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# Occurrence and Human Health Risk Assessment of Phthalate Esters in Sediments from a Riverine in Southern Thailand

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**ABSTRACT:** Phthalate esters (PAEs) are environmentally active organic pollutants that can cause endocrine disruption in humans. This study evaluated the human health risk associated with the dermal exposure to the levels of six common PAEs in sediments collected from U-Tapao River. A gas chromatograph/mass spectrometer (GC–MS) analytic method was used for the identification and quantification of PAEs. The human health risk was carried out using hazard quotient (HQ) and hazard index (HI). Of the 6 PAEs congeners measured, only 3 including di-n-butyl phthalate (DnBP), di-2-ethylhexy phthalate (DEHP) and di-isononyl phthalate (DiNP) were identified and quantified. Whereas, including benzyl butyl phthalate (BBP), di-n-octyl Phthalate (DnOP) and diisodecyl phthalate (DIDP), were not detected. The total concentrations of the 3 PAEs congeners found in the riverine sediment samples ranged from 70.0 to 1870 ng/g. The most abundant PAEs congener was DEHP ranging from 70 to 890 ng/g, followed by DiNP ranging from non-detectable (ND) to 820 ng/g, then DnBP ranging from ND to 160 ng/g. The calculated HQs and HIs were < 1, indicating that PAEs congeners posed acceptable health risk via dermal contact on adults and children. The baseline data obtained in this study will be useful for the strategic pollutant control and management in the riverine ecosystem.

**Keywords:** Phthalate esters, Sediments, Human health risk, Mixture risk, U-Tapao River

## Introduction

Phthalate esters (PAEs) are significant industrial chemicals widely used in a diversity of industrial and consumer products. PAEs function mainly as plasticizers to improve the softness, processability, flexibility and durability of polyvinyl chloride (PVCs) products, polyvinyl acetate and polyurethane resins (Wormuth *et al.*, 2006; Kawakami *et al.*, 2011). PAEs are not chemically linked to the polymeric matrix and for this reason, they easily find their way to aquatic ecosystems via discharge from industrial and municipal wastewater treatment plants, surface runoff from agricultural and aquaculture activities, leaching from municipal solid waste sites and direct and indirect dumping of PAEs-containing products and atmospheric deposition (Staples *et al.*, 1997, Net *et al.*, 2015). On entering the aquatic environment, PAEs are distributed into various environmental media including water, suspended particles, sediments and aquatic biota causing serious ecological risk on sensitive aquatic biota and entire ecosystems (Okamoto *et al.*, 2011; Net *et al.*, 2015; Gao and Wen, 2016). PAEs are potential endocrine disruptors, teratogenic and carcinogenic materials which may pose adverse effects on human health for example, such as reproductive abnormalities. The United State Environmental Protection Agency (USEPA) and the European Union (EU) classified some PAEs congeners as priority pollutants of the aquatic environment because they easily get attached to suspended solid particles and sediments and the ability to accumulate in the food web (USEPA, 2009; Sun *et al.*, 2013; Ramzi *et al.*, 2018).

Due to their high octanol and water partition coefficients plus hydrophobic characteristics, PAEs tend to be associated with suspended solid particles (SPM) that eventually settled to bottom sediments and consistently accumulate in sediments (Staples *et al.*, 1997; Net *et al.*, 2015). As a result, sediments act as long-term pollutant sinks and reservoir, and as a source of contaminant through re-suspension (Liu *et al.*, 2014). In addition, sediments play major intermediary role in PAEs uptake by aquatic biotas in the ecosystem (Gobas *et al.*, 2003). However, the ubiquity and the slow photolysis and hydrolysis rates of PAEs enhances their ability to bioaccumulate in aquatic biotas and has generated serious concerns from researchers and the public, especially with regard to the adverse effects of PAEs on microbes, algae, crustaceans, shrimps and fish in fresh or salt water aquatic ecosystems (Staples *et al.*, 1997; Gobas *et al.*, 2003; Mackintosh *et al.*, 2006; Net *et al.*, 2015). Moreover, human health can be affected by these hazardous pollutants through consumption of some species of bivalves, shrimps and fish and exposure via dermal contact; necessitating the need to evaluate the potential health risk of PAEs via sediment, since human humans will be inevitably exposed to PAEs via ingestion of contaminated surface water and edible aquatic biotas (He *et al.*, 2013; Liu *et al.*, 2016). In addition, human may be exposed to PAEs via dermal contact with contaminated sediments.

Riverine sediments are significant source and indicator for the assessment of anthropogenic pollution of chemical pollutants in aquatic environment due to their long residence time of pollutants including PAEs (Heyden and New, 2004). Currently, the contamination and ecotoxicological risk of PAEs has attracted serious attention in recent decades. Several studies on the contamination and ecological risk of PAEs in riverine sediments have been reported globally, which revealed that polluted sediments pose serious adverse effects on the aquatic ecosystem (Sun *et al.*, 2013; Wang *et al.*, 2014; Ramzi *et al.*, 2018; Arfaenia *et al.*, 2019). However, studies on the contamination of PAEs in Thailand are scarce, except for a river and a sea (Sirivithayapakorn *et al.*, 2014; Malem *et al.*, 2019). Moreover, there is limited studies of PAEs for riverine sediments in tropical regions. Nevertheless, to date, there is no reported PAEs data in U-Tapao River, Southern Thailand. Furthermore, globally, studies evaluating the human health risk of PAEs in riverine sediments are lacking.

In human health risk assessment, evaluating the potential risks for humans derived from exposure to polluted environmental media is a significant procedure used for pollutants like PAEs in air, water, sediments and food (Li *et al.*, 2017a, 2017b; Lee *et al.*, 2019). Evaluating the potential adverse effects for human depends on the route of exposure to PAEs. The exposure pathways considered include dietary and non-dietary exposure. Dietary exposure includes the routine ingestion of food items and water contaminated with pollutants (Fatoki *et al.*, 2010; Olujimi *et al.*, 2017), whereas non-dietary exposure route includes dermal contact with contaminated water, sediments, soil and personal care products; inhalation of residues in dust and particulate matters. The Hazard quotient (HQ) and Hazard Index (HI) approaches of risk assessment has been found to be very significant in performing initial exposure assessments including screening level risk assessment of organic pollutants like PAEs on human health. The Hazard quotient method of risk assessment uses point values and simple models to produce a point estimate of exposure by combing point values selected to be either health-protective (i.e. high-end values) or to represent a "typical" exposure (i.e. central tendency values). They produce an exposure estimate that is also a point estimate that falls somewhere within the full distribution of possible exposures (U.S. EPA, 1991). Hazard Quotient approach of assessments are simple to carry out, often use readily available data, and produce results that are straightforward to interpret (U.S.EPA, 1991).

U-Tapao River is a main source of freshwater draining into the outer Songkla Lake, the largest natural lagoon in Thailand. In addition, the river which is a main water resources for industrial usage, balancing of ecosystem, agriculture, aquaculture and above all for drinking water in Southern, Thailand. The water body is reported to be frequently exposed to serious environmental pollution due to rapid economic development and urbanization in the region surrounding the water body (Sirinawin and Somponchaiyakul, 2005; Gyawali *et al.*, 2012.). The river is receiving a large amount of industrial wastewater from rubber, plastic, Parawood, agrochemical and seafood processing industries at the rate of 41,000 m<sup>3</sup> per day, and the effluent are reported to have high organic contents (Sirinawin and Somponchaiyakul, 2005). In addition, elevated concentration of PAEs have been observed in industrial wastewater effluents that are frequently discharge into U-Tapao River (Worawit *et al.*, 2008). The bottom sediment of U-Tapao River has been dredged by an indigenous Thai construction company. Moreover, a previous study has reported elevated concentration of some congeners of PAEs in both water and sediments that poses high ecological risk on aquatic biotas in the aquatic ecosystem (Kingsley and Witthayawirasak, 2020). In addition, another study evaluated the health risk of PAEs via water (Kingsley and Witthayawirasak, 2020b). Nevertheless, no study has evaluated human health risk of PAEs via dermal exposures pathways from the sediments. To protect public health River, it is imperative to determine the level of PAEs in sediment, as well as their subsequent potential risk on humans. Therefore, the objectives of this study are (a) to assess the level of PAEs in sediments (b) to estimate the non-carcinogenic and carcinogenic risk of PAEs on adults and children via dermal exposure pathway. The result from this study will not only facilitate better understanding of PAEs pollution status, but also provide data for effective environmental management practice of contaminated rivers.

## Materials and methods

*Study site:* To assess the extent of PAEs contamination and potential risk in a riverine sediment, a cross-sectional study was conducted in U-Tapao River, a major riverine ecosystem is located in a tropical region in Songkla Province Southern Thailand. The freshwater source is 68 km long and approximately 3 m to 8 m deep. This waterbody originates from Bantad Mountain and flows through Hat Yai city before emptying into the outer part of Songkla Lake. The flow rate of the river ranges between <6 and 90 m<sup>3</sup> in dry and raining seasons respectively. The tropical monsoon climate of the river is strongly influenced by two monsoons: the northeast and southwest monsoon with average rainfall estimated to range from 1600 mm to 2400 mm annually. Temperature within and around the riverine ecosystem varies between 24 °C and 32 °C all through the year.

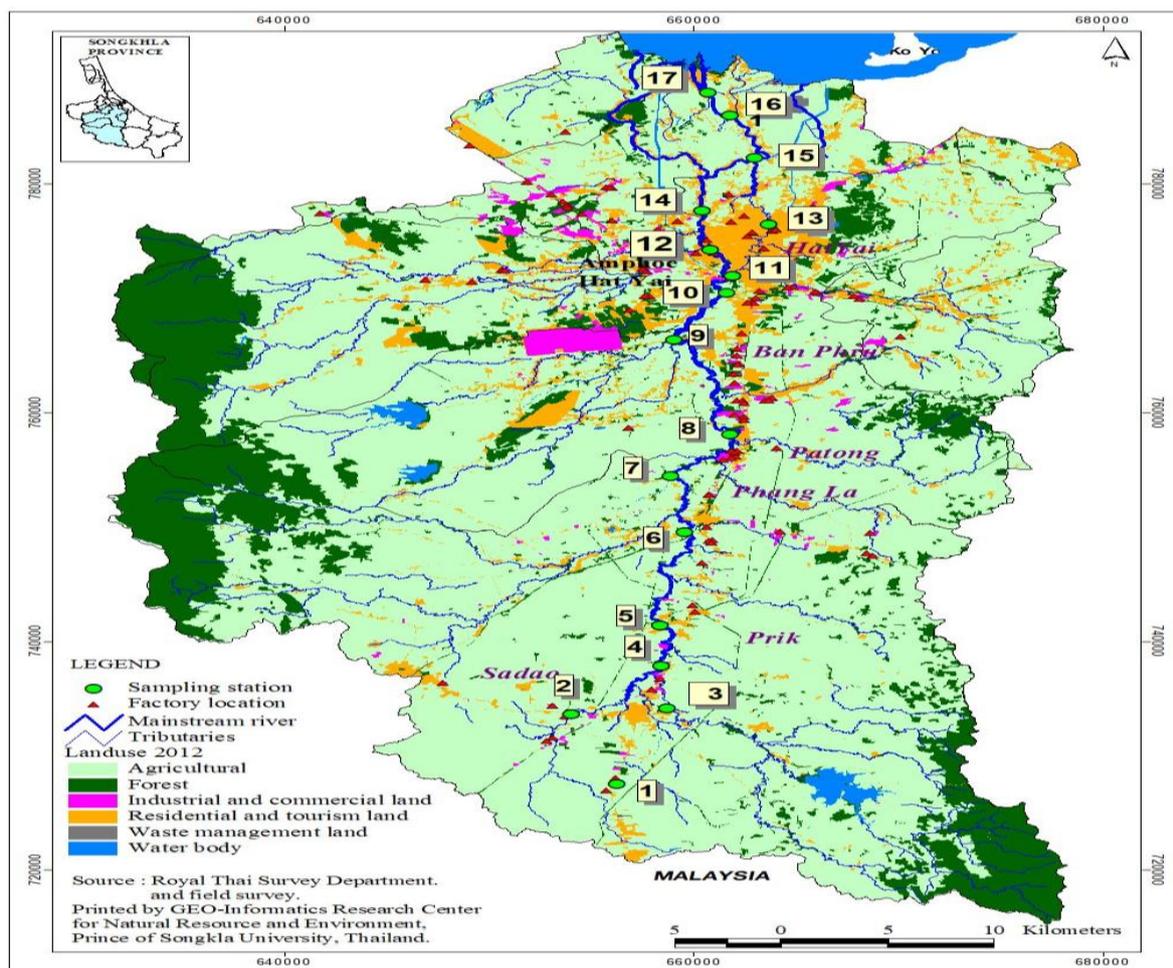
*Sampling sites and sample collection:* In these 17 sampling sites for sediments were selected along the river, from the upstream to downstream. The 17 sampling sites were classified into two different group viz: urban and rural areas. Sampling sites in urban areas include ST1, ST2, ST 3, ST4, ST6, ST7, ST9, ST10, ST12 and ST13. Sites located in the vicinity of rural area were ST5, ST8, ST11, ST14, ST15, ST16 and ST17 (Figure 1). Sediment samples were collected from 17 sampling sites by using a grab sampler and transferred onto pre-treated wide mouthed brown bottles. The bottles were immediately placed on ice and were then kept at -22 °C deep freezer in the laboratory prior to analysis. All sediment samples were analyzed within 3 days.

*Preparation of sampling equipment, glass wares and reagents:* All sampling equipment comprises of glass or stainless steel. Amber glass bottles were thoroughly washed with laboratory grade detergent, cleaned twice with HPLC grade of acetone, hexane and dichloromethane, and then heated in a muffler oven at 400 °C for at least 10 h. After baking, the bottles were re-rinsed three times with acetone, hexane, and dichloromethane, then covered with clean aluminum foil. Prior to their usage, aluminum foils were also rinsed in acetone and hexane and then heated in a hot oven at 350 °C for 10 h. Stainless steel sampling utensils such as spoons, flat trays and buckets were washed as well as wrapped with aluminum foil prior to sampling. The sediment grab sampler and glass water samplers were washed with lab-grade detergent and then washed three times with HPLC grade of acetone, n-hexane as well as dichloromethane, respectively. Mortars and pestles were cleaned using the same procedure as that for glassware but were baked at 150 °C for 10 h.

*Chemicals and materials:* Solvents used for this work included HPLC grades of Hexane, methanol, acetone, ultrapure water and dichloromethane, (Waters, U.S.A) Phthalate standards included di-n-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), di-2-ethylhexy phthalate (DEHP), di-n-octyl Phthalate (DnOP), diisononyl phthalate (DiNP), diisodecyl phthalate (DIDP) (AccuStandard, U.S.A). Internal standard solutions including phenanthrene-d10 and chrysene-d12 and surrogate standard solutions which are 2-fluorobiphenyl and 4-terphenyl-d14 were obtained from SUPELCO Inc. (USA).

*PAEs pretreatment in sediments:* The freeze-dried sediment samples collected from U-Tapao river were pretreated based on a method proposed by Cheng *et al.* (2013) with slight modification. Each five grams of sediment sample was crushed and homogenized using a mortar and pestle as well as filtered via a stainless-steel sieve (60-mesh) and placed in brown glass bottles at -20 °C pending extraction. Weighed riverine sediment samples (5.0 g) were placed into clean glass centrifuge tubes, mixed with 10 mL acetone/hexane (1:1 v/v), and 0.2 ml of 10 mg/L mixture of surrogate standard solutions (2-fluorobiphenyl and 4-terphenyl-d14). A procedural blank not containing the sediments was also prepared by using similar procedure; 1:1 (v/v) acetone/n-hexane was used to prepare a check standard mixture. Spiked sample was made by mixing standard mixture to riverine sediments sample. All samples were vortexed for 1 min and ultrasonicated for 20 min. The samples were further centrifuged at 3000 revolution per minutes (rpm) for 10 minutes. After centrifugation, the organic layer containing the extracted PAEs was siphoned out and placed in tubes by using a Pasteur pipette and the process was repeated twice with 10 mL of a 1:1 (v/v) acetone/n-hexane. The extracts were pooled together. Desulphurization was achieved by adding activated copper to the extract. The extract was further dried over anhydrous sodium sulfate, concentrated to 0.8 mL using a gentle stream of nitrogen, added to 0.2 mL of 5 mg/L internal standard (Acenaphthene-d10, Phenanthrene-d10, and Chrysene-d12) mixture solutions, and analyzed using gas chromatography (GC) with mass selective detector (MSD).

*Instrumental analysis by GC-MS:* All samples were evaluated using a gas chromatograph/mass spectrometer (GC-MS), Agilent model 6890N GC-5973 MSD (Agilent Technologies, U.S.A), functional electron influence as well as a selective ion monitoring mode with a HP-5 MS (30 m × 0.25 mm × 0.25 mm). Chromatographic separation was performed by using fused-silica capillary column. Pure helium gas (99.9999%) was used as the carrier gas and was maintained at a constant flow rate of 1 ml/min. The temperature program column oven was set to 30 °C for 1 min, raised to 280 °C at 15 °C maintained for 1 min, then increased up to 310 °C and held for 4 min. Each extract volume of 2.0 µl was injected into the GC-MS system in non-pulse and splitless mode with an injector temperature of 290 °C. The levels of PAEs in the sediments were normalized to a dry weight (dw) basis.



**Figure 1:** Map showing sampling sites for sediments in U-Tapao river (Source: Geo-informatic Research Center, Prince of Songkla University (2019) with modifications)

*Quality control and quality assurance:* To ensure that the results obtained in this work are reliable, various techniques were employed including: development of calibration curve, usage of procedural blank, establishment of lower limit of detection (LOD) and Limit of quantification, assessment of the precision; and the calculation of recovery percentage. The instrument was calibrated daily by preparing calibration curve at five different concentrations (0.01, 0.1, 0.5, 1, and 10  $\mu\text{g mL}^{-1}$ ) except for DiNP and DIDP (0.1, 1, 5, 10 and 100  $\mu\text{g mL}^{-1}$ ). All procedural blanks values were less than the detection limits. For the various PAEs congeners limit of detection (LOD) and limit of quantification (LOQ) for individual PAEs congeners were assessed on the bases of a signal-to-noise ratio of 3 and 10 times, respectively, as described by Miller and Miller, (1998). In this work LOD and LOQ ranged from 0.04 to 0.08 and 0.13 to 0.27  $\mu\text{g/kg}$ , respectively. Recovery efficiencies for the surrogate standards are between 86.8 %  $\pm$  8.6% (2-Fluorobiphenyl), and 92.7% 8.9% (4-Terphenyl-d14); and the average recovery efficiencies for the spiked samples are between 88.6 and 114.3%. All relative standard deviation (RSD) for PAEs analyzed are less than 15%.

*Human health risk assessment:* Exposure Factors Interactive Resource for Scenarios Tool (EXPOFIRST, 2011), a USEPA exposure scenario and human health risk assessment model was used to calculate the potential exposure concentration. The exposure pathways considered include dermal adsorption of detected PAEs in sediments by workers during dredging of bottom sediments of U-Tapao River and children playing in dredged sediments. In a quantitative human health risk assessment, numerical estimates of human exposure to adverse effects of chemical pollutants are expressed in terms of average daily dose. The average daily doses via dermal contact ( $\text{ADD}_{\text{derm}}$ ) were calculated by using equation 4. HQ method is used to estimate non-carcinogenic and carcinogenic risk to human and are usually evaluated via three exposure pathways including ingestion, inhalation and dermal exposure (USEPA, 1991). However, in this work dermal contact was the only pathway considered for PAEs including DnBP, DEHP and DiNP detected in the river sediment, for workers and children. The exposure factors and values used to calculate the exposure level and risk are given in Table 1.

**Table 1:** Exposure factors and values used to calculate the exposure level and risk

Factor	Descriptions	Units	Value
CF	Conversion factor	Mg/kg	1x10 <sup>-5</sup>
ED	Exposure duration	years	49 <sup>a</sup> 5 <sup>c</sup>
EF	Exposure frequency	Days/years	365
BW	Body weight	kg	60 <sup>a</sup> , 11 <sup>c</sup>
AT	Average time of exposure	days	25,550 (70 years)
ABS	Dermal absorption factor	unitless	0.1

<sup>a</sup>: adult; <sup>c</sup>: children

The estimated daily absorbed dose of PAEs via dermal contact for adults involve in dredging of bottom sediment and children playing in dredged sediments was evaluated by using equation 4.

$$ADD_{derm} = \frac{C \times AF \times ABS \times SA \times EV \times EF \times ED}{BW \times AT} \quad 4$$

where ADD<sub>derm</sub> is the average daily intake dose by dermal contact with chemical in sediment (mg/kg/day) and C is the mean environmental concentration of detected individual PAEs in sediment.

The HQ is the ratio of the ADD of the mean concentration of individual PAEs to its reference dose (RfD) for the same exposure pathway and was estimated by applying equation 5.

$$HQ = \frac{ADD}{RfD} \quad 5$$

Hazard Index (HI) of the of the three PAEs congeners detected in the sediments was calculated by using the equation below.

$$HI = \sum_{1...n}^n HQ \quad 6$$

For DEHP that has the potential for causing cancer, risk was estimated by using the equation below.

$$Risk_{dermal} = \beta \times LADD_{dermal} \quad 7$$

where the Risk<sub>dermal</sub> is the potential cancer risk due to dermal contact to PAEs contaminated riverine sediment; LADD<sub>dermal</sub> is lifetime average daily dose exposure via dermal contact; β is slope factor.

*Analysis of sediment organic matter:* 5 g of sediment sample was used to determine the organic matter levels in each subsample of sediments collected from U-Tapao River. The samples were oven dried at 105 °C for 8 h to obtain a constant weight. After drying, the samples were baked in furnace at 550 °C for 5 h, thereafter, the OM level was obtained by measuring the weight loss (Jia *et al.*, 2011).

*Statistical analysis:* Statistical analysis was performed with SPSS version 20.0 (IBM SPSS Inc., Chicago)

## Result and Discussion

*Occurrence of PAEs in sediments:* The statistical summary of PAEs concentration of PAEs measured in sediment samples collected from U-Tapao River (UR) are shown in Table 2. Of the six targeted PAEs including DnBP, BBP, DEHP, DnOP, DiNP and DIDP), only 3 congeners were detected such as DEHP, DiNP and DnBP. The total PAEs concentrations in the samples ranged from 80 to 1870 ng/g dw, with mean value of 787.4 ng/g. The average environmental concentration of individual PAEs were 385.88, 334.71 and 66.76 ng/g for DEHP, DiNP and DnBP.

**Table 2:** Individual concentration of PAEs in sediments from U-Tapao River (ng/g)

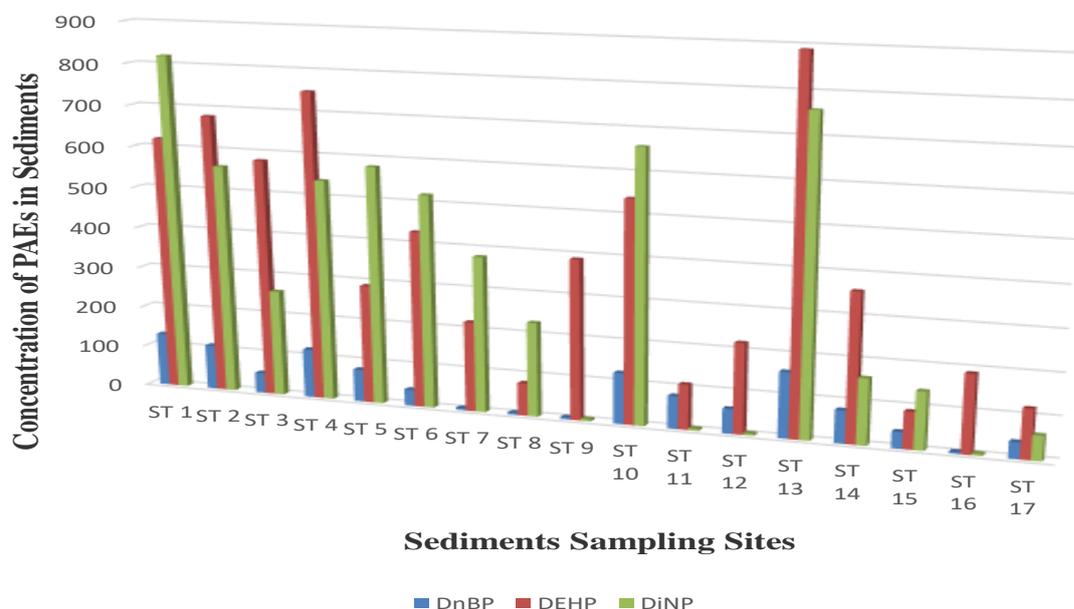
PAEs	Mean	Std. Deviation	Minimum	Maximum	FoD%
DnBP	66.76	49.40	ND	160.00	40
DEHP	385.88	252.81	80.00	890.00	100
DiNP	334.71	285.80	ND	820.00	60
BBP	ND	ND	ND	ND	-
DnOP	ND	ND	ND	ND	-
DIDP	ND	ND	ND	ND	-
ΣPAEs	787.35	588.01	80	1870.00	100

FoD = Frequency of Detection

The distribution of PAEs in the UR are shown in Figure 2. High Σ<sub>3</sub>PAEs concentration in sediment occurred at sites 13, 1, 4, 10 and 2. Sites 8, 5, 6 and 7 also had relatively high concentration. Almost all these sampling sites were located in urban area of the river ecosystem where there are industries such as rubber, plastic, Parawood

and food industries as well as residential and commercial places. Large quantity of PAEs are released from semi treated and untreated industrial and municipal wastewater, surface runoffs and atmospheric depositions discharged into rivers and finally deposited in the sediments. Several studies have reported that to date, wastewater from municipal and industrial activities are discharge into UR (Gyawali *et al.*, 2012, Musikavong and Wattanachira, 2013). Relatively low concentration of  $\sum_3$ PAEs were found at sites 11,15,16 and 17. These sites are located adjacent to aquaculture ponds for shrimps and agricultural fields. The occurrence of PAEs in agricultural areas have attributed to varying cultivation and harvesting activities including use of fertilizers, pesticides, plastic mulching and other agrochemicals (Wang *et al.*, 2014; Nui *et al.*, 2016).

Frequency of detection for individual PAEs congeners in this study, followed the order of DEHP>DiNP > DnBP. Considering the individual PAEs congener, DEHP is the most popular PAEs and account for approximately 50% of the total industrial PAEs output in many countries including Malaysia, India, China, South Africa, Nigeria and Netherland (Tan, 1995; Vethaak *et al.*, 2005; Srivastava *et al.*, 2010; Fatoki *et al.*, 2010; Adeniyi *et al.*, 2011). This work indicated that DEHP was the preponderant PAE in the riverine sediment which is attributed to high production and consumption, strong sorption and low degradation rate (Staples *et al.*, 1997; Net *et al.*, 2015). However, to reduce the human health risk as well as environmental risk, the usage of DEHP was restricted by regulation and replaced by DiNP and DIDP. Thus, it is no wonder that DiNP was found in high concentration in riverine sediments. However, our findings are consistent with few recent studies that observed high concentration of DiNP (Clara *et al.*, 2010; Chen *et al.*, 2017a). It is therefore, recommended to include DiNP when screening aquatic sediments for PAEs.



**Figure 2:** Concentration and distribution of PAEs in different sampling sites

*Human health risk assessment of PAEs in sediment:* The results of health risk assessment of both non-carcinogenic and carcinogenic risk of measured PAEs in sediment for workers and children via dermal contacts are indicated in Table 3, 4 and 5; respectively.

**Table 3:** The average daily dose, reference dose and Hazard quotient of PAEs for adults

PAEs	Mean values of PAEs (ug/g)	ADD <sub>derm</sub> (mg/kg/day)	RfD (mg/kg/day)	HQ
DnBP	0.079	$2.84 \times 10^{-6}$	$1.0 \times 10^{-1}$	$2.84 \times 10^{-5}$
DEHP	0.352	$1.43 \times 10^{-5}$	$2.00 \times 10^{-2}$	$7.15 \times 10^{-4}$
DiNP	0.359	$1.46 \times 10^{-5}$	$1.15 \times 10^{-1}$	$1.27 \times 10^{-4}$
HI				$8.70 \times 10^{-4}$

**Table 4:** Average daily dose, reference dose and hazard quotient in children

PAEs	Levels (ug/g)	ADD <sub>derm</sub> (mg/kg/day)	RfD (mg/kg/day)	HQ
DnBP	0.079	$1.12 \times 10^{-4}$	$1.0 \times 10^{-1}$	$1.12 \times 10^{-3}$
DEHP	0.352	$4.99 \times 10^{-4}$	$2.00 \times 10^{-2}$	$2.49 \times 10^{-2}$
DiNP	0.359	$5.09 \times 10^{-4}$	$1.15 \times 10^{-1}$	$4.43 \times 10^{-3}$
HI				$3.05 \times 10^{-2}$

**Table 5:** Carcinogenic risk of DEHP in sediment via dermal contact on workers and children

Human age	PAEs	LADD	Slope factor	Cancer risk
Adult	DEHP	$1.19 \times 10^{-6}$	$1.40 \times 10^{-2}$	$1.67 \times 10^{-8}$
Children	DEHP	$1.37 \times 10^{-5}$	$1.40 \times 10^{-2}$	$1.92 \times 10^{-7}$

Since DEHP is the only PAEs congeners that have been classified as carcinogenic, we evaluated the carcinogenic risk for DEHP for both adults during dredging bottom sediments in the river and children during playing in dredged sediments. HQ was applied to estimate the non-carcinogenic health risk through dermal adsorption of measured PAEs in sediments on adults and children. In addition, the adverse health effects on children playing in sediment was also evaluated. When results of  $HQ < 1$ , this is suggesting that little or no significant potential adverse effects are exerted on human health, whereas potential adverse effects on human health may be assumed if  $HQ > 1$  (U.S. EPA, 1991). According to the results, all HQ values for the detected PAEs via dermal adsorption were less than 1 for both adults and children, which suggested no potential adverse effects of measured PAEs on local residents' health through dermal contact. Based on the RfD and ADD the HQ presented in Table 4 and 5 indicated that the highest value of HQ via dermal contact observed for DEHP were  $2.49 \times 10^{-2}$  and  $7.15 \times 10^{-4}$  for non-carcinogenic in children and adults respectively. As indicated in Table 4, the highest value of carcinogenic risk was  $1.67 \times 10^{-8}$  in adults, indicating that the current values of PAEs measured in sediments cannot cause present a cancer risk in humans' adults. Similarly, in children, the carcinogenic risk value was  $1.92 \times 10^{-7}$ . These results indicate that the current level of PAEs pollution in the sediments may not pose carcinogenic risk to both adult and children via dermal exposure. Because the PAEs detected in the sediment have similar mode of action, exposure of complex pollutants may cause interactive and/or additive effects on human health, thus the total non-carcinogenic health risk from complex pollutants can be evaluated by HI (U.S. EPA, 1991). If  $HI < 1$ , it means that no significant potential adverse effects are exerted by complex pollutants on human health, whereas the complex pollutants may cause potential adverse effects if  $HI > 1$ . The result in this study showed that the calculated HI for the three PAEs congeners were less than 1; thus, the exposure of complex PAEs had no potential adverse effects on both workers and children. Although this work showed an acceptable human health and carcinogenic risk linked with dermal contacts of PAEs measured in sediments, it is worthy of note that this work only focused on six selected PAEs congeners. Other hazardous chemical pollutants not assessed in this work, might also be present in the sediment samples and would add to the potential human health risk.

## Conclusion

This baseline study was carried out to evaluate the occurrence and risk assessment of six targeted PAEs congeners including DnBP, DEHP, BBP, DnOP, DiNP and DIDP in sediments samples of U-Tapao River. Of the six PAEs congeners, only three were measured in the samples with average environmental concentrations of 66.76, 385.88 and 334.71 ng/g for DnBP, DEHP and DiNP. The Human health risk assessment indicated that the concentration of PAEs in sediment posed acceptable risk via dermal exposure on adults and children. Results from this study highlight the need for routine PAEs monitoring programs. This is beneficial in the development and implementation of regulations and strategies to control and mitigate PAEs pollution in aquatic environment, particularly in freshwater bodies.

## Conflict of interest

The authors declare no conflict of interest with respect to the authorship or publication of this work.

## References

- Adeniyi AA, Okedeyi OO, Yusuf KA: Flame ionization gas chromatographic determination of phthalate esters in water, surface sediments and fish species in the Ogun river catchments, ketu, Lagos, Nigeria. *Environ Monit Assess*, 172(1-4): 561-569. 2011.
- Arbuckle TE, Davis K, Boylan K, Fisher M, Fu J: Bisphenol A, phthalates and lead and learning and behavioral problems in Canadian children 6-11 years of age: CHMS 2007-2009. *Neurotoxicol*, 54: 89-98. 2016.
- Arfaeinia H, Fazlzadeh M, Taghizadeh F, Saeedi R, Spitz J, Dobaradaran S: Phthalate acid esters (PAEs) accumulation in coastal sediments from regions with different land use configuration along the Persian Gulf. *Ecotoxicol Environ Saf*, 169: 496-506. 2019.
- Babich MA, Chen SB, Greene MA, Kiss CT, Porter WK, Smith TP, Wind ML, Zamula WW: Risk assessment of oral exposure to diisononyl phthalate from children's products. *Regul Toxicol Pharmacol*, 40(2): 151-167. 2004.
- Backhaus T, Faust M: Predictive environmental risk assessment of chemical mixtures: A conceptual framework. *Environ Sci Technol*, 46: 2564-2573. 2012.
- Chen CF, Chen CW, Ju YR, Dong C: Determination and assessment of phthalate esters content in sediments from Kaohsiung Harbor, Taiwan. *Mar Pollut Bull*, 124: 767-774. 2017.
- Chen CW, Chen, CF, Dong C: An Distribution of Phthalate Esters in Sediments of Kaohsiung Harbor, Taiwan. *Soil Sed Contam*, 22(2): 37-41. 2013.
- Clara M, Windhofer G, Hartl W, Braun K, Simon M, Gans O, Scheffknecht C, Chovanec A: Occurrence of phthalates in surface runoff, untreated and treated wastewater and fate during wastewater treatment. *Chemosphere*, 78: 1078-1084. 2010.
- Daam MA, Satapornvanit K, Brink PJ, Den V, Nogueira AJA: Sensitivity of macroinvertebrates to carbendazim under semi-field conditions in Thailand: Implications for the use of temperate toxicity data in a tropical risk assessment of fungicides. *Chemosphere*, 74: 1187-1194. 2009.
- European Commission: Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC, Commission Directive 98/8/EC, Commission Regulation (EC) No 1488/94, Commission Directive 93/67/EEC., EUR 20418 EN/2. 2003.
- Fatoki OS, Bormman M, Ravandhalala L, Chimuka L, Genthe B, Adeniyi A: Phthalate ester plasticizers in freshwater systems of Venda, South Africa and potential health effects. *Water SA*, 36: 117-126. 2010.
- Gao D, Wen Z: 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.
- Gobas FAPC, Mackintosh CE, Webster G, Ikonoumou M, Parkerton TF, Robillard K: Bioaccumulation of phthalate esters in aquatic food-webs. *Handb Environ Chem*, 3: 201-225. 2003.
- Gyawali S, Yuangyai C, Monprapusson S: Evaluation of surface water quality using multivariate statistical techniques: A case study of U-tapao River Basin. *KMITL Sci Tech J*, 12: 7-20. 2012.
- He W, Qin N, Kong X, Liu W, He Q, Ouyang H, Yang C, Jiang Y, Wang Q, Yang B, Xu F: Spatio-temporal distributions and the ecological and health risks of phthalate esters ( PAEs ) in the surface water of a large shallow Chinese lake. *Sci Total Environ*, 461-462: 672-680. 2013.
- Heyden CJ, New MG: Sediment chemistry: A history of mine contamination remediation and an assessment of processes and pollution potential. *J Geochem Explor*, 82: 35-57. 2004.
- Huang Y, Li J, Garcia JM, Lin H, Wang Y, Yan P, Wang L, Tan Y, Luo J, Qiu Z, Chen JA, Shu W: Phthalate levels in cord blood are associated with preterm delivery and fetal growth parameters in Chinese women. *PLoSOne*, 9: e87430. 2014.
- Jia HL, Sun YQ, Liu XJ, Yang M, Wang DG, Qi H, Shen L, Sverko E, Reiner EJ, Li YF: Concentration and bioaccumulation of dechlorane compounds in coastal environment of Northern China. *Environ Sci Tech*, 45: 2613-2618. 2011.
- Kawakami T, Isama K, Matsuoka A: Analysis of phthalic acid diesters, monoester, and other plasticizers in polyvinyl chloride household products in Japan. *J Environ Sci Health Part A*, 46: 855-864. 2011.
- Kingsley O, Witthayawirasak B: Occurrence, ecological and health risk of phthalate esters in surface water of U-Tapao canal, Southern Thailand. *Toxics*, 8(3): 58. 2020a. doi: 10.3390/toxics8030058
- Kingsley O, Witthayawirasak B: Deterministic risk assessment of phthalate esters in sediments of U-Tapao Canal, Southern Thailand. *Toxics*. 8(4): 9. 2020b.
- Liu WX, Hu J, Chen JL, Fan YS, Xing B, Tao S: Distribution of persistent toxic substances in benthic bivalves from the inshore areas of the yellow sea. *Environ Toxicol Chem*, 27: 57-66. 2008.
- Lee Y, Lee J, Choe W, Kim T, Lee J, Kho Y: Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. *Environ Int*, 126: 635-643. 2019.
- Li R, Liang J, Duan H, Gong Z: Spatial distribution and seasonal variation of phthalate esters in the Jiulong River estuary, Southeast China. *Mar. Pollut Bull*, 122: 38-46. 2017.
- Li R, Liang J, Gong Z, Zhang N, Duan H: Occurrence, spatial distribution, historical trend and ecological risk of phthalate esters in the Jiulong River, Southeast China. *Sci Total Environ*, 580: 388-397. 2017.
- Liu H, Cui K, Zeng F, Chen L, Cheng Y, Li H, Li S, Zhou X, Zhu F, Ouyang G, Luan T, Zeng Z: Occurrence and distribution of phthalate esters in riverine sediments from the Pearl River Delta region, South China. *Mar Pollut Bull*, 83: 358-365. 2014.
- Liu N, Wang Y, Yang Q, Lv Y, Jin X, Giesy JP, Johnson AC: Probabilistic assessment of risks of diethylhexyl phthalate (DEHP) in surface waters of China on reproduction of fish. *Environ Pollut*, 213: 482-488. 2016.

- Liu WX, He W, Qin N, Kong X, Liu WX, He Q, Ouyang H, Yang C, Jiang Y, Wang Q, Yang B, Xu F: Spatio-temporal distributions and the ecological and health risks of phthalate esters (PAEs) in the surface water of a large, shallow Chinese lake. *Sci Total Environ*, 461–462: 672–680. 2013.
- Macdonald DD, Carr RS, Calder FD, Long ER, Ingersoll CG: Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicol*, 5: 253–278. 1996.
- Mackintosh CE, Maldonado JA, Ikonomou MG, Gobas FAPC: Sorption of phthalate esters and PCBs in a marine ecosystem. *Environ Sci Technol*, 40(11): 3481–3488. 2006.
- Malem F, Soonthondecha P, Khawmodjod P, Chunhakorn V, Whitlow H, Chienthavorn O: Occurrence of phthalate esters in the eastern coast of Thailand. *Environ Monit Assess*, 191: 627. 2019.
- Miller JC, Miller JN: Statistics for analytical chemistry. 2nd Ed. Ellis Horwood: Chichester, UK. pp. 97–100. 1998.
- Musikavong C, Wattachira S: Identification of dissolved organic matter in raw water supply from reservoirs and canals as precursors to trihalomethanes formation, *J Environ Sci Health Part A*, 48(7): 760-771. 2013.
- 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.
- Okamoto Y, Ueda K, Kojima N: Potential risks of phthalate esters: acquisition of endocrine-disrupting activity during environmental and metabolic processing. *J Heal Sci*, 57: 497–503. 2011.
- Olujimi OO, Aroyeun OA, Akinhanmi TF, Arowolo TA: Occurrence, removal and health risk assessment of phthalate esters in the process streams of two different wastewater treatment plants in Lagos and Ogun States, Nigeria. *Environ Monit Assess*, 189: 347. 2017.
- Pradit S, Pattarathomrong MS, and Panutrakul S: 2013. Arsenic cadmium and lead concentrations in sediment and biota from Songkhla Lake : A review. *Procedia Soc Behav Sci*, 91: 573–80. 2013.
- Ramzi A, Gireeshkumar TR, Habeeb Rahman, K, Manu M, Balachandran KK, Chacko J, Chandramohanakumar N: Distribution and contamination status of phthalic acid esters in the sediments of a tropical monsoonal estuary, Cochin – India. *Chemosphere*, 210: 232-238. 2018.
- Sirinawin W, Sompongchaiyakul P: Nondetrital and total metal distribution in core sediments from U-Tapao Canal, southern Thailand. *Mar Chem*, 94: 5–16. 2005.
- Srivastava A, Sharma V, Tripathi R, Kumar R, Patel D, Mathur P: Occurrence of phthalic acid esters in Gomti River Sediment, India. *Environ Monit Assess*, 169: 397-406. 2010.
- Sirivithayapakorn S, Limtrakul S: Distribution coefficient and adsorption-desorption rates of di (2-ethylhexyl) phthalate (DEHP) onto and from the surface of suspended particles in fresh water. *Water Air Soil Pollut*, 190: 45–53. 2008.
- Sirivithayapakorn S, Thuyviang K, Jansak P: Distribution and ecological risk assessment of plasticizers in the chao phraya delta, gulf of Thailand. *ASEAN Eng J Part C*, 4(1): 73–80. 2014.
- Staples CA, Peterson DR, Parkerton TF, Adams WJ: The environmental fate of phthalate esters: A literature review. *Chemosphere*, 35(4): 667-749. 1997.
- Sun J, Huang J, Zhang A, Liu W, Cheng W: Occurrence of phthalate esters in sediments in Qiantang River, China and inference with urbanization and river flow regime. *J Hazard Mater*, 248–249: 142–149. 2013.
- USEPA: Risk assessment guidance for superfund: Volume I - Human health evaluation manual (Part B, development of risk-based preliminary remediation goals). US Environ. Protection. Agency. Washington DC, pp. 1-57. 1991.
- Tan GH: Residues levels of phthalate esters in water and sediment samples from Klang River basin. *Bull Environ Contam Toxicol*, 54: 171-176. 1995.
- Vethaak AD, Lahr J, Schrap SM, Belfroid AC, Rijs GBJ, Gerritsen A, de Boer J, Bulder AS, Grinwis GCM, Kuiper RV, Legler J, Murk TAJ, Peijnenburg W, Verhaar HJM, de Voogt P: An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands. *Chemosphere*, 59: 511–24. 2005.
- Wang J, Bo L, Li L, Wang D, Chen G, Christie P, Teng Y: Occurrence of phthalate esters in river sediments in areas with different land use patterns. *Sci Total Environ*, 500-501: 113-119. 2014.
- Phthalung WN, Musikavong C, Suttinun O: The presence of aliphatic and aromatic amines in reservoirs and canal water as precursors to disinfection by-products. *J Environ Sci Health, Part A*, 51(11): 900-913. 2016.
- Worawit W, Chih-Hsiang L, Panote T, Proespichaya K: Characterization of organic substances in concentrated latex discharged effluent. The Sixth PSU Engineering Conference, Prince of Songkla University, Hat Yai, Thailand, Pp. 1–7. 8–9 May 2008.
- Yang GCC, Wang C, Chiu Y: Occurrence and distribution of phthalate esters and pharmaceuticals in Taiwan river sediments. *J Soil Sed*, 15: 198–210. 2015.
- 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(3): 372-380. 2008.
- Zhang ZM, Zhang HH, Zhang J, Wang QW, Yang GP: Occurrence, distribution, and ecological risks of phthalate esters in the seawater and sediment of Changjiang River Estuary and its adjacent area. *Sci Total Environ*, 619–620: 93–102. 2018.

