African Scientist Vol. 26, No. 1 March 31, 2025
Printed in Nigeria
1595-6881/2025 $80.00 + 0.00

https://africansciientistjournal.org

afs2025006/26109

Phthalate Esters in Raw and Finished Water from Drinking Water Treatment Plants and Human Exposure in Songkhla, Southern Thailand

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(Received February 13, 2025; Accepted in revised form February 25, 2025)

ABSTRACT: The presence of phthalate esters (PEs) in water treatment facilities has drawn a lot of interest because of the possible health risks. This research provide data on 6 PEs in the raw and finished water of three waterworks located in Songkhla Province, southern Thailand. Given that drinking water is a major way that people can be exposed to PEs, the fate of target PEs in the three conventional drinking water treatment plants was also analyzed. The results revealed that the amounts of Σ3PE in the Hat Yai (HY), Sadao (SA), and Phang La (PL) in raw water samples were relatively moderate, with mean values of 8.16, 5.54, and 5.27 µg/L, respectively. Bis(2-ethylhexyl) phthalate (DEHP) dominated the PEs concentration ranging from 1.69 to 4.84 µg/L, with mean values ranging from 1.93 to 3.71µg/L. These chemicals' distribution and occurrence were highly geographically dependent. In the meantime, the levels of PEs in the final water samples showed that PE removal was not very effective after the conventional drinking water treatment in the waterworks (51.12% to 67.5%). According to the possible ecosystem risk assessment, the raw water samples had a comparatively low risk of PEs. However, there are still dangers associated with drinking tap water contaminated by PEs; as a result, source control should receive extra attention in the source water used by the investigated provincial waterworks, and advanced treatment processes for drinking water supplies should be implemented.

Keywords: Occurrence, PEs, Raw water, Tap water, U-Tapao canal, Water treatment plant.

Introduction

Synthetic chemicals known as phthalate esters (PEs) have drawn attention in recent decades because of their widespread contamination and possible negative public health implications. In order to increase the durability, workability and flexibility of polyethylene products, PEs are mostly utilized as plasticizers (Net et al., 2015; Selvaraj et al., 2016). According to Wee and Aris (2017) and Abtahi et al. (2019), PEs are endocrine-disrupting chemicals (EDCs), and their effects could not show up until prolonged exposure. Long-term exposure to PAEs, particularly through drinking water, can cause cancer, developmental defects, polyneuropathy, and disturbance of the endocrine system, among other harmful health effects (Li *et al*., 2010; Wee and Aris, 2017; Kong *et al*., 2017; Van Zijl *et al*., 2017). Moreover, the intake of PEs contaminated water has been linked to endocrine-disrupting activities (Wee and Aris, 2017; Chiang *et al*., 2017; Abtahi *et al*., 2019). Di (2-Ethylhexyl) phthalate (DEHP) was included in the IARC class B2 (probable human carcinogen) list, with possible teratogenic and carcinogenic effects (Oehlmann *et al*., 2008). Due to the potential human health consequences, the European Union (EU) has banned the use of six PEs, including di- (2-Ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), di-n-butyl phthalate (DBP), di-isononyl phthalate (DiNP), di-isodecyl phthalate (DIDP) and di-n-octyl phthalate (DnOP) in toys and products for children (Matsumoto, 2008). Moreover, for reducing the public health risk of PEs contamination in drinking water, some countries and organizations have regulated the

guideline values of PEs in drinking water. In the United State of America (USA), the maximum contaminant level (MCL) value of DEHP is 6 μg/L (Net *et al*., 2015). World Health Organization (WHO) stipulated the level of 8 μg/L for DEHP (WHO 2011). In China, the drinking water quality standards of 8, 3, and 300 μg/L were set for DEHP, DBP, and DEP, respectively (NSC 2006); whereas, in Japan, the standards values of 100, 200, and 500 μg/L for DEHP, DBP, and BBP, respectively were stipulated for drinking water (WHO, 2011; Liu *et al.,* 2014; Net *et al.,* 2015).

One new area of public health issue is PE exposure through water from municipal water supply systems. According to studies, surface waters used as municipal source waters have higher PE levels due to industrial and domestic discharge and indiscriminate dumping of solid plastic waste (Tang *et al*., 2012, Liu *et al*., 2013; Liu *et al*., 2014; Yang *et al*., 2014; Wee and Aris, 2017). Besides, PEs in source waters are the main contributors to drinking water (Liu *et al*., 2013; Liu *et al*., 2014; Kong *et al*., 2017; Sulentic *et al*., 2018). PEs can also seep into public water supply networks that use polyvinyl chloride (PVC) or high-density polyethylene (HDPE) pipes (Liu *et al*., 2013; Dumitrascu, *et al*., 2015; Sulentic *et al*., 2018; Okpara *et al*., 2022). However, the ineffective removal of PEs by traditional drinking water treatment plants has been blamed for the presence of PEs in finished water, potentially exposing humans to PEs (Liu *et al*., 2013; Kong *et al*., 2017; Sulentic *et al*., 2018). Moreover, according to earlier research, the main ways that people are exposed to DBP, DEHP, and di-n-octyl phthalate (DnOP) are through the intake and absorption of tap water (Tang *et al*., 2012; Liu *et al*., 2013; Kong *et al*., 2017; Sulentic *et al*., 2018). Furthermore, drinking water has been found to be a significant source of PE exposure in people in France (Martine et al., 2013). However, conventional drinking water standards issued by regulatory agencies do not readily contain PEs whose detrimental impacts on public health have been established, particularly in developing nations (Liu *et al*., 2013; Kingsley and Witthayawirasak, 2020; Okpara *et al*., 2022).

The majority of drinking water treatment facilities (DWTPs) in Thailand employ traditional treatment techniques such chlorination, sedimentation, filtration, and coagulation (Tabtong *et al*., 2015; Musikavong, *et al*., 2016). PEs pollutants in raw water cannot be completely eliminated by these procedures (Liu *et al*., 2013; Kong *et al*., 2017; Okpara *et al*., 2022). Therefore, PEs may persist in drinking water after treatment (Kong *et al*., 2017; Sulentic *et al*., 2018). Additionally, PEs have been found in water bodies that provide raw water to Thailand's provincial waterworks including the Chao Phraya River and the U-Tapao canal (Sirivithayapakorn, and Thuyviang, 2010; Sirivithayapakorn *et al*., 2014; Kingsley and Witthayawirasak, 2020) Interestingly, PEs are not specifically mentioned in Thailand's drinking and surface water standards or laws (Sirivithayapakorn *et al*., 2014; Kingsley and Witthayawirasak, 2020; Okpara *et al*., 2022). Eliminating human exposure to PEs through drinking water may be hampered by the absence of regulations and established drinking water guidelines. Formulating policies pertaining to public health issues requires knowledge of the concentrations, nature, and human exposure of PEs in water supply systems. Furthermore, risk management experts employ solid empirical evidence on pollution exposure and risk estimation to establish thresholds and decide whether remediation or regulation is necessary. The U-Tapao canal supplies raw water to the three provincial waterworks investigated in this study. The provincial drinking water treatment plants produces tap water to serve about 700,000 residents (Musikavong, *et al*., 2016; Okpara *et al*., 2022). The largest drinking water treatment plant is the Hat Yai provincial waterworks which produces a water supply of about 168,000 m^3/day. The raw water from the canal has been contaminated with treated and untreated wastewater (Musikavong, *et al*., 2016; Kingsley and Witthayawirasak, 2020). Besides, an elevated concentration of PEs, including DBP, DEHP, and DiNP, was detected in the canal surface water due to several communities, industries, and agricultural areas located at the upstream and midstream of the canal (Kingsley and Witthayawirasak, 2020). Nevertheless, the concentration of PEs in the raw and finished water from the drinking water treatment plants and human exposure of the residents in the area is lacking.

Therefore, the objectives of this present study were (i) to assess PEs' concentration, makeup, and estrogenic potential in raw water; (ii) to look at how well three waterworks in Songkhla province that employ a traditional treatment method remove PEs from the water; and (iii) to assess the possibility of PEs having a negative impact on human health. Consequently, a useful contamination record in the study area may be obtained by looking into PEs in the water.

Materials and methods

Sample collection: Raw and finished water samples were drawn from the three-provincial waterworks in the study areas. Raw water or influent was collected at 0.5 m below each site of the water surface, representing the mixed water columns. The raw water was collected in pretreated brown bottles. Finished water samples were taken from the distribution points of each waterworks. Water samples were collected in 1liter prepared bottles in

triplicates, placed in an icebox, transferred to the laboratory, and held at 4 ºC refrigerators in the laboratory until analysis. An aliquot of 120 µL of 0.75 g/mL sodium thiosulfate solution was put in 1 L of finished water to block the chlorine content of tap water and prevent it from creating interference and impact the analysis. All samples were extracted within two days and analyzed within three days. The map of the locations of investigated waterworks is shown in Figure 1.

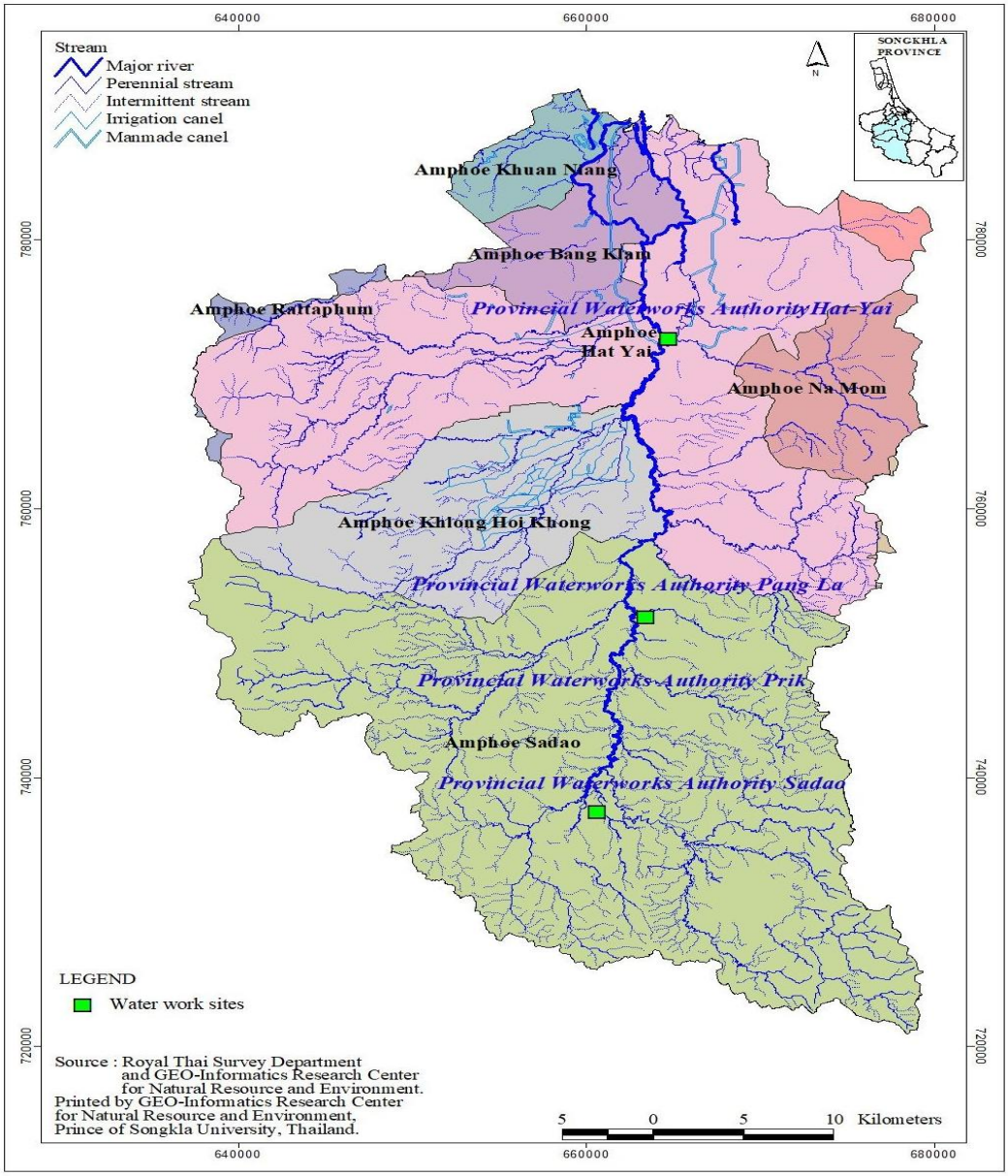

Figure 1: Map of study area

Chemicals and reagents: Standard solution of 6 PEs (DBP, BBP, DEHP, DnOP, DiNP, and DIDP) were obtained from AccuStandard, USA. Hexane, methanol, acetone, and dichloromethane, were of HPLC grades and obtained from Waters, USA. Also, Solid-phase extraction cartridge Florisil (1g 6cc, Chrom, and Sep), an internal standard of 100 mg/L of benzyl benzoate (BBZ) and anhydrous sodium sulfate were obtained from Dr. Ehrenstorfer Gmbh (Augsburg, Germany).

Sample collection, pretreatment and instrumental analysis: The pretreatment procedures for water samples were described in detail in a previous study (Kingsley and Witthayawirasak, 2020). Here, we briefly presented these procedures. Before solid-phase extraction, 1 liter of each water sample was filtered via glass fiber filters (GF/F, 0.7-µmpore size, Whatman). Florisil cartridges (1g 6cc, Chrom, and Sep) were used to extract the six targeted PEs congeners from the water samples. Finally, the extracts were reconstituted with l mL of n-hexane, and benzyl benzoate was added as an internal standard before the GC–MS analysis. The extracted PEs congeners

were analyzed using gas chromatography fixed to a mass spectrometer (GC-MS), Agilent model 6890N GC–5973 MSD (Agilent Technologies). The working condition of the GC-MS has been previously described (Kingsley and Witthayawirasak, 2020).

Quality control: All glassware was cleaned and rinsed in ethanol before being heated to 350 °C for 8 h in order to reduce the danger of contamination from PEs. In this investigation, low PEs-containing reagents such methanol, n-hexane, and ethyl acetate were employed. With n-hexane, ethyl acetate, and methanol—two reagents with comparatively low evaporation points—the rapid evaporation procedure reduced system blanks. For every extraction round of ten samples, procedural blanks and spiked samples were processed. A signal-to-noise ratio of three and ten times, respectively, was used to estimate the limit of detection (LOD) and limit of quantification (LOQ) for individual PEs congeners. For PEs examined in water, the relative standard deviation (RSD %) was all less than 15%, meaning that every precision assessment met the quality requirements.

Analysis of estrogenic activity of PEs: As endocrine disrupting compounds, PEs are able to mimic the activity of natural estrogens such as 17-β-estradiol (E2) (Céspedes *et al*., 2004). The estrogenic activity of samples due to the presence of PEs has been calculated by comparing their activity with that of this estrogen and expressed as estradiol equivalents (EEQ) (Sun *et al*., 2013; Domínguez-Morueco *et al*., 2014; Tiwari *et al*., 2018).

The estrogenic potential of PEs in raw and finished water can be represented by the estradiol equivalent (EEQ) concentration, which can be obtained by the estradiol equivalency factor (EEF) and measured environmental concentration (MEC) of pollutants (PEs), which is estimated as indicated in Equation (1).

$$EEQ = EEF \times MEC \quad (1)$$

EEF values for DBP and DEHP employed in this present study were 2.5×10^{-6} and 1.3×10^{-5} respectively, as obtained by Sun *et al*., (2013).

Total EEQ of PEs (DBP and DEHP) is estimated by using equation 2.

$$EEQ_{total} = EEQ_{DEHP} \times EEQ_{DBP} \quad (2)$$

European Commission sets the concentration causing endocrine disrupting effects as 1 ng-E2/L, indicating that the substances with EEQ larger than 1 ng-E2/L would affect the endocrine systems of aquatic organisms in the receiving water (European Commission,1996).

Human exposure assessment: The exposure of PEs in adults via the ingestion of the investigated finished water from the waterworks were calculated by using the Eq. (3) (USEPA 1989)

$$AE = \frac{C_t \times IR \times EF \times ED}{BW \times AT} \quad (3)$$

where AE (µg/kg BW/day) is the amount of pollutant exposure to adults through tap water ingestion. Ct (µg/l): represents the concentration of PEs in finished water, IR (ingestion rate), and daily water intake in liters. EF (exposure frequency): is the number of days (365) exposure in a year. ED (exposure duration): is designated as a lifetime in years (i.e., 70 years for an adult), BW (body weight) of the adult is assumed as 60 kg. AT: is averaging time, i.e., ED ×365 days.

Statistical analysis: The descriptive statistic was performed using IBM's SPSS version 20.0 and the association between the individual congeners and the total PEs found in raw water was examined using Pearson's correlation coefficient.

Result and Discussion

PEs in raw water: The concentrations of PEs in raw water samples collected from the provincial waterworks are presented in Table 1.

Table 1: PEs concentrations in raw water (µg/L)

PEs	SA (µg/L) n=4			PL (µg/L) n=4			HY (µg/L) n=4		
	Min	**Max**	**Mean±SD**	**Min**	**Max**	**Mean±SD**	**Min**	**Max**	**Mean±SD**
DBP	ND	2.04	1.89±0.15	ND	1.82	1.68±0.18	ND	3.36	2.21±0.58
DEHP	1.84	2.68	2.18±0.36	1.69	2.14	1.93±0.20	2.88	4.84	3.71±0.82
DiNP	ND	1.74	1.47±0.23	ND	1.68	1.63±0.06	ND	2.47	2.04±0.29
∑PEs	1.84	6.46	5.54±0.74	1.69	5.64	5.27±0.48	2.88	10.67	8.16±1.69

The total PE concentrations varied from 1.84 to 6.46 µg/L (mean value of 5.54±0.74µg/L) for SA, 1.69 to 5.64µg/L (mean value of 5.27±0.48µg/L) for PL, and 2.88 to 10.67µg/L (mean value of 8.16±1.69µg/L) µg/L for HY. Among the 3 PEs detected in the raw water samples, DEHP was measured at average concentrations of 2.18±0.36 for SA, 1.93±0.20 for PL, and 3.71±0.82 for HY. Considering the individual PE congeners in the investigated raw water samples, the result indicated DEHP was the most predominant accounting for 26.99 to

45% in the investigated waterworks. Followed by DBP which contributed 19.86 to 32.27% and then DiNP 13.50% to 29.72 of the Σ3PEs concentrations. This result agrees with earlier studies that reported DEHP and DBP as the predominant PEs congeners in water (Jia *et al*., 2014; Gou *et al*., 2016; Kong *et al*., 2017). The predominant DEHP values measured in raw water have been reported in different locations, including USA, China, Taiwan, and South Africa. Furthermore, the three PE congeners are essential and prevalent additives in several consumer and industrial products, household items, and personal care products, implying that these applications are the primary source of PE contamination of water (Peijnenburg and Struijs 2006, Kong *et al*., 2017). Each congener contributing to the total PEs levels can be influenced by the origin of the release. PEs are discharged into source water via several sources, including domestic and industrial wastewater, disposal of municipal and industrial solid waste, land application of sewage sludge, and PEs-containing products (Net *et al*., 2015; Abtahi *et al*., 2019).

Three of the PEs (DBP, DEHP and DiNP) found in raw water in this study are categorized as EDCs (Li *et al*., 2010; Shi *et al*., 2012; Gou *et al*., 2016; Santangeli, *et al*., 2017; Forner *et al*., 2019). In this study, the mean values of DBP in raw water were 1.89±0.15, 1.68±0.18, and 2.21±0.58 in SA, PL, and HY. A study has reported that DBP is the primary TR antagonist in water sources in the Yangtze River Delta, while DEHP and DiNP also contributed (Shi *et al*., 2012). DBP caused TR antagonist potencies in surface water samples with the equivalents ranging from 2.8×10^{1} to 1.6×10^{3} μg/L (Shi *et al*., 2012). Previous work that investigated the effect of DBP on T3-dependent activation of the TRβ gene in T3-induced metamorphosing tadpoles revealed that TR antagonist response was detected at 1.1×10^{3} μg/L DBP (Sugiyama *et al*., 2005). Besides, DBP has been reported to affect reproductive fitness adversely, and perinatal exposure to DBP could cause defectiveness and underdevelopment of epididymis, prostate, seminal vesicle, and other organs (Hu *et al*., 2013). Not many studies have evaluated DiNP in raw and tap water (Wen *et al*. 2017; Van Zijl *et al*. 2017). Therefore, it is advised to include DiNP when evaluating raw and tap water samples for PEs. The remaining 3 PEs congeners including, benzyl butyl phthalate (BBP), di-n-octyl Phthalate (DnOP), and diisodecyl phthalate (DIDP), were below the LOD and could be due to their lesser usage in Thailand at present.

A small discrepancy of the total 3PEs concentration in raw water samples of SA and PL was observed, but variation was observed at HY. The highest concentrations of the 3 PEs were measured at HY. The Σ3PEs of SA and PL were relatively low compared to HY's level because they are located far from densely urbanized areas. The HY water source collects a lot of home and industrial effluent from Hat Yai City and is encircled by busy eateries and business avenues. Table 2 displays the relationships between the concentrations of DEHP, DBP, and DiNP and the total PEs in the water samples. DEHP, DiNP, and Σ3PE were found to have significant correlations with each other. This suggests that the substances have a significant impact on the total concentrations of PEs, and that DEHP can be used as an indicator to estimate the level of other PEs in the source water under investigation.

Table 2: Pearson's correlation matrix of individual PEs concentration and total PEs in raw water

PEs	**DBP**	**DEHP**	**DiNP**	**∑PEs**
DBP	1			
DEHP	0.246	1		
DiNP	0.014	0.656*	1	
∑PEs	0.518	0.869**	0.804**	1

***** Pearson's correlation significant at the 0.05 level

****** Pearson's correlation significant at the 0.01 level

PEs profile: Numerous researches have proposed that determining the sources and biogeochemical characteristics of PEs in multimedia contexts can be aided by analyzing the congeners profile or composition (Zeng *et al*., 2008; Wang *et al*., 2014). The profiles of the detected PEs in this study are shown in Figure 2.

With contributions of 77.8 % for SA, 73.3 % for PL and 76.1 % for HY to the total PEs loads in the water, it is evident that DEHP was the most prevalent in the water sources. DBP and DiNP came in second and third, with 18.3, 45%, and 4.3% and 12%, 13%, and 17% for SA, PL, and HY, respectively. Numerous parameters, such as hydrological circumstances, degradation, accumulation pattern, sedimentary dispersion, water solubility and source configuration may be reflected in the profile pattern of PEs congeners. In the polymer sector, DEHP is widely used as a plasticizer (Zeng et al., 2008). Because they are longer and branch alkyl PEs, DEHP and DiNP are more likely to sorb in sediment and to degrade. The findings show various trends in the intake of plastic contaminants over the sampling periods. DBP is utilized in epoxy resins and special adhesive formulations, which are crucial indicators that the PEs at the sampling locations are from industrial pollution, as a chemical factory is located close to the water source.

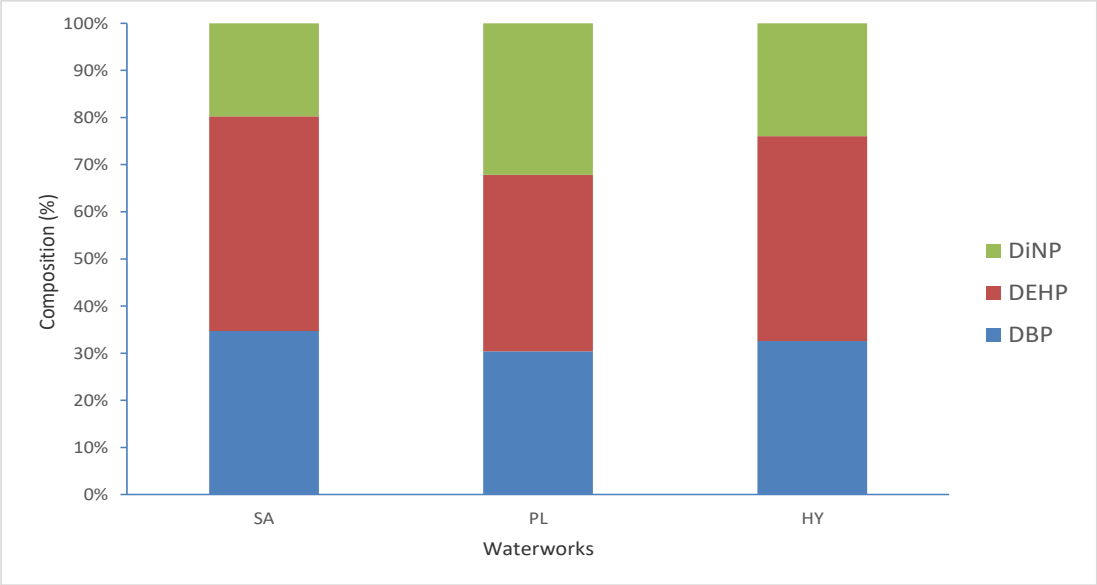

Figure 2: PEs composition of the raw water samples in investigated provincial waterworks

PEs in finished water from treatment plants: The measured concentrations of PEs in the finished water samples are shown in Table 3.

Table 3: PEs concentrations in finished water (µg/L)

PEs	**SA (µg/L) n=4**			**PL (µg/L) n=4**			**HY (µg/L) n=4**		
	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD
DBP	ND	0.78	0.63±0.14	ND	0.68	0.54±0.12	ND	1.07	0.75±0.21
DEHP	0.59	0.98	0.81±0.17	0.53	0.85	0.69±0.16	1.02	1.24	1.12±0.09
DiNP	ND	0.64	0.54±0.08	ND	0.52	0.48±0.08	ND	0.99	0.75±0.18
∑PEs	0.59	2.40	1.98±0.39	0.53	1.99	1.71±0.36	1.02	3.30	2.62±0.48

Like the raw water, only DBP, DEHP, and DiNP were detected in the finished water as other congeners were below the LOD. The total PE concentrations in finished water ranged from 0.59 to 2.40 µg/L (mean value of 1.98±0.39µg/L) for SA, 0.53 to 1.99µg/L (mean value of 1.71±0.36µg/L) for PL, and 1.02 to 3.30µg/L (mean value of 2.62±0.48µg/L) for HY. The total levels of PEs in finished water in this study was not consistent with previous study from Spain (1.034µg/L; Domínguez-Morueco *et al*., 2014) and France (0.427 µg/L; Martine *et al*., 2013). In contrast, Tang *et al*. (2012) observed much higher drinking water levels of PEs in China to be as high as 96 µg/L affecting children's serum sex hormone levels in the polluted area. The most crucial congener in the finished water was DEHP, with the mean concentration of 1.12, 0.81, and 0.69 µg/L, for the HY, SA, and PL suggesting the highest composition of total PE levels in the finished water. Following DEHP is DBP with mean concentrations of 1.07, 0.63, and 0.54 for HY, SA, and PL, and DiNP with mean levels of 0.75 for HY, 0.54 for SA and 0.48 µg/L for PL. The occurrence of DiNP in tap water may pose adverse health effects. A Norwegian study evaluating urinary PEs biomarkers showed that DiNP increased asthma risk in children (Bertelsen *et al*., 2013). In vitro data have indicated that DiNP enhances the allergic response by upregulation of IL-4 (Lee *et al*., 2004). It has been suggested that DiNP induces asthma by modulation of the Th1/Th2 equilibrium (Hwang *et al*., 2017). Besides, a study has reported that DiNP is related to a shorter AGD in boys at the age of 21 months, which is of concern since AGD has been associated with male genital congenital disabilities and impaired reproductive function in adult males.

There was a small variance in the detected concentrations of the examined PEs in the completed water samples that were taken from the three waterworks. DEHP, DBP, and DiNP concentrations in the HY were greater than those in the SA and PL for the finished water from the various effluents, whereas DBP, DEHP, and DiNP and DEHP concentrations were comparatively similar in the SA and PL. The removal of PEs by these three waterworks varied greatly without consistent removal efficiency, ranging from 51.8% to 67.2% in the current study. This outcome is consistent with other research that found that CDWTP has a low removal effectiveness of these PE groups (Liu et al., 2013; Kong et al., 2017). Less than 51.8% of DBP was removed in the SA, which was the lowest removal efficiency. No sound removal efficiencies were found for the PEs in any of the three

waterworks, suggesting that conventional drinking water treatment is unable to effectively remove these priority contaminants, independent of the kind of water supply.

CDWTP involves physical techniques to deal with the colloids and particles. Numerous investigations on ecological fates of PEs have shown that the primary process for their removal in water bodies is microbial action or oxidation (Yang *et al*., 2014; Gao and Wen, 2016). As a result, the basic methods for eliminating PEs from the water should be integrated into the treatment procedure. However, more research would seem to be needed because the removal efficiencies of PEs by these sophisticated drinking water treatments in waterworks are restricted.

Comparison with other water bodies: Although research of the concentrations of DBP and DEHP in raw and finished water have been reported, the data on DiNP are scarce (Van Zijl *et al*. 2017; Kingsley and Witthayawirasak, 2020). In this study, the results of DBP and DEHP concentrations published in the literature for raw and finished water in conventional drinking water treatment plants (CDWTP) and advanced drinking water treatment plant (ADWTP) are presented in Table 4.

Table 4: Comparison of DBP and DEHP levels obtained in this study with others in literature

Location	**Method of treatment**	**Raw water**		**Finished water**		**References**
		DBP (µg/L)	**DEHP (µg/L)**	**DBP (µg/L)**	**DEHP (µg/L)**	
Taiwan	CDWTP	<MDL-0.76	<MDL-2.50	<MDL-0.84	<MDL-2.88	Guo *et al*. (2016)
China	CDWTP	0.05-4.49	0.13-6.57	0.02-1.71	0.05-2.36	Liu *et al*. (2013)
China	CDWTP	0.02-0.08	0.18-0.75	0.01-0.03	0.07-0.31	Kong *et al*. (2017)
USA	CDWTP	1.44-8.34	2.67-5.94	(mean, 2.73)	2.43-2.68	Loraine and Pettigrove (2006)
USA	ADWTP	0.05-0.06	0.12-0.17	ND	ND	Benotti *et al*. (2009)
China	ADWTP	14.00-100	0.46-7.00	0.07-0.19	0.01-0.05	Hu *et al*. (2013)
Taiwan	ADWTP	0.08-0.09	0.13-0.16	0.01-0.07	0.02-0.12	Yang *et al*. (2014)
Thailand	CDWTP	ND-3.36	1.69-4.84	ND-1.07	0.59-1.24	Present study

As shown in Table 4, the levels of DEHP and DBP in raw and finished water samples in the CDWTP of the present study were below those documented for South Carolina, USA and Harbin city, Northeast China (Liu *et al*., 2013) and above those documented for East China and Taiwan (Guo *et al*., 2016, Kong *et al*., 2017). According to Guo *et al*. (2016), the concentration of DEHP in raw water was slightly higher than the level in finished water, which the authors attributed to PEs leaching from the pipes into the water. The levels of DEHP and DBP in finished water samples in CDWTP were greater than those of finished water in ADWTP, suggesting that the ADWTP might be more effective at the removing of PEs congeners from raw water. However, it is not always a viable option due to much higher operational cost. Thus, strategies to limit source contamination and effectively remove PEs from raw water are also recommended and may include the development of more effective water treatment technologies and public awareness campaign (Van Ziji *et al*., 2017).

Oestrogenicity of raw and finished water: The oestrogenic activity due to the presence of PEs was calculated for each provincial waterworks. For raw water, the calculated mean value of EEQ for DBP were found as 0.0047 for SA, 0.0042 for PL and 0.0055 for HY while those of DEHP were 0.028 for SA, 0.025 for PL and 0.048 for HY. For finished water, the calculated mean value of EEQ for DBP were found as 0.0016 for SA, 0.0014 for PL and 0.0019 for HY while those of DEHP were 0.011 for SA, 0.009 for PL and 0.015 for HY. The EEQTotal for all the water samples were less than 1 ng-E2/L, indicating that on average, the phthalates alone could not probably cause endocrine disruption in aquatic organism in the raw and finished source water. As can be seen, DEHP presented the highest oestrogenicity values in all cases, with these values being higher in the raw water than in finished drinking water, probably due to the fact that the latter is treated.

Exposure assessment of PEs in water: Because of their endocrine disruptive properties, PEs have been a serious public health problem in recent decades when they have been found in source water and finished drinking water (Shi et al., 2012; Tang et al., 2012; Liu et al., 2013). Consuming tap water has been found to be a major way for people to be exposed to Pes (Shi *et al*., 2012; Dumitrascu, *et al*., 2015). Besides, drinking water is a significant exposure pathway to PEs in adults and children (Dumitrascu, *et al*., 2015; Sulentic *et al*., 2018). In this present study, to evaluate the potential and harmful effects of PEs in humans, quality guidelines for source and drinking water standards were used. The result of this study suggested that the mean DEHP and DBP concentrations were below the Reference doses (RfDs) recommended by United State Environmental Protection Agency (USEPA) WHO and China. Thus, the current concentrations do not harm human health. This finding is agreeable with previous studies (Liu *et al*., 2013; Kong *et al*., 2017; Okpara *et al*., 2022).

Nevertheless, PEs are EDCs that can negatively impact both humans and wildlife's endocrine systems' ability to operate normally. These effects might not show up until the exposure is extensive or chronic, and they might also be permanent. The findings of this study indicate that PEs were found in drinking finished water, which is

something that people may consume on a regular basis. This suggests that tap water is a major source or pathway of exposure to these organic contaminants that affect hormones. The highest concentration of PEs, including DBP, DEHP, and DiNP detected in the finished water, occurred at HY, where the daily intake for adults was 0.00442, 0.00742, and 0.00428 µg/kg/day, respectively. Based on the current study's findings, the estimated daily intake levels of DEHP are significantly lower than the US EPA reference dose of 20 µg/kg/day, the EFSA total daily intake of 50 µg/kg/day for the risk of increased liver weight, the ADI for female reproductive malformations (11.51 µg/kg/day) recommended by the Consumer Product Safety Commission (CPSC), and the developmental risk of testicular toxicity for women of reproductive age and adolescents. Besides, the daily intake of DEHP obtains in this study are lower than values reported in India (0.027µg/kg/day) and Taiwan (0.0823 and 0.115µg/kg/day, male and female), but similar to those documented in France (0.00105 µg/kg/day). The daily intake of DBP via drinking finished water was much lower than the RfD of 100µg/kg/day, recommended by the USEPA. Since all of the values estimated in this investigation were well below the suggested limits, there was no discernible harm to human health.

Additionally, the estimations fell short of the range of 0.08 to 69.6 µg/kg/day for overall dietary intake (DI), which was determined when numerous exposure pathways were taken into account (Gavala *et al*. 2004; Net *et al*. 2015). This evaluation of Thai residents' exposure highlights the need for additional research to identify other essential sources of PEs in Thailand, particularly those obtained by ingestion (others than water), given the potential negative effects of PEs on their endocrine properties, associated potential decline in fertility, and potential carcinogenic properties (Deblonde et al. 2011). Since drinking water adds to the daily continuous absorption of PEs, careful monitoring is advised. This study also suggests that epidemiologic research is required to assess the possible consequences of long-term exposure to PEs in Thai citizens. Moreover, the insignificant health risk should not be disregarded because drinking tap water may also contribute to a number of additional health problems brought on by various contaminants, including pesticides, heavy metals, and disinfection products, which could result in a significant overall burden of disease (Abtahi et al., 2019). Overall, humans are not at risk from the existing levels of PEs in the raw and finished water from the SA, PL, and HY.

However, organisms metabolize PEs to some extent. Future studies should therefore ascertain the possible impacts of metabolites (Gou et al. 2016). It's also important to remember that it was challenging to do a thorough risk assessment due to the absence of information from other PEs. Additionally, future study should take into account additional studies that estimate the intake of PEs among Thai inhabitants using both epidemiological and food analysis methods.

Conclusion

This study provided data on phthalate esters (PEs) in raw and finished water of three waterworks located in Songkhla Province, southern Thailand. The results revealed that the amounts of Σ3PEs in the raw water samples were relatively moderate. These chemicals' distribution and occurrence were highly geographically dependent. The levels of PEs in the final water samples showed that PE removal was not very effective after the conventional drinking water treatment in the waterworks. The risk assessment indicated that there was no risk associated with the PEs in the water samples. However, source control should receive extra attention in the source water used by the investigated provincial waterworks, and advanced treatment processes for drinking water supplies should be implemented.

References

Abtahi M, Dobaradaran S, Torabbeigi M, Jorfi S, Gholamnia R, Koolivand A, Darabil H, Kavousii A, Saeedi R: 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. Environ Res, 173: 469-479. 2019.

Bertelsen IR, Lødrup Carlsen KC, Calafat AM, Hoppin JA, Håland G, Mowinckel P, Carlsen K, Løvik M: Urinary biomarkers for phthalates associated with asthma in Norwegian children. Environ Health Perspect, 121(2): 251–256. 2013.

Benotti MJ, Trenholm RA, Vanderford BJ, Holady JC, Stanford BD, Snyder SA: Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. Environ Sci Technol, 43(3): 597–603. 2009.

Céspedes R, Petrovic M, Raldúa D, Saura U, Pina B, Lacorte S, Viana P, Barceló D: Integrated procedure for determination of endocrine-disrupting activity in surface waters and sediments by use of the biological technique recombinant yeast assay and chemical analysis by LC–ESI-MS. Anal Bioanal Chem, 378: 697–708. 2004.

Chiang C, Mahalingam S, Flaws J: Environmental contaminants affecting fertility and somatic health. Seminars Reprod Med, 35(03): 241–249. 2017.

Deblonde T, Cossu-Leguille C, Hartemann P: Emerging pollutants in wastewater: A review of the literature. Int. J. Hygiene Environ Health, 214(6): 442–448. 2011.

Domínguez-Morueco N, González-Alonso S, Valcárcel Y: Phthalate occurrence in rivers and tap water from central Spain. Sci Total Environ, 500-501: 139–146. 2014.

Dumitrascu I, Gurzau A, Gurzau EA: Pilot study on determination of phthalates from drinking water system supply of Cluj-Napoca by solid phase extraction and GC-MS analysis. Wulfenia J, 22: 345–358. 2015.

European Commission: Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No. 1488/94 on Assessment for Existing Substances. Office for Official Publications of the European Communities, Luxembourg, pp. 328-334. 1996.

Forner I, Constantinos P, Ioannis CM, Maria F, Fabiana P, Di Marzo V, Calduch-Giner J, Pérez-Sánchez J, Carnevali O: Effects of diisononyl phthalate (DiNP) on the endocannabinoid and reproductive systems of male gilthead sea bream (Sparus aurata) during the spawning season. Arch Toxicol, 93: 727–741. 2019.

Gavala HN, Yenal U, Ahring BK: Thermal and enzymatic pretreatment of sludge containing phthalate esters prior to mesophilic anaerobic digestion. Biotechnol Bioeng, 85: 561–567. 2004.

Gao DW, Wen ZD: Phthalate esters in the environment: A critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. Sci Total Environ, 541: 986–1001. 2016.

Gou YY, Lin S, Que DE, Tayo LL, Lin DY, Chen KC, Chen FA, Chiang PC, Wang GS, Hsu YC, Chuang KP, Chuang CY, Tsou TC, Chao HR: Estrogenic effects in the influents and effluents of the drinking water treatment plants. Environ Sci Pollut Res, 23(9): 8518–8528. 2016.

Hu X, Shi W, Wei S, Zhang X, Feng J, Hu G, Chen S, Giesy JP, Yu H: Occurrence and potential causes of androgenic activities in source and drinking water in China. Environ Sci Technol, 47(18):10591-10600. 2013.

Hwang YH, Paik MJ, Yee ST: Diisononyl phthalate induces asthma via modulation of Th1/Th2 equilibrium. Toxicol Lett, 272: 49–59. 2017.

Jia Y, Wang F, Zhang L, Shan C, Bai Z, Sun Z, Shen B: A comprehensive assessment of human exposure to phthalates from environmental media and food in Tianjin, China. J Hazard Mater, 279: 133–140. 2014.

Kingsley O, Witthayawirasak B: Occurrence, ecological and health risk of phthalate esters in surface water of U-Tapao canal. Toxics, 8: 58. 2020.

Kingsley O, Witthayawirasak B: Deterministic assessment of the risk of phthalate esters in sediments of U-Tapao Canal, Southern Thailand. Toxics, 8: 93. 2020.

Kong Y, Shen J, Chen Z, Kang J, Li T, Wu X, Fan L: Profiles and risk assessment of phthalate acid esters (PEs) in drinking water sources and treatment plants, East China. Environ Sci Pollut Res, 24(30): 23646–23657. 2017.

Lee MH, Park J, Chung SW, Kang BY, Kim SH, Kim TS: Enhancement of Interleukin-4 production in activated CD4+ T Cells by diphthalate plasticizers via increased NF-AT binding activity. Int Arch Allergy Immunol, 134(3): 213–222. 2004.

Li N, Wang D, Zhou Y, Ma M, Li J, Wang Z: Dibutyl phthalate contributes to the thyroid receptor antagonistic activity in drinking water processes. Environ Sci Technol, 44(17): 6863–6868.

Liu Y, Chen Z, Shen J. Occurrence and removal characteristics of phthalate esters from typical water sources in Northeast China. J Anal Methods Chem, 2013: 419349. 2013.

Liu X, Shi J, Bo T, Zhang H, Wu W, Chen Q: Occurrence of phthalic acid esters in source waters: A nationwide survey in China during the period of 2009 to 2012. Environ Pollut,184: 262–270. 2014.

Liu X, Shi J, Bo, T, Li H, Crittenden JC: Occurrence and risk assessment of selected phthalates in drinking water from waterworks in China. Environ Sci Pollut Res, 22(14): 10690–10698. 2015.

Loraine GA, Pettigrove ME: Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in Southern California. Environ Sci Technol, 40: 687–95. 2006.

Martine B, Marie-Jeanne T, Cendrine D, Fabrice A, Marc C: Assessment of adult human exposure to phthalate esters in the urban centre of Paris (France). Bull Environ Contam Toxicol, 90(1): 91–96. 2012.

Matsumoto M, Hirata-Koizumi M, Ema M: Potential adverse effects of phthalic acid esters on human health: A review of recent studies on reproduction. Regul Toxicol Pharmacol, 50(1): 37–49. 2008.

Musikavong C, Srimuang K, Tachapattaworakul Suksaroj T, Suksaroj C: Formation of trihalomethanes of dissolved organic matter fractions in reservoir and canal waters. J Environ Sci Health Part A, 51(9): 782–791. 2016.

National Standard of the People's Republic of China (NSC): China's Standard for Drinking Water Quality. Ministry of Health of the People's Republic of China and Standardization Administration of the People's Republic of China, GB 5749–2006. 2006. Available online: http://tradechina.dairyaustralia.com.au/wp-content/uploads/2018/08/GB-5749-2006-Standards-for-Drinking-Water-Quality.pdf (accessed on 13 September 2024). (In Chinese)

Net S, Sempéré R, Delmont A, Paluselli A, Ouddane B: Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ Sci Technol, 49:4019–4035. 2015.

Oehlmann J, Oetken M, Schulte-Oehlmann U: A critical evaluation of the environmental risk assessment for plasticizers in the freshwater environment in Europe, with special emphasis on bisphenol A and endocrine disruption. Environ Res, 108:140–149. 2008.

Okpara KE, Phoungthong K, Agbozu I, Edwin-Isotu E, Techato K: Phthalate esters in tap water, southern Thailand: Daily exposure and cumulative health risk in infants, lactating mothers, pregnant and nonpregnant women. Int J Environ Res Public Health, 19: 2187 2022.

Peijnenburg WJGM, Struijs J: Occurrence of phthalate esters in the environment of the Netherlands. Ecotoxicol Environ Saf, 63:204– 215. 2006.

Santangeli S, Maradonna F, Zanardini M, Notarstefano V, Gioacchini G, Forner-piquer I, Habibib H, Carnevali O: Effects of diisononyl phthalate on Daniorerio reproduction. Environ Pollut, 231:1051–1062. 2017.

Selvaraj KK, Mubarakali H, Rathinam M, Harikumar L, Sampath S, Shanmugam G, Ramaswamy BR: Cumulative exposure and dietary risk assessment of phthalates in bottled water and bovine milk samples: A preliminary case study in Tamil Nadu, India. Human Ecol Risk Assess, 22(5):1166–1182. 2016.

Shi W, Hu XX, Zhang FX, Hu GJ, Hao YQ, Zhang XW, Liu HL, Wei S, Wang XR, Giesy JP, Yu HX. 2012. Occurrence of thyroid hormone activities in drinking water from Eastern China: contributions of phthalate esters. Environ Sci Technol, 46(3):1811–1818.

Sirivithayapakorn S, Thuyviang K: Dispersion and ecological risk assessment of di (2-ethyl hexyl) phthalate (DEHP) in the surface waters of Thailand. Bull. Environ Contam Toxicol, 84: 503–506. 2010.

Sirivithayapakorn S, Thuyviang K, Jansak P: Distribution and ecological risk assessment of plasticizers in the Chao Phraya Delta, Gulf of Thailand. ASEAN Eng J, 4: 73–80. 2014.

Sugiyama S, Shimada N, Miyoshi H, Yamauchi K: Detection of thyroid system-disrupting chemicals using in vitro and in vivo screening assays in Xenopus laevis. Toxicol Sci, 88: 367–74. 2005.

Sulentic RO, Dumitrascu I, Deziel NC, Gurzau AE: Phthalate exposure from drinking water in romanian adolescents. Int J Environ Res Public Health, 15(10): 2109. 2018.

Sun Y, Huang H, Sun Y, Wang C, Shi XL, Hu HY, Kameya T, Fujie K: Ecological risk of estrogenic endocrine disrupting chemicals in sewage plant effluent and reclaimed water. Environ Pollut, 180: 339–344. 2013.

Tabtong W, Boontanon SK, Boontanon N: Fate and risk assessment of perfluoroalkyl substances (PFAS) in water treatment plants and tap water in Bangkok, Thailand. Procedia Environ Sci, 28: 750–757. 2015.

Tang CY, Li AQ, Guan YB, Yan L, Cheng XM, Ping L, Qunl S, Xinluo Y, Qihuang H, Chen Y, Xincu L: Influence of polluted SY River on child growth and sex hormones. Biomed Environ Sci, 25: 291–296. 2012.

Tiwari M, Sahu SK, Pandit GG: Environmental distribution and ecotoxicological concerns of phthalic acid esters in creek ecosystem. J Environ Sci Health A Tox Hazard Subst Environ Eng, 54(4):328-333. 2019.

Yang GCC, Yen CH, Wang CL: Monitoring and removal of residual phthalate esters and pharmaceuticals in the drinking water of Kaohsiung City, Taiwan. J Hazard Mater, 277: 53–61. 2014.

USEPA (United State Environmental Protection Agency) Risk Assessment Guidance for Superfund Volume 1Human Health Evaluation Manual (Part A); EPA/540/1–89/002; Office of Emergency and Remedial Response. US Environmental Protection Agency: Washington, DC, USA. 1989.

Van Zijl MC, Aneck-Hahn NH, Swart P, Hayward S, Genthe B, De Jager C: Estrogenic activity, chemical levels and health risk assessment of municipal distribution point water from Pretoria and Cape Town, South Africa. Chemosphere, 186: 305–313. 2017.

Wang J, Bo L, Li L, Wang D, Chen G, Christie P, Tenga Y: Occurrence of phthalate esters in river sediments in areas with different land use patterns. Sci Total Environ, 500:113–119. 2014.

Wee SY, Aris AZ: Endocrine disrupting compounds in drinking water supply system and human health risk implication. Environ Int, 106: 207–233. 2017.

Wen Z, Huang X, Gao D, Liu G, Fang C, Shang Y, Du J, Zhao Y, Lv L, Song K: Phthalate esters in surface water of Songhua River watershed associated with land use types, Northeast China. Environ Sci. Pollut Res. 25(8): 7688–7698. 2017.

World Health Organization: Guidelines for drinking-water quality—4th ed. WHO Press, Geneva. 2011

Zeng F, Cui K, Xie Z, Liu M, Li Y, Lin Y, Zeng Z, Li F: Occurrence of phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South China. Environ Int 34: 372–338. 2008.