

Occurrence And Seasonal Disparity Of Emerging Endocrine Disrupting Chemicals In A Drinking Water Supply System And Associated Health Risk

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Abstract

Contamination of drinking water with endocrine-disrupting chemicals (EDCs) raises concerns over the security and long-term sustainability of clean water supplies as well as human exposure via daily water intake. In this study, the seasonal disparity and occurrence of six phthalates and bisphenol A in the drinking water supply system and associated health risk were examined. DEHP was the most prevalent phthalate esters congener ranging from 1.14 - 8351.85 µg/L (winter) and 0.552 - 410.29 µg/L (summer) surpassing the permissible limit. Meanwhile, BPA concentrations were found under the permissible limit. The results suggested that PAE concentration displayed significant seasonal variations with the highest in winter and the lowest in the summer. The exposure to PAEs and BPA from drinking water was assessed, and the results indicated a possible health risk to humans with a Hazard Quotient (HQ) for DEHP. The findings necessitate an immediate scrutiny of these EDCs in drinking water supply system and are critical for implementing effective technologies at the WTP scale to ensure the quality and safety of drinking water in order to ascertain human and environmental health.

Introduction

The safety and purity of drinking water are critical to human health across the world. As a result of uncontrolled anthropogenic activity, surface water is exposed to a myriad of contaminants, making clean drinking water a primary focus. Contamination of drinking water with EDCs such as Phthalate esters (PAEs) and Bisphenol A (BPA) has physiological consequences by simulating hormones or interfering with their production, release, and metabolic pathways. Low molecular weight phthalates like dimethyl phthalate (DMP), diethyl phthalate (DEP) and Benzyl butyl phthalate (BBP) are challenging chemicals as they mimic endocrine hormones and play a role in several non-communicable diseases like infertility, diabetes, obesity, neurological diseases, and aberrant growth patterns¹. Whereas, high molecular weight phthalates such as di(2-ethylhexyl) phthalate (DEHP), Di-n-butyl phthalate (DBP), and Di-n-octyl phthalate (DNOP) are suspected carcinogens, that could harm the liver, excretory system and reproductive system. Of all known PAE congeners, DMP, DEP, DEHP, DBP, DNOP and BBP were identified as priority pollutants due to their targeted influence on the human health².

PAEs are semi-volatile, polar organic molecules, with high solubility³. These plasticizers are not firmly attached to the matrix, even minor changes in environmental parameters such as temperature, pH, and pressure might cause them to migrate to the surroundings⁴. They are widely used in a variety of industries including construction, pharmaceuticals, food packaging, and medical equipment⁵. For instance, Polyvinyl chloride (PVC) comprises 40% DEHP, whereas BBP is found in polyurethane, polysulfide and acrylic-based polymers. DBP is used as a plasticizer in PVC and rubber as well as in paints and cosmetics as a solvent and fixative. DNOP is widely used in floors, coverings, conveyor belts and other applications. Furthermore, PAEs like DMP and DEP have a wide range of uses in cosmetics and baby care products manufacturing⁶. The presence of PAEs such as DMP, DEP, DEHP, DBP, DNOP, and BBP has been detected in drinking water, raising serious concerns about human health^{7,8}. For drinking water,

the threshold value for DEHP (category B, includes probable human carcinogens) has been set to 6 µg/ L and 8 µg/ L by EPA and WHO respectively⁹.

BPA is primarily employed as a monomer in the manufacturing of flame retardants polycarbonate, epoxy and unsaturated polyester-styrene resins. The resulting materials are frequently utilized as can coatings, powder paints, dental fillings, and household items such as bottles, cutlery and containers. BPA is currently produced at a rate of about 8 million tonnes per year, with the international market expected to remain stable at around 7300 k tonnes by 2023¹⁰. BPA-containing goods are officially prohibited in some American states and Canada due to their endocrine disruptive properties, yet they are nevertheless widely used in other nations¹¹. It can be released into the surrounding environment during commercial processing and as leachates from the finished products. One of the important sources of human exposure to BPA is drinking water and might be associated with a number of chronic human disorders including cardiovascular disease (CVD), birth abnormalities, respiratory and kidney problems and breast cancer according to epidemiological research. It has also been found to have estrogenic activity, which could increase the risk of cancer by interrupting the developmental process^{12,13}.

In most of the countries, natural reservoirs such as rivers, lakes, dams, etc are the primary source for drinking water treatment plant (DWTP). Direct sources, such as untreated and treated discharges and indirect sources such as runoff and leachates are the two main causes of EDCs contamination in surface water. Between the drinking water source and the consumers, the DWTP is the last point of exposure for EDCs and unfortunately the traditional drinking water treatment facilities are insufficient for eliminating these pollutants, resulting in their dissemination in the drinking water supply¹⁴. Despite of the extensive use and prevalence of plasticizers in the environment, developing countries like India still lack the awareness and strict guidelines on environmental monitoring of these pollutants. In India, surface water such as dams, rivers, and lakes are widely used for drinking water which often receive untreated industrial effluents. Moreover, there is no baseline data available for PAEs and BPA in Indian drinking water. Hence, this study has been carried out to detect and quantify the EDCs in drinking water system and their associated health risks.

The present study was undertaken to quantify selected EDCs i.e., PAEs and BPA across the drinking water supply system, evaluate their potential influence on drinking water security and assess their health risk. The Hazard quotient (HQ) was used to estimate the human health risk caused by the targeted EDCs in the drinking water. The seasonal distribution pattern of these pollutants was also investigated in order to establish the correlation between the abundance of phthalate esters and BPA with that of temperature variation.

Results And Discussion

Occurrence and seasonal distribution of \sum_6 PAEs and BPA in the drinking water supply system

The detection frequencies (DF) of the six PAEs ranged from 24–100% in the winter season whereas; in summer it is below the detection level in case of BBP to 100% (DEP, DBP, DEHP) in the sampling areas. In a study conducted by ¹⁵, PAEs detection frequencies ranged from 1.8–81.8%. According to our results, DEHP was the major phthalate with the highest detection frequency of 100% (Supplementary Table 1), which is consistent with previous findings that reported its highest detection rate with 61% ¹⁶, 93.3% ¹⁷ and 92% ¹⁸, indicating the ubiquity of DEHP in source and drinking water samples. The detection frequency for BPA is 100% in summer season whereas in winter it lies in the range of 64–100% as presented in Supplementary Table. 1, similar DF (67.6%) was reported for the surface water by ¹⁹. The earlier recorded detection frequency for BPA in drinking water was 5% (North America), 52% (Europe), and 59% (Asia) whereas for surface water it was reported 17% ²⁰.

The relative abundance of different PAE congeners in source water varied in the order DEHP > DBP > DMP > DEP > DNOP > BBP and DEHP > DNOP > DBP > DEP > BBP > DMP for winter and summer, respectively. The area-wise concentration of each PAE in source, WTP, and drinking water samples (OH and DW) during winter and summer seasons are presented in Fig. 1 and Fig. 2. The average concentrations of PAEs (Σ_6 PAEs) lies in the range of 3927.89–7553.94 $\mu\text{g/L}$ and 4.665–410.48 $\mu\text{g/L}$ (surface water), 4173.91–8633.57 $\mu\text{g/L}$ and 3.31–9.81 $\mu\text{g/L}$ (WTP), 3.02–1527.29 $\mu\text{g/L}$ and 0.722–90.47 $\mu\text{g/L}$ (overhead water), 1.86–1438.20 $\mu\text{g/L}$ and 0.77–57.75 $\mu\text{g/L}$ (drinking water), for winter and summer respectively. Significant seasonal variations were observed for all PAE congeners, with a higher concentration of total PAEs detected in the winter season than in summer. Overall, the PAE concentrations in source water samples were found to be more than WTP effluents and drinking water samples. The results of this study suggest that WTP might be able to remove phthalates to some extent, but still, a substantial quantity of phthalates has been detected in drinking water.

Five phthalates viz. DMP, DEP, DEHP, DBP and DNOP were frequently detected in all the samples except BBP (detected in summer only); of all, DEHP was consistently high in terms of concentration and occurrence during the two seasons. A significant seasonal variation was observed in five of the PAEs in the household over-head (OH) tank water samples and drinking water (DW) samples. The concentration of different PAEs was observed to be significantly varying with the season for the source water samples (Supplementary Table 2).

A high concentration of DEHP in source water may indicate its stronger sorption capacity and lower degradation rate. The abundances of DEHP, DBP, and DNOP in the surface water could be linked to their huge production and rampant usage. DEHP was the most prominent species in the water samples with a concentration range of 84.49 to 8351.85 $\mu\text{g/L}$, which is much higher than the earlier reported concentration of 1.28 to 5.28 $\mu\text{g/L}$ ²¹ and 1.684 $\mu\text{g/L}$ ⁹ in drinking water. Many previous studies have also reported similar results ^{7,15,22}. The reported DEHP concentrations were up to 2.6 $\mu\text{g/L}$ and 27.1 $\mu\text{g/L}$ in the treated wastewater ^{23,24} and 490 mg/kg dry weight in the sludge ²⁵. The abundance of DEHP in the surface waters could be attributed to industrial effluents which are routinely discharged into rivers.

Moreover, the predominance of DEHP in the air may also contribute to the profusion of PAEs in source water²², and being a long alkyl chain PAE its mineralization is slow²⁶.

Toxicological data on DNOP are extremely limited to date; therefore, its health and environmental risks are still ambiguous. Distribution of DMP and DEP in terms of concentration and abundance were found to be least of all the detected PAE congeners in source and drinking water, similar to those observed in the Jiulong River estuary, Southeast China²⁷. The measured Σ_6 PAE concentrations unveiled notable seasonal variations with the highest value in winter and the lowest value in summer, which are consistent with the previous observation²⁸. The lower concentrations of Σ_6 PAE in the summer could be partly due to high photolytic activity, microbial degradation, and oxidation^{29–31}. Additionally, PAEs concentration in the air surrounding the source water might vary over seasons and could be one of the contributing factors for seasonal variations in PAEs levels. Besides this, a shift in the microbial communities and their relative abundance were subject to the seasonal variation that could change the rate of microbial mediated degradation.

The ongoing trend of phthalate contamination in drinking water calls for scrutiny as chronic/long-term exposure to PAEs has been linked to several health-related ailments including endocrine system disruption, cancer, developmental aberrations etc.³². Besides, WTPs should also implement upgraded technologies that can remove phthalates more efficiently during the water treatment process.

Area wise BPA concentrations in source and drinking water were summarised in Fig. 4. Its concentration ranges 0.307–0.726 $\mu\text{g/L}$ and 0.884–1.42 $\mu\text{g/L}$ in surface water, 0.05–0.422 $\mu\text{g/L}$ and 0.812–1.373 $\mu\text{g/L}$ in WTP, 0.06–1.188 $\mu\text{g/L}$ and 0.166–3.059 $\mu\text{g/L}$ in OH water, 0.002–1.418 $\mu\text{g/L}$ and 0.185–2.843 $\mu\text{g/L}$ in DW for winter and summer, respectively (Fig. 3). From the four study areas, only OH water samples collected from Bhongadwar showed a statistically significant seasonal variation ($p = 0.01755$), whereas no significant seasonal difference was observed in any of the other study areas, for both the OH and DW samples (Supplementary Table.2). An earlier study has reported a much higher concentration of BPA i.e., 85.5 $\mu\text{g/L}$ and 2.230 $\mu\text{g/L}$ in surface and drinking water, respectively³³. In the summer season, the BPA concentrations in the water samples were generally high and it seemed to be well distributed in terms of occurrence which was consistent with the results reported by³⁴ while Luo et al. (2019) observed the opposite trend. The high abundance of BPA in summer could be related to the temperature, as it gets leached out under high temperature or acidic/alkaline environments^{35,36}. The concentration of BPA in our study was higher than that observed in three rivers (Kaveri, range 6.6–136 ng/L; Vellar, range 2.8–6 ng/L and Tamiraparani, range 9.8–36 ng/L) in Southern India¹⁸. Furthermore, Arnold et al. (2013) reported 0.099 $\mu\text{g/L}$, 0.014 $\mu\text{g/L}$, and 0.317 $\mu\text{g/L}$ concentrations for North America, Europe, and Asia, respectively.

Among the phenolic compounds, BPA is the most reported chemical in surface water around the world^{37–39}. The average concentration of BPA in the Ganga River was found to be 0.04–4.46 $\mu\text{g/L}$ ⁴⁰. Lalwani et al. (2020) reported 1.42 $\mu\text{g/L}$ and 14.8 $\mu\text{g/L}$ concentrations in the Cooum River and Yamuna River of India, respectively. Among the reported data, the highest BPA concentration was observed in the Yamuna River

of India, till date. Though BPA was found in source and drinking water, the mean concentrations were lower than those of PAEs irrespective of the seasons and detected concentration lies within the admissible limit. The source water is usually chlorinated in WTP, it may also affect the BPA concentration in the drinking water supply as it degrades quickly in highly chlorinated water³⁷. Furthermore, an earlier study had shown the abiotic process mediated transformation and mineralization of BPA under anoxygenic conditions, suggesting that it is susceptible to degradation under such conditions⁴¹. Therefore, it can be inferred that the seasonal fluctuations (due to weather conditions like temperature, intensity of sunlight, rainfall etc) have a strong relationship with that of EDCs concentration and their distribution in source and drinking water³⁶.

Human healthrisk

We calculated the daily consumption of PAE congeners and BPA based on the maximum concentration in drinking water. The hazard quotient (HQ and HQ-AA) associated with PAEs and BPA exposures in different seasons are summarized in Table 1. Of all, DEHP has a higher (> 1.0) HQ and HQ-AA irrespective of the season, showing a higher risk for human health. This result is in contrast to the study conducted by Zare et al. (2018), which showed that HQ-AA for DEHP is less than 1.0 in Iran⁴². In a similar line, Abtahi et al. (2019) reported a much lower HQ for DEHP in Tehran⁴³. The exposure of other targeted PAEs and BPA does not cause adverse health effects, as HQ and HQ-AA values were found to be less than 1.0. According to the HQ and HQ-AA values, the risk of PAE congeners were found to be in order of DEHP > DBP, BBP, DEP and DEHP > DBP, BPA, BBP for winter season, whereas in summer the risk order is DEHP > DBP, DEP and DEHP > BPA, DBP respectively in the studied area. This suggests that seasonal variation has a more significant impact on high-risk phthalates than low-risk species which was also supported by the findings of¹⁵.

Table 1
Human Exposures and Risk Assessment of PAEs and BPA through Drinking Water.

WINTER					
Analytes	EDI (ug/kg bw/day)	HQ (RfD)	HQ (RfD-AA)	Contribution via Drinking water	Excess Cancer risk
DMP	2.662	-	-	-	-
DEP	0.193	0.0002	-	-	-
DBP	33.450	0.334	0.334	334.496	-
BBP	0.338	0.002	0.001	0.068	-
DEHP	702.750	35.137	23.425	1405.500	9.838
DNOP	0.358	-	-	-	-
BPA	0.096	-	0.008	-	-
SUMMER					
Analytes	EDI (ug/kg bw/day)	HQ (RfD)	HQ (RfD-AA)	Contribution via Drinking water	Excess Cancer risk
DMP	0.046	-	-	-	-
DEP	0.012	1.51875E-05	-	-	-
DBP	1.106	0.011	0.011	11.057	-
BBP	-	-	-	-	-
DEHP	73.276	3.664	2.443	146.552	1.026
DNOP	0.030	-	-	-	-
BPA	0.192	-	0.015	-	-
(-) indicates non availability of data					

Material And Methods

Study area and sample collection

The study was conducted in Jabalpur city of Madhya Pradesh state of India. The sampling area covers all community water sources like rivers (Narmada and Gaur), reservoirs and dams and the public water supply systems. Four WTPs at different locations, namely Ranjhi, Bhongadwar, Lalpur and Ramnagra were chosen for the study (Fig. 4). Samples were collected from the source as well as distribution areas of these WTPs and also the WTP itself for a comprehensive assessment of transmission of EDCs in the

water supply chain. In each WTP distribution area, water samples were collected from 25 households. All these samples were collected during the winter season (Jan-2021) and summer season (June-2021) to study the seasonal variations. Samples were collected in pre-cleaned 1L amber glass bottles, using phthalate-free caps and were preserved with 80mg/L of sodium thiosulfate to quench residual chlorine in the finished water. The samples were packed and transported in cold condition to the laboratory overnight and stored in the dark at 4°C until extraction. The source (influent for drinking water treatment plants) and WTP effluent (i.e., finished drinking water ready for distribution) samples were collected on the same day with the assumption that the source water characteristics would not vary significantly throughout the day.

Chemicals and Reagents

A standard stock solution containing phthalate esters mixture (606-M) of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), din-octyl phthalate (DNOP) (each at a concentration of 0.2mg/mL in methanol) and Bisphenol A (10mg/mL) were purchased from AccuStandard Chem. Co. (CT, USA). HPLC grade acetone, methanol, dichloromethane and sodium chloride (99.5%) was obtained from Merck (Darmstadt, Germany). Working standard solutions for calibration were prepared from the stock standard solutions and stored at 4°C.

Sample Extraction and Analysis

Extraction of phthalates and BPA were done via salt-assisted liquid-liquid extraction (SALLE) as described in EPA (method 3510). Water-immiscible solvents, like dichloromethane (DCM) and n-hexane, were tested to extract and pre-concentrate the PAEs and BPA from the water samples. DCM was found to be the suitable solvent for selective extraction of all the targeted six PAEs and BPA with maximum recovery in comparison to n-hexane. A serial liquid-liquid (LLE) extraction was performed in a 2 L separatory funnel, with 1 liter of the sample (containing 990ml water sample, 10 ml 0.5 M phosphate buffer (pH = 7), and 50 g NaCl) and was extracted out thrice with 60 mL dichloromethane (DCM) each time. After each extraction, the organic layer was allowed to separate for 10 mins. The pooled extracts were evaporated on a rotary evaporator (45°C and 60 rpm). The dried extracts were dissolved in 5ml of GC/MS grade methanol and concentrated up to 1 ml under a stream of N₂ at 65°C. This eluate was transferred to GC vials and used for the GC-MS analysis. To check the extraction efficiency, milli-Q was spiked with PAEs and BPA and extracted using the same method.

Gas chromatography (Thermo fisher Trace 1300 model) coupled with a mass spectroscopy ISQ 7000 (Thermo Fischer, Italy) was used for the quantification of phthalates and BPA. Data acquisition and processing were performed using Chromeleon Console software. A TG-5MS Trace (30 m × 0.25mm × 0.25 μm) fused silica capillary column was used. The flow rate of the carrier gas He (99.999% purity) was kept constant at 1.5 mL/min. The sample (1 μL) was injected into GC in split-less mode with an inlet temperature of 280°C. Initially, the column temperature was programmed at 80°C for 1 min and then elevated to 290°C at the rate of 10°C/min with a holding time of 8 mins for PAEs. For BPA, an initial temperature of 100°C was provided for 2 mins then increased to 290°C at the rate of 20°C/min with a holding time of 8 mins. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV

and an emission current of 60 μ A. Detector temperature was maintained at 280°C. MS was operated in full-scan mode from m/z 40–400 for qualitative analysis. Acquisition for quantitative analysis was performed in the single-ion monitoring (SIM) mode along with characteristic ions (Table.2) and quantification was done with an external calibration method.

Quality assurance and Quality control

In order to prevent the backgroundcontamination of PAEsand BPA, all the employed glassware and apparatus were cleaned via analytical grade acetone and heated at 250°C for 2hrs.The limit of detection (LOD) and limit of quantification (LOQ) for all the six phthalates and BPA were calculated based on a signal-to-noise ratio of 3 and 10 times respectively. Details of quality assurance for phthalates and BPA analysis, including the limit of detection (LOD), the limit of quantification (LOQ), R^2 , and precision values (% RSD) details are given in Table.2. During the GC-MS analysis, for every set of 10 samples, a set of blanks and standards were also run to ensure the performance of the instrument. The ion chromatograms of PAEs and BPA were obtained using GC/MS depicted in Fig. 5.The calibration curve for each targeted phthalate and BPA are provided in the supplementary file (Supplementary Fig. 1)

Table 2
QA/QC parameters for Phthalates and BPA extraction and analysis

Analytes	MW	CAS Number	Retention time (Min)	Monitored ions (m/z)	LOD (μ g/L)	LOQ (μ g/L)	R^2	Precision (% RSD)
Dimethyl phthalate	194	131-11-3	9.8	163,77	0.002	0.006	0.999	2.01
Diethyl phthalate	222	84-66-2	11.5	149,177	0.0034	0.01	0.997	1.57
Di-n-butyl phthalate	278	84-74-2	15.4	149	0.01	0.03	0.995	1.80
Benzyl butyl phthalate	312	85-68-7	18.95	149,206,91	0.006	0.02	0.998	6.17
Bis(2-Ethylhexyl) phthalate	390	117-81-7	20.4	149,167,279	0.008	0.026	0.995	2.61
Di-n-octyl phthalate	390	117-84-0	21.8	149,279	0.006	0.018	0.998	5.49
Bisphenol A	228	80-05-7	10.5	213,119,228	0.02	0.086	0.986	1.66

Human health risk assessment

To validate the safety of drinking water from the viewpoint of carcinogenic and endocrine-disrupting potential, daily intakes of targeted phthalates were estimated based on their maximum concentrations detected in drinking water. The risks assessment for the selected compounds was assessed based on the toxicity data available in the Integrated Risk Information System (IRIS) of the Environmental Protection Agency (EPA) and World Health Organization (WHO).

The exposure levels and risk of phthalates for adults were calculated by using the following formula ⁴⁴.

$$EDI = \frac{MC \cdot IR}{BW}$$

where,

EDI represents estimated daily intake (EDI) of PAEs and BPA, MC represents maximum concentration of the analyte, IR represents ingestion rate of drinking water (assumed as 4.05L/day) per kg body weight (BW) of an adult. The calculated value is expressed in terms of ug/kg body weight/day⁴⁵.

Non-carcinogenic risks induced by PAEs and BPA on human health were estimated using Hazard Quotient (HQ). This is determined using EDI, reference dose (RfD; ug/kg body weight/day) for increased mortality as reported in USEPA 2012, and RfD for anti-androgenicity ^{46,47} as follows:

$$HQ = \frac{EDI}{RfD}$$

HQ and HQ-AA (calculated using RfD for anti-androgenicity) > 1, indicates potential human health risk and vice versa.

Additionally, the contribution of the daily intake of DBP, BBP, and DEHP via consumption of drinking water was computed as:

$$\text{Contribution by drinking water} = \left(\frac{EDI}{TDI} \right) \times 100$$

where,

TDI is the Tolerable daily intake, defined as the estimated amount of a substance in drinking water, expressed on a bodyweight basis (mg/kg or mg/kg of body weight), that can be ingested over a lifetime without appreciable health risk (WHO, 2008).

The risk of developing cancer could be assessed via an excess cancer risk as follows:

$$\text{Excess Cancer Risk} = \text{CSF} \times \text{EDI}$$

where,

CSF is the slope factor used to determine the cancer risk associated with the oral exposure of either carcinogen or probable human carcinogen. The CSF value for DEHP is 1.4×10^{-2} per mg/kg/day. The acceptable range for the assessment of excess cancer risk is 10^{-5} to 10^{-6} , as per US EPA (2012).

Statistical analysis

All statistical analysis were conducted using R version 4.1.0 using the packages ggplot2 (version 3.3.5), ggpubr (version 0.4.0) and dplyr (version 1.0.7). As per the requirement for the data analysis, descriptive analyses such as median and interquartile range (IQR) were calculated. Shapiro-Wilk test was performed to check the normality of the data. The scores were found to be significantly deviating from the normal distribution at a $p \leq 0.05$ significance level. Therefore, Wilcoxon signed-rank test, a non-parametric statistical hypothesis test was used for comparing the PAE and BPA concentrations across the household water samples to assess whether their population median rank differs. A $p \leq 0.05$ was considered to be statistically significant throughout the analysis.

Conclusions

This study provides an overview of the occurrence and concentrations of PAEs and BPA in the source and drinking water of Jabalpur, India. Our findings imply that temperature variation significantly affects the relative abundance and distribution pattern of targeted EDCs i.e., PAEs and BPA. These EDCs are ubiquitously found throughout the source water and drinking water with high detection values for DEHP, DNOP, and DBP. Source water samples containing high levels of phthalates reflect intensive anthropogenic activities (industrial and agricultural practices) and abiotic factors. DEHP in source and drinking water surpassed the threshold value, thus posing a significant risk to human health. Moreover, it also highlights the inefficiency of WTP in managing these emerging pollutants in developing countries like India. Thus, biomonitoring is needed across the country, especially in areas where anthropogenic activities are high, and industrial waste management policies should be imposed to minimize contamination of hazardous pollutants in drinking water. Concurrently, alternatives of these plasticizers should be developed to substitute such toxic chemicals. This study emphasizes the importance of adequate phthalate monitoring in India's drinking water system to ascertain the human and environmental health status.

Declarations

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Declaration of Competing Interest

The authors declare no conflict of interest.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Author Credit statement

MK, PS, NP and MMJ: Manuscript writing samples extraction & analysis. VV, SS, DKS and MK: Conceptualization, Manuscript Editing, data analysis & Project administration. RRT: Overall review.

References

- 1 Kumar, M. *et al.* Environmental Endocrine-Disrupting Chemical Exposure: Role in Non-Communicable Diseases. *Frontiers in public health***8**, 553850, doi:10.3389/fpubh.2020.553850 (2020).
- 2 Liu, Y., Chen, Z. & Shen, J. Occurrence and removal characteristics of phthalate esters from typical water sources in northeast china. *Journal of analytical methods in chemistry***2013**, 419349, doi:10.1155/2013/419349 (2013).
- 3 Tahboub, Y. R., Zaater, M. F. & Khater, D. F. Semi-volatile organic pollutants in Jordanian surface water. *Arabian Journal of Chemistry***10**, S3318-S3323 (2017).
- 4 Zaater, M. F., Tahboub, Y. R. & Al Sayyed, A. N. Determination of phthalates in Jordanian bottled water using GC-MS and HPLC-UV: environmental study. *Journal of chromatographic science***52**, 447-452 (2014).
- 5 Tankiewicz, M., Olkowska, E., Berg, A. & Wolska, L. Advancement in Determination of Phthalate Metabolites by Gas Chromatography Eliminating Derivatization Step. *Frontiers in chemistry***7**, 928, doi:10.3389/fchem.2019.00928 (2019).
- 6 Ramzi, A. *et al.* Distribution and contamination status of phthalic acid esters in the sediments of a tropical monsoonal estuary, Cochin - India. *Chemosphere***210**, 232-238, doi:10.1016/j.chemosphere.2018.06.182 (2018).

- 7 Liu, X., Shi, J., Bo, T., Li, H. & Crittenden, J. C. Occurrence and risk assessment of selected phthalates in drinking water from waterworks in China. *Environmental science and pollution research international***22**, 10690-10698, doi:10.1007/s11356-015-4253-9 (2015).
- 8 Lane, R., Adams, C., Randtke, S. & Carter Jr, R. Bisphenol diglycidyl ethers and bisphenol A and their hydrolysis in drinking water. *Water research***72**, 331-339 (2015).
- 9 Otero, P. *et al.* Improved method for rapid detection of phthalates in bottled water by gas chromatography-mass spectrometry. *Journal of chromatography. B, Analytical technologies in the biomedical and life sciences***997**, 229-235, doi:10.1016/j.jchromb.2015.05.036 (2015).
- 10 Vasiljevic, T. & Harner, T. Bisphenol A and its analogues in outdoor and indoor air: Properties, sources and global levels. *The Science of the total environment***789**, 148013, doi:10.1016/j.scitotenv.2021.148013 (2021).
- 11 Huang, Y. Q. *et al.* Bisphenol A (BPA) in China: a review of sources, environmental levels, and potential human health impacts. *Environment international***42**, 91-99, doi:10.1016/j.envint.2011.04.010 (2012).
- 12 Li, X., Ying, G. G., Su, H. C., Yang, X. B. & Wang, L. Simultaneous determination and assessment of 4-nonylphenol, bisphenol A and triclosan in tap water, bottled water and baby bottles. *Environment international***36**, 557-562, doi:10.1016/j.envint.2010.04.009 (2010).
- 13 Kalmykova, Y., Bjorklund, K., Stromvall, A. M. & Blom, L. Partitioning of polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachates and stormwater. *Water research***47**, 1317-1328, doi:10.1016/j.watres.2012.11.054 (2013).
- 14 Wee, S. Y., Aris, A. Z., Yusoff, F. M. & Praveena, S. M. Occurrence of multiclass endocrine disrupting compounds in a drinking water supply system and associated risks. *Scientific reports***10**, 17755, doi:10.1038/s41598-020-74061-5 (2020).
- 15 Luo, X., Shu, S., Feng, H., Zou, H. & Zhang, Y. Seasonal distribution and ecological risks of phthalic acid esters in surface water of Taihu Lake, China. *The Science of the total environment***768**, 144517, doi:10.1016/j.scitotenv.2020.144517 (2021).
- 16 Torres, N. I. *et al.* The influence of hydrogeological and anthropogenic variables on phthalate contamination in eogenetic karst groundwater systems. *Environmental pollution***237**, 298-307, doi:10.1016/j.envpol.2018.01.106 (2018).
- 17 Srivastava, A. *et al.* Occurrence of phthalic acid esters in Gomti River Sediment, India. *Environmental monitoring and assessment***169**, 397-406, doi:10.1007/s10661-009-1182-4 (2010).
- 18 Selvaraj, K. K., Shanmugam, G., Sampath, S., Larsson, D. J. & Ramaswamy, B. R. GC-MS determination of bisphenol A and alkylphenol ethoxylates in river water from India and their ecotoxicological risk assessment. *Ecotoxicology and environmental safety***99**, 13-20 (2014).

- 19 Lalwani, D. *et al.* Nationwide distribution and potential risk of bisphenol analogues in Indian waters. *Ecotoxicol Environ Saf***200**, 110718, doi:10.1016/j.ecoenv.2020.110718 (2020).
- 20 Arnold, S. M. *et al.* Relevance of drinking water as a source of human exposure to bisphenol A. *Journal of exposure science & environmental epidemiology***23**, 137-144 (2013).
- 21 Kingsley, O. & Witthayawirasak, B. Occurrence, Ecological and Health Risk Assessment of Phthalate Esters in Surface Water of U-Tapao Canal, Southern, Thailand. *Toxics***8**, doi:10.3390/toxics8030058 (2020).
- 22 Lee, Y. M. *et al.* Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. *Environment international***126**, 635-643, doi:10.1016/j.envint.2019.02.059 (2019).
- 23 Gani, K. M., Rajpal, A. & Kazmi, A. A. Contamination level of four priority phthalates in North Indian wastewater treatment plants and their fate in sequencing batch reactor systems. *Environmental Science: Processes & Impacts***18**, 406-416 (2016).
- 24 Kotowska, U., Kapelewska, J. & Sawczuk, R. Occurrence, removal, and environmental risk of phthalates in wastewaters, landfill leachates, and groundwater in Poland. *Environmental pollution***267**, 115643, doi:10.1016/j.envpol.2020.115643 (2020).
- 25 Çifci, D. İ., Kinacı, C. & Arıkan, O. A. Occurrence of phthalates in sewage sludge from three wastewater treatment plants in Istanbul, Turkey. *Clean–Soil, Air, Water***41**, 851-855 (2013).
- 26 Stamatelatou, K., Pakou, C. & Lyberatos, G. Occurrence, toxicity, and biodegradation of selected emerging priority pollutants in municipal sewage sludge. (2011).
- 27 Li, R., Liang, J., Duan, H. & Gong, Z. Spatial distribution and seasonal variation of phthalate esters in the Jiulong River estuary, Southeast China. *Marine pollution bulletin***122**, 38-46, doi:10.1016/j.marpolbul.2017.05.062 (2017).
- 28 Zhang, Z.-M. *et al.* Pollution characteristics, spatial variation, and potential risks of phthalate esters in the water–sediment system of the Yangtze River estuary and its adjacent East China Sea. *Environmental pollution***265**, 114913 (2020).
- 29 Boll, M., Geiger, R., Junghare, M. & Schink, B. Microbial degradation of phthalates: biochemistry and environmental implications. *Environmental microbiology reports***12**, 3-15, doi:10.1111/1758-2229.12787 (2020).
- 30 da Silva Costa, R. *et al.* Potential risk of BPA and phthalates in commercial water bottles: a minireview. *Journal of water and health***19**, 411-435, doi:10.2166/wh.2021.202 (2021).
- 31 Tran, B. C., Teil, M. J., Blanchard, M., Alliot, F. & Chevreuil, M. BPA and phthalate fate in a sewage network and an elementary river of France. Influence of hydroclimatic conditions. *Chemosphere***119**, 43-

51 (2015).

32 Dada, E. O. & Ikeh, R. K. Phthalate and Metal Concentrations in Drinking Water in Lagos, Nigeria. *Journal of health & pollution***8**, 180603, doi:10.5696/2156-9614-8.18.30 (2018).

33 Radwan, E. K., Ibrahim, M. B. M., Adel, A. & Farouk, M. The occurrence and risk assessment of phenolic endocrine-disrupting chemicals in Egypt's drinking and source water. *Environmental science and pollution research international***27**, 1776-1788, doi:10.1007/s11356-019-06887-0 (2020).

34 Milanović, M. *et al.* Seasonal variations of bisphenol A in the Danube River by the municipality of Novi Sad, Serbia. *Journal of the Serbian Chemical Society***81**, 333-345 (2016).

35 Sun, P. *et al.* Sorption and leaching behaviors between aged MPs and BPA in water: The role of BPA binding modes within plastic matrix. *Water research***195**, 116956 (2021).

36 Luo, R. *et al.* Singlet oxygen-dominated non-radical oxidation process for efficient degradation of bisphenol A under high salinity condition. *Water research***148**, 416-424, doi:10.1016/j.watres.2018.10.087 (2019).

37 Santhi, V. A., Sakai, N., Ahmad, E. D. & Mustafa, A. M. Occurrence of bisphenol A in surface water, drinking water and plasma from Malaysia with exposure assessment from consumption of drinking water. *The Science of the total environment***427-428**, 332-338, doi:10.1016/j.scitotenv.2012.04.041 (2012).

38 Shehab, Z. N., Jamil, N. R. & Aris, A. Z. Occurrence, environmental implications and risk assessment of Bisphenol A in association with colloidal particles in an urban tropical river in Malaysia. *Scientific reports***10**, 20360, doi:10.1038/s41598-020-77454-8 (2020).

39 Staples, C. *et al.* Distributions of concentrations of bisphenol A in North American and European surface waters and sediments determined from 19 years of monitoring data. *Chemosphere***201**, 448-458, doi:10.1016/j.chemosphere.2018.02.175 (2018).

40 Chakraborty, P. *et al.* Surveillance of plasticizers, bisphenol A, steroids and caffeine in surface water of River Ganga and Sundarban wetland along the Bay of Bengal: occurrence, sources, estrogenicity screening and ecotoxicological risk assessment. *Water research***190**, 116668, doi:10.1016/j.watres.2020.116668 (2021).

41 Im, J. & Loffler, F. E. Fate of Bisphenol A in Terrestrial and Aquatic Environments. *Environmental science & technology***50**, 8403-8416, doi:10.1021/acs.est.6b00877 (2016).

42 Zare Jeddi, M. *et al.* Biomonitoring and Subsequent Risk Assessment of Combined Exposure to Phthalates in Iranian Children and Adolescents. *International journal of environmental research and public health***15**, doi:10.3390/ijerph15112336 (2018).

- 43 Abtahi, M. *et al.* Health risk of phthalates in water environment: Occurrence in water resources, bottled water, and tap water, and burden of disease from exposure through drinking water in tehran, Iran. *Environmental research***173**, 469-479, doi:10.1016/j.envres.2019.03.071 (2019).
- 44 Jeddi, M. Z., Rastkari, N., Ahmadkhaniha, R. & Yunesian, M. Endocrine disruptor phthalates in bottled water: daily exposure and health risk assessment in pregnant and lactating women. *Environmental monitoring and assessment***188**, 534, doi:10.1007/s10661-016-5502-1 (2016).
- 45 Selvaraj, K. K. *et al.* Phthalate esters in water and sediments of the Kaveri River, India: environmental levels and ecotoxicological evaluations. *Environmental geochemistry and health***37**, 83-96 (2015).
- 46 Apel, P. *et al.* Time course of phthalate cumulative risks to male developmental health over a 27-year period: Biomonitoring samples of the German Environmental Specimen Bank. *Environment international***137**, 105467 (2020).
- 47 Kortenkamp, A. & Faust, M. Combined exposures to anti-androgenic chemicals: steps towards cumulative risk assessment. *International journal of andrology***33**, 463-474, doi:10.1111/j.1365-2605.2009.01047.x (2010).

Figures

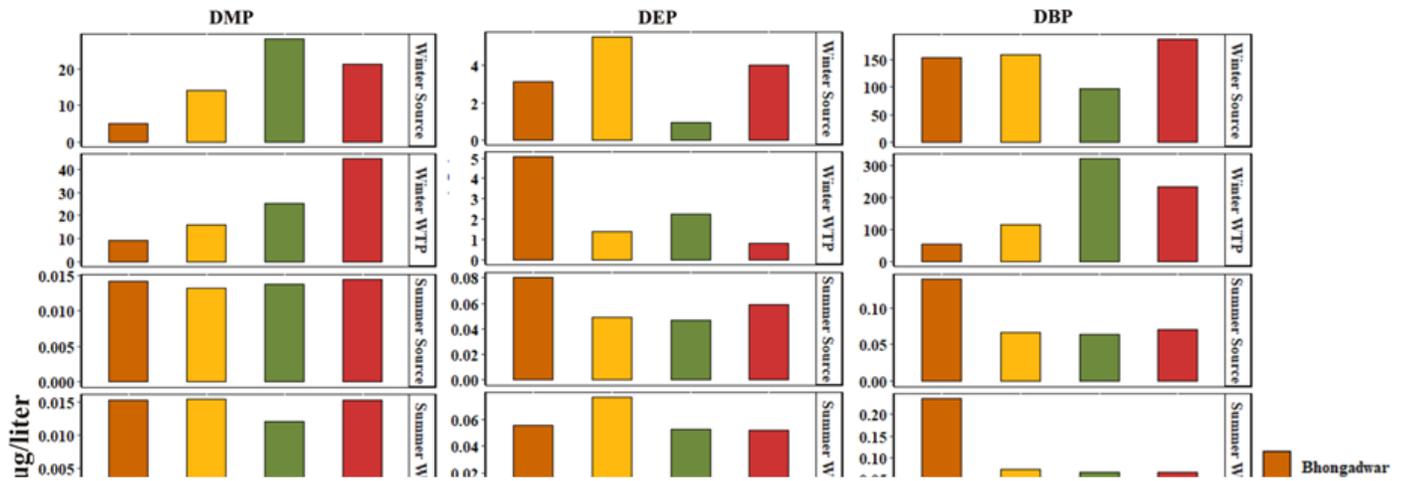


Figure 1

Area wise and seasonal comparison of dimethyl phthalate (DMP), diethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Benzyl butyl phthalate (BBP), di (2- ethylhexyl) phthalate (DEHP) and Di-n-octyl phthalate (DNOP) The data for WTP water samples (Summer) was not presented in the figure as all the targeted PAEs were not detected in any of the area.

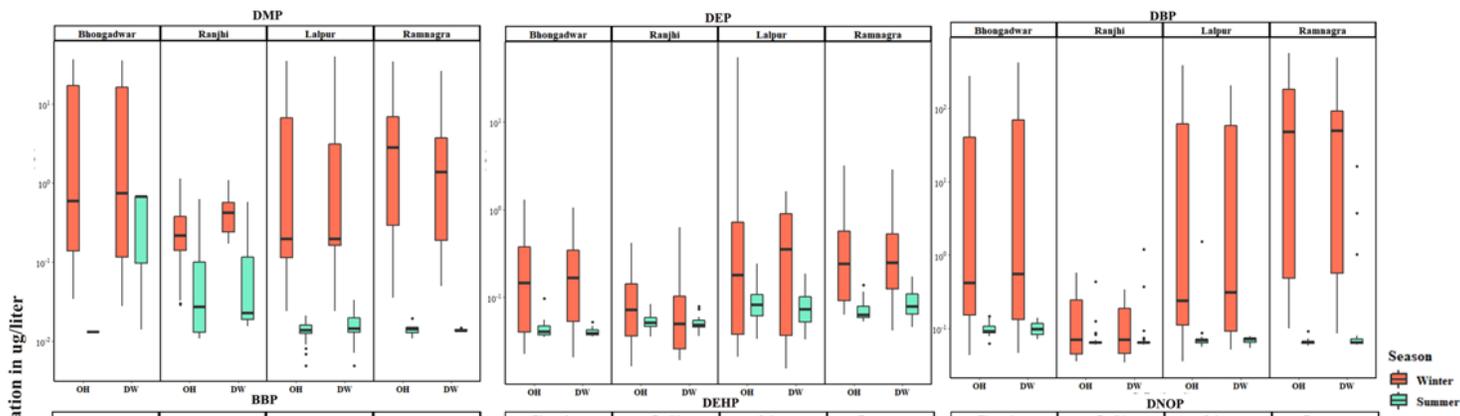


Figure 2

Area wise concentration of Phthalates (ug/l) in Overhead and Drinking water during winter and summer season. Box whisker plots showing the lower quartile, mean, upper quartile ranges of concentrations of dimethyl phthalate (DMP), diethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Benzyl butyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP) and Di-n-octyl phthalate (DNOP) in Overhead (OH) and Drinking water (DW) samples over two seasons. BBP was detected only in one sample during summer thus not shown in the above figure.

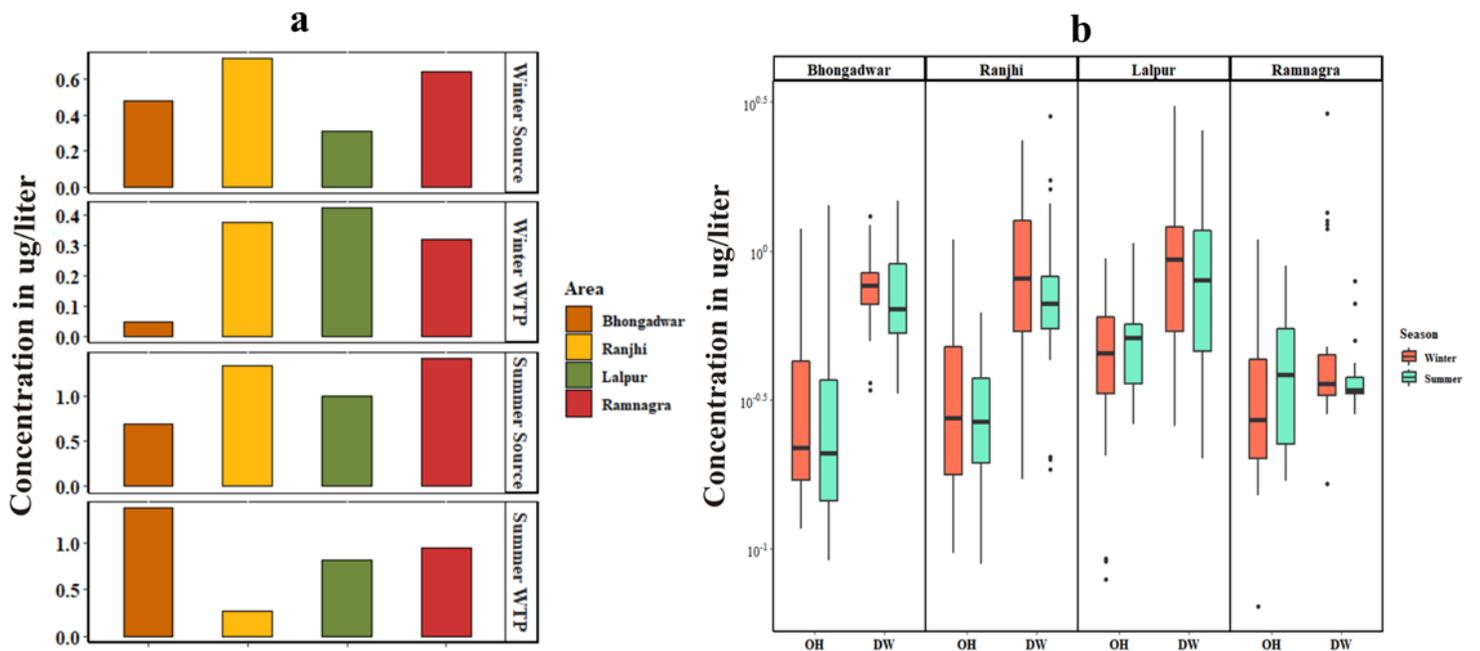


Figure 3

a. Area wise and seasonal comparison of Bisphenol A (BPA) concentrations in source and WTP water samples, b. Area wise concentration of Bisphenol A ($\mu\text{g/L}$) in Overhead and Drinking water during winter and summer season. Box whisker plots showing the lower quartile, mean, upper quartile ranges of concentrations of BPA in Overhead (OH) and Drinking water (DW) samples over two seasons.

Figure 4

GIS Map illustrates the sampling sites of the Jabalpur city.

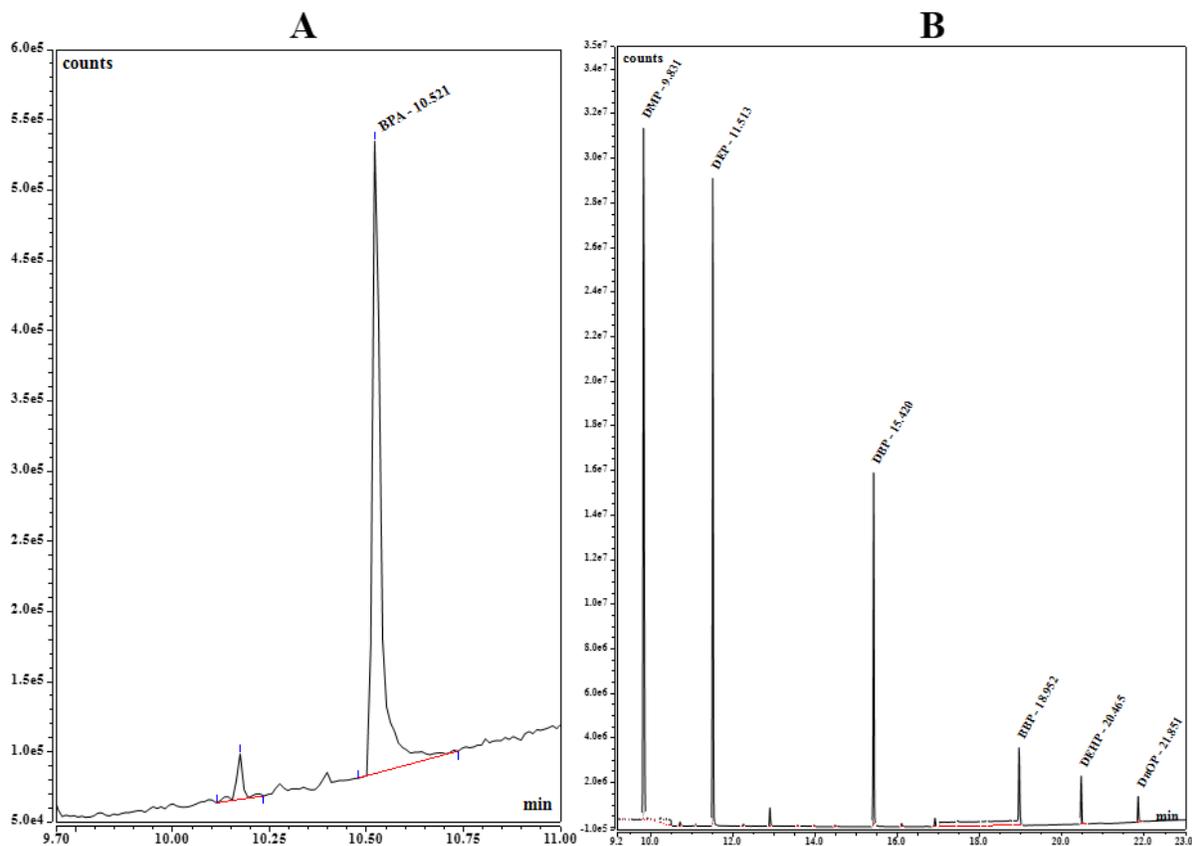


Figure 5

Ion Chromatogram of (a) BPA and (b) PAEs Congeners and their peak identities are as follows: DMP (Dimethyl phthalate), Di-ethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Benzyl butyl phthalate (BBP), Di (2-ethylhexyl) phthalate (DEHP), and Di-n-octyl phthalate (DNOP).

Supplementary Files

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