivers in India, the Kaveri. Water and sediment samples were collected during 2010–2012 representing the major stretch of the river and extracted by solid-phase and ultrasonic methods, respectively, and analyzed for six major phthalates by using a gas chromatograph–mass spectrometer. The analytical recovery for phthalates in water and sediment ranged from 79 to 121 %. Results indicated that diethyl phthalate (DEP) and dimethyl phthalate were found in every sample, whereas butylbenzyl phthalate and diethylhexyl phthalate (DEHP) were detected in 92 % of the water samples. Likewise, in sediment samples, DEP was found most often (94 %). The total phthalates in water samples ranged from 313

to 1,640 ng/l, whereas in sediments it was 2 to 1,438 ng/g dw (dry weight) with DEHP having the highest concentration. Human health risk assessment based on drinking water consumption showed no potential risk for phthalates and also DEHP levels were safe with respect to USEPA guideline (6,000 ng/l). Further, DEHP and di-*n*-octyl phthalate levels in water were expected to pose little threat to sensitive organisms in the riverine ecosystem as per ECOSAR chronic values. In case of sediment, the DEHP concentration was well above the USEPA sediment guideline value. To our knowledge, this is the first study to describe the levels and ecotoxicological risks of phthalates in Kaveri River, India.

Keywords Phthalates · Sediment · Kaveri River water · Health risk assessment · Endocrine disruptors

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Introduction

Plasticizers are known for their immense use in formulation and the manufacture of plastic products are now considered to pose environmental threats via multiple mechanisms including endocrine disruption. Phthalates are plasticizers mainly used to increase plasticity or fluidity of plastic products (mainly polyvinyl chloride) which has an extensive usage in gelling agents, stabilizers, dispersants, lubricants, binders, and emulsifying agents, etc. (USEPA 2012).

Therefore phthalates are found in a variety of end-application such as packaging, children's toys, adhesives and glues, paints, pharmaceutical and personal care products, detergents, textiles, vinyl flooring, electronics, medical devices (Latini 2005). Phthalates in Indian toys were detected up to 16.2 % mass (Johnson et al. 2011). Global plasticizer consumption is estimated to be 6.4 million tons with 52 % being consumed by the Asia Pacific region itself and phthalates account for 87 % of the produced plasticizer (Cullen 2012). In India, data on phthalate production is unavailable, however phthalic anhydride (the major raw material of phthalates) production during 2012–2013 was 225,262 metric tons, in addition to the imported quantity of 43,420 metric tons (DGOS 2013). Due to substantial worldwide use, phthalates were ubiquitously found in the atmosphere, sewerage, storm water, soil, natural waters, as well as sediment (Berge et al. 2013; Hongjun et al. 2013; Martine et al. 2013; Teil et al. 2013).

The large-scale production and consumption of consumer products resulted in unavoidable exposure of phthalates by human and wildlife at elevated levels (Oehlmann et al. 2009; Casals-casas and Desvergne 2011). Exposure to phthalate(s) via oral intake for prolonged periods may cause serious health issues such as birth defects (reduced anogenital distance in baby boys), altered semen quality, hormonal and endocrine disruptions (premature breast development, shortened gestation, fertility, testicular dysgenesis, childhood social impairment, obesity), asthma, breast cancer, etc. (Colon et al. 2000; Casals-casas and Desvergne 2011). Furthermore, effects on receptors such as insulin receptor (Rengarajan et al. 2007), aryl hydrocarbon receptor, and androgen receptor (Kruger et al. 2008), and other cellular targets (Mankidy et al. 2013) have been well elucidated. The USEPA (2012) has classified DEHP under probable human carcinogen (Class B2) and BBP under possible human carcinogen (Class C). Due to the potential risk, some phthalates (including DEHP, DBP (dibutyl phthalate) and BBP) have also been restricted/banned in the inclusion of toys and childcare articles sold in the United States (CPSIA 2008), European Union (Directive 2005/84/EC), and Canada (Hazardous Product Act 2010). Although few phthalates have been banned for use in cosmetics in Asia and the United States, the majority of them are not restricted at all. As a proactive measure, Chemsec, an international non-profit organization, has included 11

phthalates (DEHP, DBP, BBP, DEP, and six others) in their latest "Substitute It Now!" (SIN) chemical list (Chemsec 2013).

Ecotoxicological studies of these phthalates showed plausible effects on aquatic organisms at environmental concentrations (i.e., ng/l to $\mu\text{g/l}$) and so their potential effect on wildlife populations may not be ruled out (Oehlmann et al. 2009). Especially, sediments may act as an ultimate repository of these contaminants entering water resources that are mostly insoluble in water (Petrovic et al. 2001). For instance, DEHP-exposed (0.01–10.0 $\mu\text{g/l}$) eggs of Medaka fish resulted in increased mortality, decreased body weight, and distortion of sex ratio in embryos (Chikae et al. 2004). Recent findings demonstrated that DBP and DEP (5–500 $\mu\text{g/l}$) could induce antioxidant and immune responses in zebra fish embryos (Xu et al. 2013).

Rivers are vulnerable to emerging pollutants released through anthropogenic activities. In developing countries like India, where the riverine systems are known to receive wastewaters, the water quality is worse in the majority of the rivers (CARDS 2011; Ramaswamy et al. 2011). Although classical organohalogen (chlorinated pesticides, PCBs, and PBDEs) contamination and risk assessments have been well studied in environmental and biological matrices (Chakraborty and Zhang 2012; Takeoka et al. 1991), very little is known on the phthalates esters, and therefore the health status of rivers is still not fully understood. One of the important rivers in southern India is the Kaveri, known to serve humankind for centuries. Due to agricultural, industrial, and urbanization activities, contaminants such as pesticides, heavy metals, radionuclide, and various organic pollutants have already been addressed in this river (as cited in Ramaswamy et al. 2011). Very recently, studies pertaining to emerging contaminants such as pharmaceutical and personal care products and phenolic compounds in this river were reported by us (Ramaswamy et al. 2011; Selvaraj et al. 2014; Shanmugam et al. 2014). However, phthalates have not been studied in this river so far. Therefore, the present study was aimed to determine the phthalates in water and sediments from the Kaveri River with respect to spatial and temporal scale. Further, a preliminary aquatic and human-health risk assessment for understanding the environmental safety status of the river with respect to phthalates was performed for the first time in India.

Materials and methods

Study area and sample collection

The river subjected in this study, the Kaveri (Cauvery), originates at Talakaveri (11°9'N, 79°52'E) of Western Ghats in India. Having a stretch of 800 km, the major part of the river runs down through the provinces of Karnataka and Tamil Nadu, before joining the sea at the Bay of Bengal. This is considered one of the most important and largest rivers in southern India because its basin covers an area of 81,155 km² (i.e., 2.7 % of the country's land). Importantly, about 50 % of its drainage area lies in Tamil Nadu province (CARDS 2011) and is highly exploited (95 % abstraction of water) for multiple purposes such as irrigation, drinking, and industrial processes.

The water and sediment samples were collected during March 2012 (dry season). The archived sediment samples (March–April 2010 and 2011) were also included for analysis. The sampling includes 16 locations (Fig. 1) covering the major part of the Kaveri River basin (14 riverine and two estuarine), starting from Mettur Dam (R1; Stanley reservoir) to debouching place at Muthupet (R15) and Picharavarm

(R16). The details of the sampling locations are provided in Table S1. The surface-water samples were collected using amber glass bottles (1 l) prewashed successively with detergent, tap water, ultrapure water, and sample water. Grab samples of sediment were collected in clean polypropylene bags. The sample collection point was always set away from convergence of wastewater/effluent outlet. The sampled locations comprise rural and urban environments, which were in the proximity to agricultural areas, cities, and industries. The collected samples were placed in iceboxes and immediately transferred to the laboratory where water samples were stored at 4 °C and extracted within a week, and sediment samples were stored at –20 °C until chemical extraction.

Preparation of stock standards and chemicals

Stock solutions of phthalates in ethyl acetate were prepared from EPA phthalate esters mix (4S8231) procured from Supelco Analytical (Philadelphia, PA, USA). Internal standard, Phenanthrene d-10 was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The solvents (ethyl acetate and methanol) and other chemicals used were of HPLC and analytical grade, respectively. Sodium

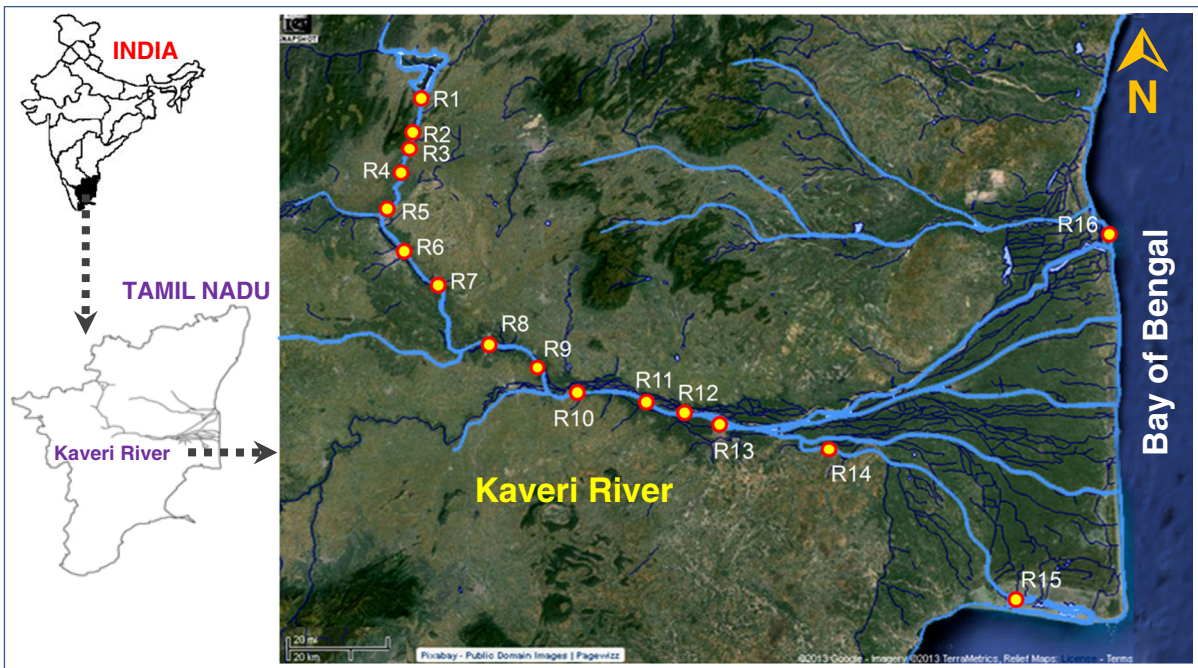


Fig. 1 Map showing the water and sediment sampling locations of Kaveri River, India

sulfate, silica gel (60–120 mesh), and glass wool were baked at 200 °C overnight before use.

Preparation of glassware

All glassware was sequentially washed with 10 % soap solution (Laboline, Fischer Scientific India Pvt. Ltd., Mumbai) and tap water, and rinsed with 50 % hydrochloric acid and ultrapure water (ELGA, USA). The washed glassware was air dried, covered with aluminum foil (Hindalco, Mumbai), and sterilized in a hot-air oven (Heco, Chennai, India) at 200 °C overnight. While processing the water samples, precautions were taken to avoid contact with plastics to minimize the background concentration of phthalates.

Extraction of phthalates from water

Extraction of phthalates from water samples was performed by solid-phase extraction (SPE) according to the method of Wang et al. (2005) with minor modifications. Briefly, the water sample (500 ml at pH 7) was passed through a preconditioned C18-E cartridge (1,000 mg/6 ml; Phenomenex, Torrance, CA, USA) at a flow rate of 5 ml/min in a vacuum manifold (Phenomenex). Then the loaded cartridge was dried and subsequently eluted with 20 ml of ethyl acetate. Then, the eluate was dehydrated using anhydrous sodium sulfate, condensed, and transferred to 2-ml glass vials with a Teflon-lined screw cap for gas chromatograph–mass spectrometer (GC–MS) analysis.

Extraction of phthalates from sediment

One gram of dried and homogenized sediment was mixed with 20 ml of ethyl acetate in an amber glass bottle (20 ml capacity), and covered with aluminum foil. The sample was then sonicated for 30 min in an ultrasonicator (33 kHz, 100 W; PCI Analytics, India). After extraction, the solvent fraction was decanted into a conical flask and sodium sulfate (1 g) was added to dehydrate it. Finally, the extract was condensed completely and reconstituted with 1 ml ethyl acetate before being analyzed in GC–MS with/without column cleanup.

Column cleanup

The sediment extract (1 ml in ethyl acetate) from ultrasonication was introduced onto a silica gel

chromatographic column to remove interfering molecules. The glass column (1.3 cm dia. × 24 cm length) was packed with glass wool at its base and 2 g of silica gel slurry in 15 ml of ethyl acetate. Anhydrous sodium sulfate was added above the silica gel (1 cm). The column was then washed with 20 ml of ethyl acetate and the sediment extract was loaded on to column and eluted with 20 ml of ethyl acetate. The final eluate was condensed to 1 ml and transferred to a glass vial for GC–MS analysis.

Instrumental conditions

The quantification of phthalates was performed using GC–MS (QP-2010; Shimadzu, Japan) working in the electron impact mode at 70 eV. Analyte separation was achieved with Rtx column (60 m × 0.25 mm i.d., 0.25- μ m film thickness) with the following conditions: the injection port temperature was held at 280 °C; the column temperature was initially held at 150 °C for 1 min and then raised to 300 °C at 8 °C/min and to 320 °C at 7 °C/min and held for 10 min. Sample injection (1 μ l) was performed using AOC-20i auto sampler in the splitless mode and with helium (99.999 % purity) as the carrier gas. The transfer line and ion source temperatures were set as 270 and 230 °C, respectively. MS was operated in full-scan mode from m/z 35–500 for qualitative analysis. Acquisition for quantitative analysis was carried out in the single-ion monitoring mode along with two characteristic ions (Table 1). Furthermore, quantification was performed with an external calibration method.

Quality assurance and quality control

The SPE extraction method for water was validated by spiking 500 ng of phthalate standard mix in 500 ml of river water. Similarly, 1 g of sediment was spiked with 100 ng of phthalate standard mix for the validation of ultrasonic extraction. The obtained mean recovery was satisfactory (water) and good (sediment) for the adopted methods. The external calibration method showed linear correlations ($R^2 > 0.999$) for all phthalates from the 1–200 μ g/l range. The limit of detection (LOD) and limit of quantification (LOQ) for individual phthalates were estimated based on a signal-to-noise ratio of 3 and 10 times, respectively. For every set of five samples, blank was run to check for

Table 1 QA/QC parameters for phthalates extraction and analysis

Phthalate	CAS no.	Log K_{ow}^a	Target ions (m/z)	Retention time (RT)	Linearity R^2	LOD ($n = 7$) ng/ml	LOQ ($n = 7$) ng/ml	Sediment recovery (%) (100 ng/g) ($n = 3$)	Precision (% RSD)	Water recovery (%) (1,000 ng/l) ($n = 3$)
Dimethyl phthalate (DMP)	131-11-3	1.6	163, 164, 133	8.77	0.999	0.80	2.68	85	11.1	109
Diethyl phthalate (DEP)	84-66-2	2.42	149, 177, 150	10.4	0.999	0.47	1.55	108	7.3	118
Di- <i>n</i> -butyl phthalate (DBP)	84-74-2	4.5	149, 150, 104	15.13	0.999	0.75	2.49	105	5.9	121
Butylbenzyl phthalate (BBP)	85-68-7	4.73	149, 206, 123	20.25	0.999	1.22	4.07	108	6.2	33
Di-2-ethylhexyl phthalate (DEHP)	117-81-7	7.27	149, 167, 150	21.27	0.999	0.94	3.15	79.4	7.4	116
Di- <i>n</i> -octyl phthalate (DOP)	117-84-0	8.1	149, 150, 279	23.49	0.999	0.75	2.49	93	8.9	45

^a Ellington and Floyd (1996)

interferences and/or cross-contamination. The recovery, precision (% RSD), LOD, and LOQ are given in Table 1. The standard and sample chromatograms are shown in Fig. S1.

Human health risk assessment

The exposure levels and risk of phthalates in local population were calculated by using the Eq. (1) (USEPA 1989).

$$AE = (C_w \times IR \times EF \times ED)/(BW \times AT) \tag{1}$$

where AE ($\mu\text{g}/\text{kg bw}/\text{day}$) is the contaminant exposure to adult through ingestion of drinking water, C_w ($\mu\text{g}/\text{l}$) represents concentration of phthalate in drinking water, IR (ingestion rate) is the daily water intake in liters, EF (exposure frequency) is the number of days (365) exposure in a year, ED (exposure duration) is designated as lifetime in years (i.e., 70), BW (body weight) of adult is assumed as 60 kg and AT is averaging time, i.e., $ED \times 365$ days.

From the calculated AE, the hazard quotient (HQ) was derived to estimate non-carcinogenic risk (USEPA 1989) as per Eq. (2).

$$HQ = AE/RfD \tag{2}$$

where RfD represents individual phthalate reference dose as given in USEPA (2013). The RfD for DEP, DBP, BBP, DEHP, and DOP were 800, 100, 200, 20, and 10 $\mu\text{g}/\text{kg}/\text{day}$, respectively.

Further, to estimate overall non-carcinogenic risk posed by all phthalates, their respective HQs were summed and expressed as hazard index (HI). Like HQ, $HI > 1$ indicates potential adverse health effects (Wu et al. 2010).

Freshwater and sediment risk assessment

The aquatic risk assessment as risk quotient (RQ) was calculated as per formula (4), the ratio between the measured environmental concentration (MEC) and predicted no effect concentration (PNEC) of aquatic organisms, which is detailed elsewhere in our earlier studies (Ramaswamy et al. 2011; Selvaraj et al. 2014; Shanmugam et al. 2014).

$$RQ = MEC/PNEC \tag{3}$$

where the detected maximum concentrations of phthalate in water were regarded as the MEC ($\mu\text{g/l}$). For calculating the PNECs, the lowest chronic toxicity of green algae, daphnia, and fish was selected and an assessment factor of 10 was applied to it. The predicted chronic toxicity values for the organisms were obtained through ECOSAR (v1.1) software based on a structure–activity relationship (USEPA 2011). The MEC/PNEC ratio >1 indicates the given substance of concern, whereas the ratio <1 suggests no significant concern.

Further, the sediment risk assessment was performed by comparing the measured sediment concentration with screening benchmark values (SCB) of phthalates given by USEPA (2006).

Results and discussion

Experimental design

The study was aimed to estimate phthalate levels in water and sediments of rivers and to evaluate its potential risk to aquatic species and humans. Initially, the performance of solid-phase extraction and ultrasonication method for phthalates extraction from water and sediment, respectively were carried out. Then the methods were used to extract phthalates and further quantified in GC–MS. The results thus obtained were used to understand the abundance and spatio-temporal variation of phthalates in the Kaveri River. Further, the concentrations were applied in formulas 1–3 to calculate the risk of phthalates to humans and aquatic organisms.

Performance of method

The extraction method for water showed recovery of 109–121 % for phthalates, except for BBP (33 %) and DOP (45 %), which gave low recovery (Table 1). For sediment, the extraction method without column clean up gave good recovery in the range of 79.4–108 % (Table 1). However, it was noticed that recoveries for BBP (186 %) and DEHP (121 %) levels were beyond the acceptable range. Such background concentration may be due to usage of more solvent and glassware in the experiment as opined by Petrovic et al. (2001).

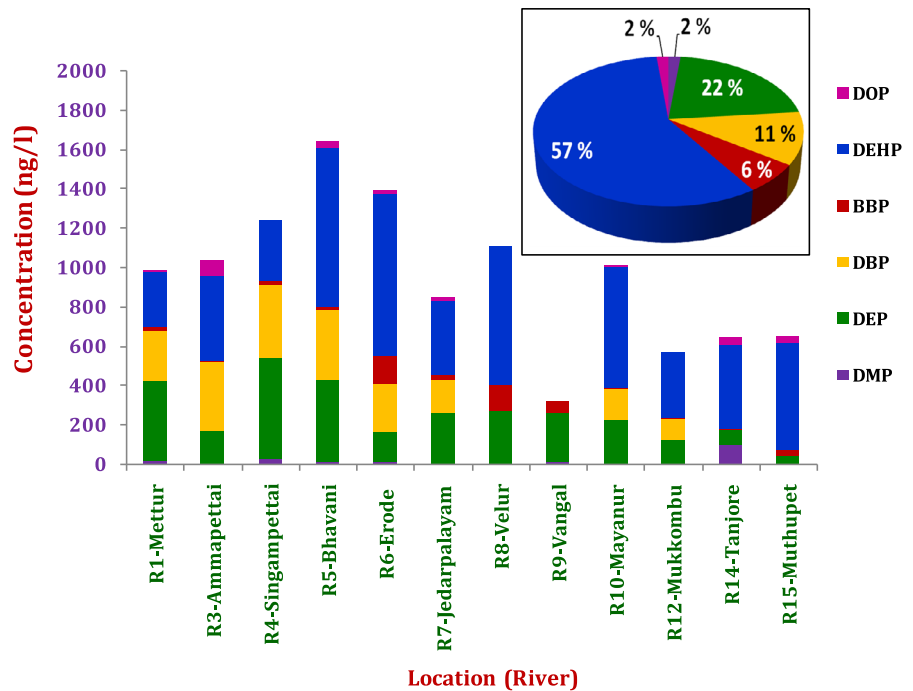
Therefore, the samples were processed without column cleanup.

Phthalates in river water

The results of phthalate concentration in the Kaveri River water (Fig. 2) indicate that DEP was ubiquitous in all of the samples. Similarly, DMP, BBP, and DEHP were also frequently detected (92 %), whereas DBP and DOP were detected in 67 % of the samples. The phthalates were measured in the range of ND (not detected)—822 ng/l. The mean levels of DMP (21.3 ng/l), BBP (39 ng/l), and DOP (28.8 ng/l) were one order of magnitude lower than DEP (241 ng/l), DBP (250 ng/l), and DEHP (514 ng/l). The total phthalates were in the range of 313–4,640 ng/l with DEHP constituting 57 % followed by DEP (22 %) and DBP (11 %) (Fig. 2). Further, the percentage composition of phthalates (DEHP, DEP, DBP, BBP, DOP, and DMP) observed in this study indicates their usage as mentioned in Olujimi et al. (2010).

Among the individual phthalates, DEHP and BBP were quantified up to 822 and 145 ng/l in Erode (R6), respectively. Also, in nearby location Bhavani (R5), DEHP, BBP, and DEP were quantified at higher concentrations. This may be due to extensive industrial activities around these two towns. In fact, they are known to be the hub for apparel manufacturing and also houses many other industries such as paper mills, leather, rubber, and chemicals. All these industrial effluents and domestic wastewater are discharged into the river at many points from these towns. In addition to phthalates, preservatives and pharmaceutical compounds were already reported at higher levels in Bhavani (triclosan, 139 ng/l; Ramaswamy et al. 2011) and Erode (acetylsalicylic acid, 240 ng/l; Shanmugam et al. 2014) by us. Dithethyl phthalate (520 ng/l) and DBP (372 ng/l) were predominant in Singampettai (R4) location, which is part of the upstream location. Since R4 is rural, domestic wastewaters are not expected to contribute significantly, however effluents from industries upstream (town of Mettur) may contribute. In case of DMP, Tanjore (R14) recorded the highest level (94 ng/l) and the potential source was anticipated to be domestic discharge and agriculture run off (insecticides) because DMP is added in shampoos, aftershave, pesticides, etc., as reported by Olujimi et al. (2010). Also, the severity of anthropogenic influence in this location may be perceived from

Fig. 2 Cumulative concentration of phthalates in the Kaveri River water and its contribution percentage (*inside box*)



our earlier study reporting the highest levels of bisphenol A (2,100 ng/l) and octylphenol (16.3 ng/l) (Selvaraj et al. 2014), and pharmaceutical compounds such as acetyl salicylic acid (660 ng/l) (Shanmugam et al. 2014).

The level of DMP in the Kaveri River (ND—94 ng/l) was in the range of concentrations reported in China, France, the Netherlands, and Malaysia (Table 2), whereas, it is an order of magnitude lower than Baboolrod River of Iran (870 ng/l). DEP reported (36–520 ng/l) in this study was 1–2 orders of magnitude lower than Netherlands’s Dommel River (2,300 ng/l; Vethaak et al. 2005) and, however, comparable with other rivers. Dibutyl phthalate was highly recorded in rivers from the USA (up to 4,140 ng/l; Solís et al. 2007) and also in the Netherlands (up to 3,100 ng/l), which is about ten times higher than the Kaveri River. In India, DBP and BBP were the only phthalates previously reported in Bahruli River (Assam Province) below the detection limit by Roy and Kalita (2011). The concentration of BBP (5.4–145 ng/l) in the Kaveri River was comparable with other rivers elsewhere in Table 2. Like other phthalates (DMP, DEP, DBP), the maximum DEHP measured in Indian rivers (822 ng/l) was an order of magnitude lower than Netherlands’s Dommel River (5,000 ng/l) and Mediterranean River of Spain

(4,980 ng/l). Unlike other phthalates, DOP was scarcely reported (India, the Netherlands, China, and Malaysia) and the levels were comparable.

Phthalates in Kaveri River sediment

The GC–MS quantification of phthalates in sediment (2010–2012) shows that they are ubiquitous in riverine environment (shown in Fig. 3). Phthalates such as DEP (94 %), DBP, and DEHP (88 %) were detected in most of the samples, whereas DOP, BBP, and DMP were detected in only 66, 31, and 13 % of the samples, respectively. The total phthalates were recorded at the lowest levels at Tiruchrappalli (2 ng/g dw) during 2010 and at the highest levels at Erode (1,438 ng/g) during 2011. Diethylhexyl phthalate was quantified at a higher concentration in most of the locations (mean 278 ng/g), followed by DBP (35.5 ng/g), DEP (16.5 ng/g), BBP (2.6 ng/g), DOP (2.5 ng/g), and DMP (1.6 ng/g).

Among the locations, all the phthalates were detected at Erode (R6) sediment during 2011 and the water concentration was also high. The probable reason is already discussed in the above section. Further, higher mean concentration recorded in Jedarpalayam (located downstream of Erode) is also likely due to the upstream locations. Although Mettur

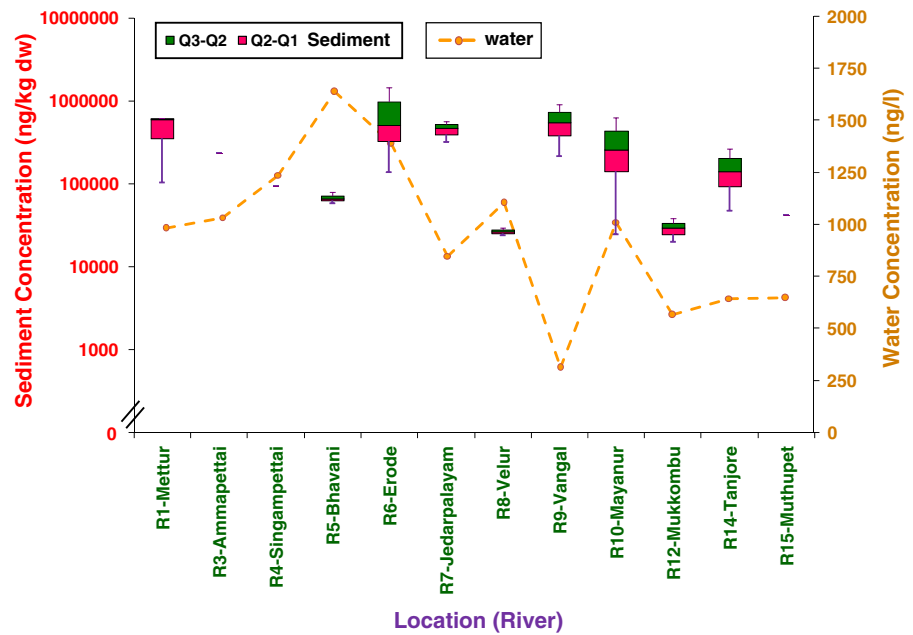
Table 2 Comparison of phthalates reported in rivers of India and other countries

Country	River	DMP	DEP	DBP	BBP	DEHP	DOP	Reference
<i>Water (ng/l)</i>								
Netherlands	Dommel	10–190	70–2,300	70–3,100	10–1,800	900–5,000	<loq–80	Vethaak et al. (2005)
Sweden	Hoje	^a	10–30	20–60	^a	10–40	^a	Bendz et al. (2005)
USA	Eleven Point, White	^a	^a	140–4,140	40–350	^a	^a	Solís et al. (2007)
Iran	Babolrood	870	670	^a	^a	^a	^a	Hadjmohammadi et al. (2011)
Spain	Muga, Fluvia, Ter, Besos, Llobregat, Ebro	^a	50–280	^a	<LOQ–20	120–4,980	^a	Sanchez-Avila et al. (2012)
China	Yangtze	<10–25	<10–211	105–286	10–21	<10–836	<10–20	He et al. (2011)
France	Seine	26–184	71–181	67–319	ND	160–314	ND	Dargnat et al. (2009)
Malaysia	Selangor	2–15	10–49	47–213	4–13	66–389	ND–9	Santhi and Mustafa (2013)
India	Bharalu	^a	^a	BDL	BDL	^a	^a	Roy and Kalita (2011)
India	Kaveri	ND–94	36–520	ND–372	5.4–145	ND–822	ND–85	Present Study
<i>Sediment (ng/g dw)</i>								
Taiwan	Zhonggang, Keya, Erren, Gaoping, Donggang and Danshui	^a	BDL	300–30,300	^a	500–23,900	^a	Yuan et al. (2002)
Germany	Rhine, Elbe, Ruhr, Mosel, Havel, Spree, Oder	^a	^a	450	^a	700	^a	Fromme et al. (2002)
Japan	Furu	^a	^a	^a	^a	1,000–2,000	^a	Yuwatani et al. (2006)
Netherlands	Lateral, Nodsea, and Twente canals	^a	^a	90	^a	4,300	^a	Peijnenburg and Struijs (2006)
China	Yellow	ND – 3,012	ND - 1,310	1,750–5,780	540–63,040	ND	4,000–69,120	Sha et al. (2007)
India	Gomti	BDL–490	BDL–350	BDL–340	^a	BDL–3,240	BDL–530	Srivastava et al. (2010)
India	Kaveri	ND–3.71	ND–185.2	ND–664	ND–7.8	ND–1,400	ND–8.54	Present study

ND not detected, BDL below detection limit

^a Not performed

Fig. 3 Phthalates distribution in water (line) and sediment (box plot) along the course of Kaveri River



(Stanley reservoir) recorded a reasonable level (mean 440 ng/g) of phthalates, the reason could not be elucidated because of the lack of data in the catchment area. Not only phthalates but also triclosan was detected at higher level (8,419 ng/kg dw; Ramaswamy et al. 2011) in this location, considered to be pristine. Next to Mettur, Ammapettai (R3) showed lower levels of phthalates (230 ng/g), which may be due to chemical and other industries situated in Mettur. The rural locations such as Vangal and Mayanur (300–556 ng/g) may be impacted mainly due to domestic water discharges along with paper and sugar industries. Low levels recorded in Tiruchirappalli (R13) (Table S3), despite its high population, may be due to high flow dynamics of the river, which causes frequent washing of sediment and/or deposition of new silt. In case of a mangrove location, Picharavam (R16), the total phthalates were found to be 293 ng/g with maximum contribution from DEHP (276 ng/g) and this may affect the sensitive mangrove ecosystem. The only possible reason for high DEHP is the domestic waste discharge into the mangrove waters.

Further, the trend of higher DEHP, DEP, and DBP in sediment was also observed in water samples. Based on mean total phthalates concentration, a decreasing temporal trend was observed with the decreasing order from 2010 (329 ng/g) to 2012 (198 ng/g).

Decreasing phthalates levels towards the downstream was observed not only in sediment but also in water (Fig. 3) and the pattern strongly coincides with the industrial locations. The slight increase in phthalate concentration at downstream locations (R14–15) may be due to the limited dilution (restricted river flow) and input of wastewaters from a large number of settlements (Tiruchirappalli town) in its upstream. While the water concentration provides the recent source of phthalates, however, the sediment pattern reflects the phthalates accumulation/persistence over years (i.e., temporal concentration) (Fig. 3). Especially in Erode (R6) higher phthalates in both matrices indicates contamination of the river for years. In case of Bhavani town (R5), the sediment levels were lower than water. This may be due to the washing out of sediment at the juncture due to the convergence of two rivers, the Bhavani and the Noyyal. Further, the accumulation of phthalates such as DMP, DEP, DBP, and DEHP in sediment were clearly associated with its octanol–water partition coefficient (Fig. 4). For BBP and DOP, despite its higher log K_{ow} , the decreased accumulation may reflect its lesser usage (Olujimi et al. 2010). In the case of water, a similar pattern relative to sediment was observed (except for DBP), and it shows that phthalate occurrence in water is less determined by their octanol–water partition

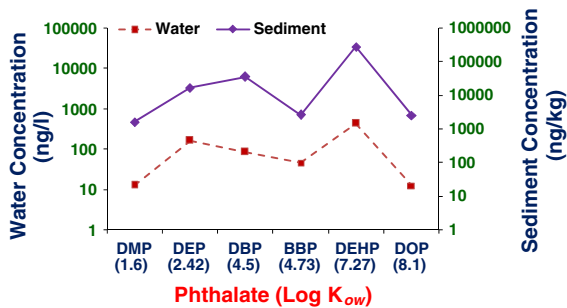


Fig. 4 Comparison of mean phthalates concentration in Kaveri River with its octanol-water partition coefficient

coefficient and more dependent on the wastewater input.

The level of phthalates in Kaveri River was 10–1,000 times lower than maximum concentration reported for the Yellow River in China, except DEHP (Sha et al. 2007). Further, the maximum DMP level observed in Gomti River (northern India) was higher than the Kaveri River (southern India). Further, DOP in Kaveri River (ND—8.54) was two orders of magnitude lower than Gomti river (BDL-530 ng/g dw) (Table 2). In the present study, DEP and DBP levels were comparable with other reported rivers. In case of DEHP, elevated levels were observed in all rivers, except China (ND; Sha et al. 2007).

Drinking water risk assessment

In India, around 75 % of sewage/wastewater is discharged into local water bodies without treatment, while the rivers directly serve as a drinking-water source (Ramaswamy et al. 2011). In this regard, it is important to know the health status of the river water. The studies pertaining to human health risk assessment with respect to emerging contaminants (ECs) in rivers are generally lacking in India except for pharmaceutical and phenolic compounds made by us (Selvaraj et al. 2014; Shanmugam et al. 2014). In order to ascertain the human health implications, adult exposure and relative risk (hazard quotient) for phthalates were calculated (Table 3). The maximum estimated exposure for DEHP was 0.027 $\mu\text{g}/\text{kg}$ bw/day with a HQ of 0.0014. Further, the HQs and HI (0.0018) were well below unity (Table 3), signifying no risk of phthalates from consumption of the Kaveri River water. Generally, HQ or HI values >1 signifies

Table 3 Human exposure and risk assessment of phthalates via drinking Kaveri River water

Phthalate	Adult exposure (AE) ($\mu\text{g}/\text{kg}$ bw/day)	RfD ^a ($\mu\text{g}/\text{kg}/\text{day}$)	HQ
DMP	0.003	—	—
DEP	0.017	800	0.000022
DBP	0.012	100	0.00012
BBP	0.005	200	0.000024
DEHP	0.027	20	0.0014
DOP	0.003	10	0.00028

^a USEPA (2013)

potential adverse health effects and suggests further monitoring/evaluation study (Wu et al. 2010).

The mean level of DEHP (800 ng/l) found in the Kaveri River was about seven times lower than USEPA's MCL (maximum contamination level) of 6,000 ng/l (USEPA 2012). Although the exposure concentration is considered safe in terms of non-carcinogenic risk and MCL, the contribution from other sources (food, cosmetics, etc.) is imperative for performing actual cumulative exposure. Recently, Guo et al. (2011) described that phthalate exposure in the Indian population was the second highest (389 ng/ml) among several Asian countries, next to China, and contributed mainly by the metabolites of DEP (mono ethyl phthalate, 49 %) and DEHP (mono ethylhexyl phthalates, 32 %). Although, the phthalate levels were much lower than the USEPA's RfD (Table 3), there are emerging reports describing the toxicity at levels relative to RfD by using in vitro models. Hsieh et al. (2012) demonstrated that BBP and DBP at 1 μM concentration induced proliferation, migration, invasion, and tumor formation in estrogen receptor (ER)-negative breast cancer cells. Further, that study revealed a novel oncogenic mechanism of phthalates in breast cancer cells, which is independent from estrogenic activities. Moreover, monoethyl phthalate (170 $\mu\text{g}/\text{g}$ creatinine) was positively correlated with breast cancer in women patients of northern Mexico (Lopez-Carrillo et al. 2010).

Aquatic risk assessment

Since rivers receive wastewater treatment plants effluents, untreated wastewater, and urban/agricultural runoff, the continuous exposure of low doses of

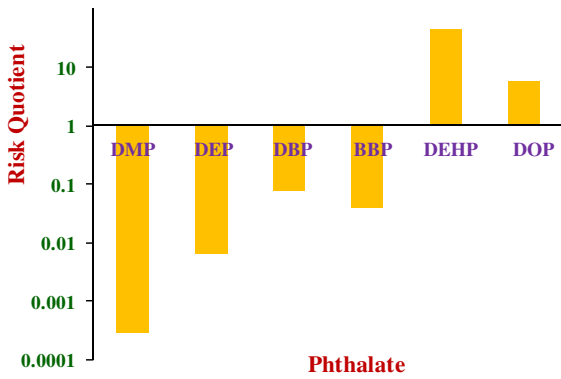


Fig. 5 Aquatic risk assessment (water) for phthalates in Kaveri River, southern India

endocrine-disrupting compounds to resident aquatic organisms cannot be avoided (Ramaswamy et al. 2011). Although phthalates were quantified in ng to µg level, they may likely pose some threat to aquatic organisms. Therefore risk-assessment studies are imperative for assessing the rivers’ health status. In the present study, ECOSAR chronic values were used to derive a risk quotient. The calculated RQ for DMP, DEP, DBP, and BBP were below unity, whereas it was 43 and 5.6 for DEHP and DOP, respectively (Fig. 5). There are few studies that report phthalate toxicity at environmental concentrations. Sung et al. (2003) reported that phthalates such as DEHP, DBP, and others (at 100 µg/l) could damage hemocytes and influence the defense mechanism of freshwater prawn, *Macrobrachium rosenbergii*. Further, a recent study describes that DEHP at 5,000 ng/l induces oxidative stress and alters immune-related genes in zebrafish embryos (Xu et al. 2013). Therefore, probable risks due to phthalates may be anticipated in aquatic wildlife of the Kaveri River.

The sediment risk assessment of phthalates was performed by comparing the maximum concentration

of phthalates with the screening benchmark values given in Table 4 (USEPA 2006). None of the phthalates quantified exceeded the SCB freshwater guideline level except for DEHP, which is eight times higher than SCB. A similar trend was observed in estuarine environments (Pichavaram), where the DEHP level was 1.5 times higher than estuarine SCB (Table 4). This assessment clearly demonstrates that phthalates other than DEHP in sediment are not expected to pose any risk to ecologically sensitive benthic species (e.g., worms, clams, oysters). However, the sediment can be an extended/archived source of anthropogenic compounds in the water column. Since phthalate is one of the pseudo-persistent pollutants, its prolonged exposure may cause plausible health effects in fish and other non-target aquatic species.

Conclusions

This study provides an overview of the occurrence and concentrations of phthalates in the Kaveri River, India. Phthalates are ubiquitously found throughout the Kaveri River with high detections of DEHP, DEP, and DBP. Elevated levels of phthalates observed in upstream locations with intensive anthropogenic activity (industrial). Phthalates in river water did not show any human health risks. Aquatic health risk assessment revealed probable risk due to DEHP and DOP, whose RQs were 43 and 5.6, respectively. The sediment risk assessment also showed DEHP as a phthalate of concern. The results emphasize the need for adequate monitoring of phthalates in Indian rivers in order to ascertain the human and environmental health status. This is the first study to demonstrate the toxicological status of phthalates in Indian rivers. Further, the report will serve as baseline data to

Table 4 Screening benchmark (SCB) for phthalates in river and coastal sediment

Phthalate	River sediment MEC (µg/kg)	River sediment SCB ^a (µg/kg)	Estuarine sediment MEC (µg/kg)	Coastal sediment SCB ^a (µg/kg)
DEP	185	603	1.3	200
DBP	664	6,470	8.5	1,160
BBP	7.8	10,900	1.4	16,800
DEHP	1,400	180	276	182

^a USEPA (2006)

support regulatory decision-making at local and national levels.

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