Risk Assessment of Phthalate Esters in Surface Water and Tap Water of U-Tapao Canal Songkhla Province Southern Thailand

Okpara Kingsley E.

A Thesis Submitted in Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Environmental Management
Prince of Songkla University
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Author	Mr. Okpara Kingsley E.
Major Program	Environmental Management

Major Advisor	**Examining Committee:**
....	....Chairperson
(Asst. Prof. Dr. Banchong Witthayawirasak)	(Assoc. Prof. Dr Wattasit Siriwong)
	....Committee
	(Assoc. Prof. Dr Chatchai Ratanachai)
	....Committee
	(Assoc. Prof. Dr Bachong Witthayawirasak)
	....Committee
	(Asst. Prof. Dr Thitiworn Chusong)
	....Committee
	(Dr Peerapat Kosolsaksakul)

The Graduate School, Prince of Songkla University, has approved this thesis as fulfillment of the requirements for the Doctor of Philosophy Degree in Environmental Management.

....
(Prof. Dr. Damrongsak Faroongsarng)
Dean of Graduate School

This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgment has been made of any assistance received.

………………...…....…..................Signature
(Assoc. Prof. Dr. Banchong Witthayawirasak)
Advisor

……………....……………….........Signature
(Mr. Okpara Kingsley E.)
Candidate

I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

………………………Signature
(Mr. Okpara Kingsley E.)
Candidate

Thesis Title Risk Assessment of Phthalate Esters in Surface Water and Tap Water of U-Tapao Canal Songkhla Province, Southern Thailand
Author Mr. Okpara Kingsley E.
Major Program Environmental Management
Academic Year 2019

ABSTRACT

PAEs are synthetic chemical compounds that causes endocrine disrupting effects in aquatic organisms such as algae, crustaceans fish and aquatic mammals, terrestrial biota as well as human. In human, prolonged exposure to PAEs may cause adverse health effects such as birth defects, alteration of semen quality, disruption of the hormonal and endocrine systems which may result to premature breast development, reduced gestation period, infertility in both male and female organism, testicular dysgenesis, childhood social impairment, obesity, asthmatic attack and breast cancer in human. Because of their ubiquitous presnces and potentila risk in aquatic ecosystems and human, a cross sectional study on the contamination of PAEs in water and sediment was carried out in U-Tapao canal, Songkla Province, southern Thailand. In addition, the efficiency of removing PAEs by water filtration plants, the sedimentary transfer of PAEs, ecological and human health risks of PAEs were also assessed. Samples of surface water, tap water and sediment were collected and analyzed by GC-MS for six PAEs including di-n-butyl phthalate (DnBP), butyl-benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DnOP)), di-iso-nonyl phthalate (DiNP), di-iso-decyl phthalate (DIDP). Seventeen sampling sites were chosen for surface water and sediments. Tap water samples were collected from four waterworks that received raw water from U-Tapao canal. All samples were collected during August 2018 to February 2019. The individual levels of PAEs detected in surface water ranged from 1.28±0.15 to 5.28±0.89 µg/L, non-detectable (ND) to 3.36±0.22 µg/L and ND 3.44±0.27µg/L for DEHP, DnBP and DiNP, respectively. The removal efficiency of PAEs by the conventional water filtration plants ranged from 43%, 16.4% and 14.3% for DnBP, DiNP and DEHP, respectively. The estmated inventory indicated sedimentary PAEs transfer of 12.2 tons into Songkhla lake in a period of 5 years, suggesting annual transfer of 2.44 tons and a potential source of PAEs pollution of the largest natural lagoon in Thailand. The distribution of PAEs along the network of the canal revealed that the sampling sites in the urban region were more contaminated with PAEs than those in rural region, thus associating the major source of PAEs pollution of the investigated canal to urbanization. The ecological risk assessment indicated that PAEs posed moderate to high risks on sensitives organisms such as algae, crustaceans and fish in U-Tapao canal ecosystem. Human health risk assessment revealed that, the hazard quotient (HQ) for DnBP, DEHP and DiNP were below1, indicating acceptable risk of PAEs via ingestion or bathing of tap water. In addition, the Hazard Index (HI) via ingestion and bathing of tap water were less than1indicating acceptable risks. Which implies that none of these PAEs congeners will cause any bad health effects on children, adolescents and adults through ingestions and bathing of tap water. Similarly, the cancer risk evaluated for DEHP, the only PAEs congener classified as carcinogenic agent showed acceptable risk compared to 1.0×10^{-6} as stipulated by WHO. This suggest that the level of DEHP in the investigated tap water cannot trigger cancer risk in children, adolescents and adults via ingestion and bathing. However, considering the fact that PAEs are endocrine disrupting organic pollutants, there is need to include PAEs in routine chemical monitoring programs and initiatives to limit both point and non-point source of PAEs pollution of the canal. This will greatly enhance the prevention and protection of this freshwater, which is a major water resource for drinking water, balancing aquatic ecosystem, industrial and agricultural utilizations from further PAEs contamination. In addition, to mitigate ecological and human health risks of the sensitive aquatic habitats and Thai residents who use water and consume aquatic foods from the canal, respectively.

Keywords: Phthalate esters (PAEs), Occurrence, Distribution, Ecological risk, Human health risk, Canal, Removal efficiency and Sedimentary transfer.

DEDICATION

This Thesis is dedicated to my beloved Queen Okpara Esther and Princesses (Daniella, Chimeka, Ohamachi and Chizimenum).

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Okpara Kingsley E.

LIST OF ABBREVIATIONS AND ACRONYMS

ALC	Aquatic life criteria
ECD	Electron Capture Detector
EDI	Estimated Daily Intake
EFSA	European Food Safety Authority
EI	Electron Ionization
USEPA	United State Environmental Protection Agency
FCM	Food Contact Material
USFDA	United State Food and Drug Administration
FID	Flame Ionization Detector
GC/MS	Gas Chromatography Mass Spectrometer
HDPE	High -Density Polyethylene
IARC	International Agency for Research on Cancer
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
MCL	Maximum Contaminant Level
NHANES	National Health and Nutrition Examination Survey
NIAS	Non-Intentional Added Substance
PAE	Phthalate ester
DMP	Dimethyl phthalate
DEP	Diethyl phthalate
DBP	Dibutyl phthalate
BBP	Benzyl Butyl phthalate
DEHP	Di (2-ethyl hexyl phthalate)
D-n-OP	Di n octyl phthalate
DiNP	Di-iso-nonyl phthalate

DiDP	Di-iso-decyl phthalate
DiBP	Di-iso-butyl phthalate
MEP	Monoethyl phthalate
MBP	Monobutyl phthalate
MiBP	Mono-iso-butyl phthalate

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CHAPTER ONE

INTRODUCTION

1.1 Background

Phthalates or phthalate esters (PAEs) are synthetic organic compounds that belong to the group of 1,2-benzoldicarbonic acid (Staple et al., 1997). Phthalate esters are commonly used as plasticizers. A plasticizer is defined as an additive that is incorporated into a plastic to impart softness, flexibility and toughness in order to facilitate the manufacturing process (Net et al., 2015). PAEs are mainly used as plasticizers in the production of plastics, rubber, polyvinyl chloride (PVC) and other polyethylene products to improve their flexibility, workability and durability (Wormuth et al., 2007; Wang et al., 2014; Zhang et al., 2018). In addition, PAEs are used to improve the quality of a large diversity of consumer and industrial products, such as coating of pharmaceutical coatings, gels, dispersants, lubricants, binders, medical devices, waxes, detergents, textile fabrics, children's toys (Stapels et al., 1997; Latini 2005; Huang 2008; Adeniyi et al., 2011; Selvaraj et al., 2014). PAEs accounted for 70% of 8.4 million tons of plasticizers that were produced and consumed worldwide in 2014 and were forecasted to increase to 10.3 million tons in 2019 with PAEs contributing 65% (Zhang et al., 2018a). Previous works have reported that PAEs are top offenders in the growing list of endocrines disrupting chemical compounds, which are natural or synthetic, that interfere or disrupts with normal endocrine functions (He et al., 2013; Net et al., 2015; Olujimi et al., 2017). Several PAEs, including (DMP), di (2-ethylhexyl) phthalate (DEHP), and dibutyl phthalate (DnBP) are listed as priority pollutants in many countries (Zheng et al., 2014; Net et al., 2015). Given the biogeochemical cycling as well as the physicochemical properties of PAEs, phthalates are ubiqitous in various environmental matrices, including air (Lee et al., 2019), surface water (Li et al., 2017), tap water (Domingue-Morueco et al., 2014), sediments (Sun et al., 2013; Liu et al., 2014), aquatic biota (Cheng et al., 2013) and humans (Kim et al., 2011; Liu et al., 2012). Currently, the occurrenc, distribution, source, migration and potential ecological risks of PAEs in the aquatic environment have attracted wide attention globally (Liu et al., 2014; Net et al., 2015).

Similar to other anthropogenic chemical compounds, PAEs enter aquatic environment through various route, including direct or indirect sources of wastewater discharge, surface runoff as well as atmospheric deposition(Clara et al., 2010; Net et al., 2015; Gao and Wen, 2016; Gani et al., 2017). As a result of their low solubility, PAEs in aquatic ecosystem are closely related with suspended solid particles and ultimately accumulate in bottom sediments. In the past few decades, PAEs congeners have been measured in the water phase or/and sediment of large rivers, including Yellow River, and Pearl River, Ogun River and Khlang River (Tan, 1995; Sha et al., 2007; Adeniyi et al., 2011; Liu et al., 2014), lakes, including the Epe and Lagos Lakes in Nigeria, and Lake Taihu in China (He et al., 2013; Adeogun et al., 2015).

PAEs are ubiquitous and resistant to degradation which will subsequently result to potential accumulation in aquatic communities (Staples et al., 1997; Net et al., 2015). As a result, PAEs may cause adverse effects to aquatic biota and can distress the overall aquatic ecosystems. Thus, understanding the potential ecological risk of PAEs in aquatic environments, together with algae, crustacean and fish in a river system is a significant issue as well as generating serious concerns (Staples et al., 1997). The acute toxicity of PAEs including DMP, DEHP, DnBP and BBP for different aquatic biota have been measured as 29–337, 10.3–131, 0.35–6.29, and 0.21–5.3 mg/L, respectively, the potential ecological risk was positively correlated with the alkyl chain lengths of these PAEs (He et al., 2013). Humans are exposed to PAEs via dietary consumption, bioaccumulation in aquatic food web, ingesting and bathing of contaminated water and the extensive use or exposure to PAEs in numerous industrial products during production, storage, transportation and utilization (Staples et al., 1997; Cheng et al., 2013). For the reason that, PAEs causes numerous potential risks via exposure, a comprehensive assessment of the environmental and human health risks of PAEs is essential. To get accurate, as well as appropriate data, studies on the ecotoxicity of PAEs have been done (Adams et al., 1995; Staples et al., 1997, 2011; He et al., 2013; Al-Saleh et al., 2017; Li et al., 2017). Staples et al. (2000) stated that America and the Netherlands calculated the predicted no-effect concentrations (PNECs) and the findings revealed that PAEs posed no ecological risk to all the aquatic biota in North American and Western European surface water. However, Li et al. (2017) have reported that DEHP posed high risk at a concentration exceeding 0.62µg/L on aquatic biota in Jiulong River in China, while DnBP posed moderate risk with concentrations between 0.03-1.77µg/L. Nevertheless, there is lack of scientific information about the risks of PAEs in aquatic environment for developing nations including Thailand (Zeng et al., 2008; Sirivithayapakorn et al., 2014).

1.2 Rationale of present study

The U-Tapao canal is one of the most important water resources of the Songkla Lake in Southern Thailand (Chuvanich et al. 2017; Gyawali et al., 2011). The U-Tapao canal, is 68 km long which flows from Bantad Mountain through Hat Yai City before emptying into Songkla Lake (Gyawali et al., 2011). Hat Yai city, is the main city in the watershed; which is a center of economic development, industrialization, urbanization, tourism and commercial hubs in Songkla province, southern Thailand (Chuvanich et al., 2017). The canal serves as a major water resources for industries, agriculture, balancing of ecosystems and provision of tap watersource for people living in the catchment area (Muskavong and Wattanachira, 2013; Chuvianch et al., 2017).

Most factories and commercial places are located on the banks of canal; 24.9%, 65% and 10.1% are situated at the upstream, midstream as well as downstream of the U-Tapao canal respectively. The factories and commercial places located at the bank of the canal in Sadao districts include 32 rubber, 14 Parawood, 9 Plastic, 8 concrete, 2 mining, 3 Food and 3 Others (Gyawali et al., 2012). For Klong Hot Khog district, the factories and commercial places located in this region of the canal include 4 Concrete and 1 Parawood. In Na Mom district; there were 1 concrete, 2 rubber, 2 parawood, 2 plastic and 2 food industries. In Bang klam district; 5 concrete, 8 rubber, 8 parawood, 4 plastic, 5 Other service industries are located along the banks of the canal. Finally, in Hat Yai district there were 16 concrete, 36 rubber, 28 parawood, 13 plastic, 9 mining, 24 Food industries and 49 other Services (Gyawali et al., 2012). In addition, U-Tapao Canal ecosystem is rich in macrobenthic fauna, boasting of four phyla and 67 species which include a specie of porifera, 26 species of Annelida, 21 species of Mollusca, 15 species of Arthropoda. The major taxa were annelids (polychaetes 22 species), arthropods (crustaceans 15 species) and molluscs (pelecypods 13 species and gastropods eight species). Cyclophorid shells were also found in the basin. The U-Tapao canal is also vital to the economy of the area, in 2006, over 13,574 pig farms and 3,698 shrimps' farms were located around the watershed. In addition, over, 900 industries were located around the basin including rubber, parawood, plastic, concrete, furniture, metal and food industries (Pornpinatepong et al., 2010; Gyawali et al., 2012).

However, the ongoing industrialization and urbanization competes with traditional uses which include fishing, aquaculture, agricultural activities, in addition to industrial usage and provision of safe plus potable water to residents in the locality. With the population and industrial pressures increasing along the U-Tapao Canal, exposure to serious threats of these ecosystems from both organic and inorganic chemical contaminants, which can accumulate in the aquatic media or food chains is inevitable. Furthermore, chemical pollution of source water and tap water from the canal will be injurious to human health (Pornpinatepong et al., 2010; Gyawali et al., 2012).

Furthermore, the canal currently suffers from growing pollutions of hazardous organic and inorganic chemical compounds. Despite significant quantities of hazardous chemical being manufactured, used, and discharged into the water body, little is known about their release or about their pollution status in water and sediments as well as the ecological and human health risk caused by rapid economic development in the area. Due to the rapid economic development in recent decades, the river system is facing accelerated environmental degradation (Gyawali et al., 2012; Musikavong et al., 2016; Chuvanich et al., 2017)

However, a few numbers of specific studies conducted in the U-Tapao Canal have produced clear indication that certain effluent containing persistent, bioaccumulative and toxic chemical compounds, are being discharged by industries and municipalities which are deteriorating the watershed. For instance, wastewater effluent containing high organic content was reported to be discharged into U-Tapao Canal, at the rate of 41,000 m^3 per day from rubber, parawood and seafood industries (Sirinawin and Somponchaiyakul, 2005). In addition, a study reported the presence of high concentration of PAEs in wastewater effluents from latex industries which are incessantly discharged into the water body. Many researchers have reported that the water quality of U-Tapao Canal is seriously deteriorated by anthropogenic source (Pornpinatepong et al., 2010; Gyawali et al., 2012; Gyawali et al., 2013a; Chinaving et al., 2017). Moreover, elevated levels of hazardous chemical compounds including heavy metals (Pradit et al., 2012; Pradit et al., 2013), DDT (Kumblad et al., 2001) dissolved organic matter and trihhalomethane (Musikavong et al.,, 2013), Trihalomethane of dissolved organic matter fraction (Musikavong et al., 2016), Nitrogen (chinaving et al., 2017) were detected in the canal ecosystem.

Although these studies deliberated above are not intended to provide an all-inclusive overview of the situation in U-Tapao Canal, however they demonstrate that the aquatic environment is currently facing chemical pollution. The potential for accumulation of organic chemicals compounds in the aquatic environmental media such as water, sediments and biota are already been seen, though the extent of the problem so far is not fully clear. There is a pressing need to evaluate and establish the degree of the chemical pollution and develop suitable solutions together with the establishment of a priority substance list with the aim of ultimately eradicating all releases of hazardous substances. In this regard, a preventive and sustainable approach to the risk management of hazardous chemical compounds in the aquatic environment is required, starting with robust research in occurrence, distribution, ecolgocal and human health risk assessment of chemical pollutants.

The fact that numerous hazardous chemical pollutants identified in the U-Tapao Canal are restricted or banned in other more developed markets, or have been prioritized for eradication by different international and national organization, should be a wake-up call to the authorities and all stakeholders to start addressing this delinquent now, if possible in aquatic environments in Thailand.

However, Thailand has embarked on national programs to deal with chemical pollution of aquatic environment, but the scope of current programs has ignored phthalate esters. Therefore, this study can inform policy makers to include phthalate esters in the routine assessment or monitoring of these endocrine disrupting organic pollutant in aquatic environment.

Moreover, there is no reported scient data for scientific information on the occurrence of PAEs in surface water and sediment of U-Tapao Canal that houses several industries in Southern Thailand. In addition, based on available published literature, there is no information of PAEs in aquatic environment in Southern Thailand. Furthermore, at global level, studies involving distribution and contamination of phthalate esters in surface water and sediments of suburban river ecosystem in reference to the impact of land use pattern are limited. Several studies on the distribution and contamination of PAEs in riverine ecosystems, revealed that theses organic contaminates are posing serious risks on aquatic ecosystems (Sun et al., 2013; Wang et al., 2014; Ramzi et al., 2018; Arfeania et al., 2019).

Based on these backgrounds, this present work was carried out with the intended to provide baseline scientific information of the presence along with distribution pattern of certain PAEs species including DnBP, BBP, DEHP, DnOP, DiNP and DIDP in U-Tapao Canal, in Songkla Province, Southern Thailand. The surface water and sediment are being analyzed by gas chromatography and spectrometer (GC-MS), to address the present contamination status of PAEs in the canal. Physicochemical parameters of water and sediment that influences the occurrence and distribution of PAEs in the canal will also be evaluated. PAEs pollution of the canal might be a potential threat to source water and tap waterin the study area. Moreover, the conventional or traditional water treatment plants are not designed to efficiently remove PAEs. Furthermore, prolonged ingestion of contaminated source water and tap waterfrom the canal may generate a serious public health concern. Hence, it is important to investigate the concentrations of PAEs in commonly consumed tap waterin order to evaluate the possible human health risk from consumption and bathing of contaminated water. Unfortunately, the accumulation of PAEs in Thailand riverine ecosystems has been paid less attention and no study has been carried out so far in river ecosystems in Southern Thailand. Therefore, the purpose of this research work was to evaluate the presence of certain PAEs congeners in surface water and sediment, giving prominence to ecological and human health risk assessment in U-Tapao canal. Likewise, the occurrence and removal efficiency of PAEs in main tap water supply plants in the area will be assessed. This information will facilitate better understanding of the pollution status of the six most common PAEs and the potential risk on human and aquatic biota. Furthermore, the baseline of the scientific information of PAEs in this canal will be useful to policy makers and related regulatory agencies for significant and future strategies of the pollutant control and management of PAEs in canal ecosystems.

1.3 Research Questions

a) What are the concentrations, distribution and ecological risk of PAEs in surface water in U-Tapao Canal?
b) What are the concentrations, distribution and ecological risk of PAEs in sediments of U-Tapao Canal?
c) What is the removal efficiency of PAEs in water filtration plants and human health risk for children, adolescent and adult via ingestion and dermal contact via bathing of tap water?

1.4 Research Objectives

The specific objectives addressed by this work include

a) To investigate the concentrations, distribution and ecological risk in surface water of U-Tapao Canal.
b) To investigate the PAEs concentrations, distribution and ecological risk in the sediments of U-Tapao Canal.
c) To determine the PAEs concentration, removal efficiency of water treatment plants where conventional or traditional water treatment plant is utilized for processing tap water, as well as assess the human health risk for children via ingestion and bathing of tap water.

1.5 Expected Outcomes

a) Provide useful scientific information for policy makers as wel as other stakeholders on the pollution status and the influence of urbanization on the occurrence of PAEs in U-Tapao canal, which will be beneficial for future pollution control strategies for the management and remediation of PAEs in U-Tapao canal.

b) The study will provide information on the removal efficiency of the PAEs by conventional or traditional water filtration plants and contribute to the characterization of exposure of Thai citizens to these compounds in tap water for the first time, which will be very useful, to policy makers, risk assessor, regulators and managers of public water supply for the protection, prevention and adequate management of public water supply system and protection and control of aquatic environment as well as human exposure.

c) To provide scientific information for policy makers and regulatory agencies for formulation of intervention standards for the protection, prevention, control, reduction and management of PAEs contamination of aquatic ecosystem.

d) To provide baseline data for future research on phthalate esters in U-Tapao canal.

1.6 Research scope

This research will restrict itself to assessment of phthalate acid esters in surface water and sediments of U-Tapao Canal, Songkla Province, southern Thailand. In addition, the study will evaluate the occurrence and removal efficiency of PAEs in source water and tap water from four waterworks that are equipped with raw water from U-Tapao Canal. Moreover, the ecological risk of PAEs in water and sediments will be assessed as well as the human health risk of PAEs in tap water on exposed Thai residents, including children, adolescents and adults via ingestion and bathing of tap water. Only six most common PAEs congeners are targeted in this work, they include dibutyl phthalate (DnBP), benzyl butyl phthalates (BBP), di (2-ethylhexyl) phthalates (DEHP), di-n-octyl phthalates (DnOP), di-iso-nonyl phthalates (DiNP), and di-iso-decyl phthalates (DiDP).

CHAPTER TWO

LITERATURE REVIEW

2.1 Structural identity and Physicochemical Properties of Phthalates

2.1.1 Structural identification of Phthalate esters

Chemically, the different phthalate acid esters congeners share the identical basic chemical structure but differ in the length and ester side chain. All PAEs congeners have the general structure showed in Figure 2.1, where R1 and R2 denote ester side chains that usually differ in chain length and structure (ECHA, 2009). PAEs congener side groups can be similar or dissimilar, in addition, the nature of the side groups determines both the identity of the PAEs congener and its physicochemicals and toxicological properties. Figure 2.2, 2.3, 2.4, 2.5, 2.6, and 2.7 shows the chemical structures of DnBP, BBP, DEHP, DnOP, DIDP and DiNP respectively.

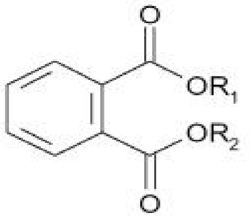

Figure 2.1 General structure of ortho-phthalate

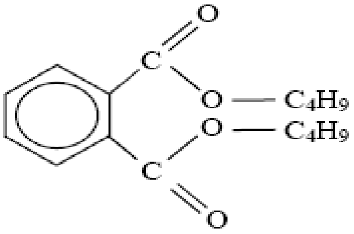

Figure 2.2 Structure of Di-n-butyl phthalate (DnBP)

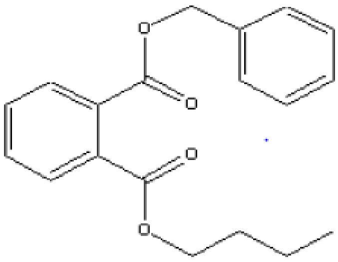

Figure2.3 Structure of Benzyl butyl phthalate (BBP)

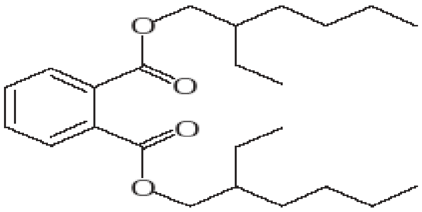

Figure2.4 Structure of Bis (2-ethylhexyl) phthalate (DEHP)

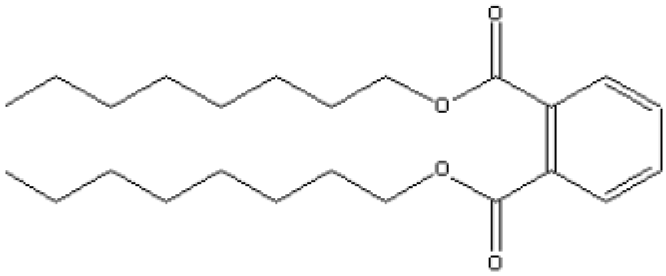

Figure2.5 Structure of Di-n-octyl phthalate (DnOP)

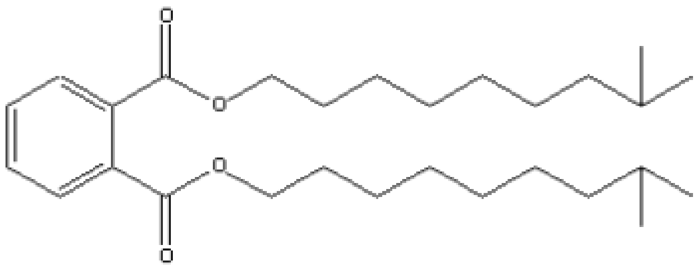

Figure2.6 Structure of Di-isodecyl phthalate (DIDP)

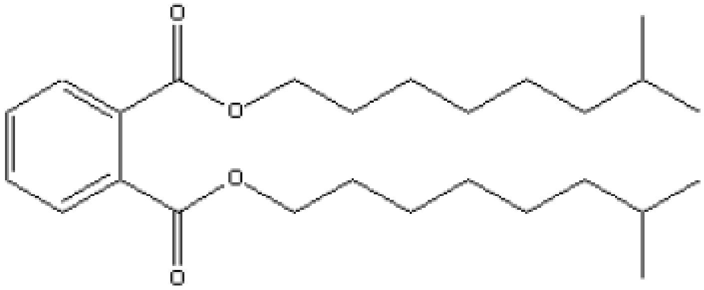

Figure 2.7 Structure of Di-iso-nonyl phthalate **(DiNP)**

2.1.2 Physical and Chemical Properties

Physicochemical properties control the general characteristics of a chemical pollutants, in addition, they are used to evaluate the suitability of different chemical pollutants for different types of applications. Such chemical characteristics also play a vital part in evaluating the environmental fate and of the substances, as well as their toxicity to humans and aquatic life (Staples et al., 1997). The physical and chemical properties of the 6 PAEs assessed in this work are shown in Table2.1. The main physicochemical parameter that influences the biogeochemical behavior, fate and transport as well as their exchange between different environmental compartments (atmosphere, lands, water and biota), includes water solubility (S_W), vapor pressures (Vp), Henry's law constants (H), air–water partitioning (K_{AW}), octanol-air partitions (K_{OA}), octanol–water partitionings (K_{OW}) and organic carbon partitionings (K_{OC}) (Staples et al., 1997; Cousin and Mackay, 2000). In general, the solubility of PAEs in aqueous environment displays an overall pattern of decreasing values with increasing alkyl chain length. Medium-chain phthalates displays low to moderate solubilities in water phase as well as very low to low. Water solubility (S_W) influences the distribution between environmental matrices which include water vs soil vs sediment vs atmosphere and Vice versa (Staples et al., 1997). K_{OW} regulates the affinity of an organic compound with the lipid molecules in living organisms, this explain why K_{OW} is useful in the prediction of the tendency of a contaminant to concentrate in aquatic organisms and yields a quality results (Staples et al., 1997). For PAEs, Log K_{OW} increases as the alkyl chain length increases, signifying greater bioconcentration Vp drops more than 7 orders of magnitude with increasing alkyls chains lengths. Moreover, H shows the predisposition of a chemical compound to escape from water into air. *H* can be evaluated from Vp and S_W. Chemical compounds with *H* values of 1.01×10^{-2} Pa·m^3/mol are commonly considered to have insignificant volatility.

Table 2.1 Physicochemical properties of some common PAEs

Phthalate esters	Formula	Molecular weight (g/mol)	Solubility in water at 25°C (mg/L)	Vapor pressure at 25°C (mmHg)	Octanol-water partition coefficient Log Kow	Sorption coefficient Koc(L/Kg) (sediment and soil)
Dibutyl phthalate (DBP)	$C_{16}H_{22}O_4$	278.34	2.35	2.01×10^{-5}	4.50	1.460×10^{3}
Benzyl butyl phthalate (BBP)	$C_{19}H_{20}O_4$	312.37	2.8	8.25×10^{-1}	4.91	1.567×10^{5}
Di(2-ethylhexyl) phthalate (DEHP)	$C_{24}H_{38}O_4$	390.57	2.70×10^{-1}	1.42×10^{-7}	7.60	1.654×10^{5}
Di-n-octyl phthalate (DnOP)	$C_{24}H_{38}O_4$	390.5	2.49×10^{-1}	1.39×10^{-1}	8.10	1.654×10^{5}
Di-iso-nonyl phthalate (DINP)	$C_{26}H_{42}O_4$	418.6	3.59×10^{-5}	5.40×10^{-7}	9.37	2.158×10^{5}
Di-iso-decyl phthalate (DIDP)	$C_{28}H_{46}O_4$	446.7	2.80×10^{-1}	5.28×10^{-7}	10.36	1.589×10^{6}

Source**:** Cousin and Mackay **(**2000), Net et al. (2015)

2.2 Production and application of PAEs

Industrial use of PAEs as plasticizers to confer flexibility and durability on plastic products that started in the 1930s has rapidly expanded broadly worldwide (Net et al., 2015). Low molecular weights PAEs which include dimethyl phthalate (DMP), diethyl phthalate (DEP), as well as DnBP are major constituents of industrial solvents, diluents in perfumes, adhesives, waxes, inks, medicinal products, pesticides, fertilizers materials, and cosmetics (Wee and Aris 2017). DMP and DEP are used to improve fragrance of perfume by reducing the evaporation rate of the perfume, thus lengthening the duration of the scent; while a small quantity of DnBP gives nail polish a chipresistant characteristic. PAEs with longer alkyl chains are majorly applied as plasticizers in industries that produce plastic and related materials to improve flexibility, durability, workability, processability as well as general handling properties, 80% of PAEs produced are used for this purpose (Wee and Aris 2017). The most commonly used phthalate esters considered in this work include dibutyl phthalate (DBP), denzyl butyl phthalates (BBP), di (2-ethylhexyl) phthalates (DEHP), di-n-octyl phthalate (DnOP), di-iso-nonyl phthalates (DiNP), and di-iso-decyl phthalates (DiDP). Their global and regional production and consumption, especially as well as their diversity of application are addressed below:

2.2.1 Production and application of DnBP

DnBP is manufactured by esterification of n-butyl alcohol with phthalic anhydride in the presence of a catalyst such as sulfuric acid or p-toluene sulfonic acid. The ECHA DnBP (2009) report indicated that the annual global production volume of DnBP in 2005 was more than 22 million pounds per year. In the U.S from 1986 to 2002, production of DnBP ranged from 10 to 50 million pounds. Asia and Pacific Region countries each produced amounts of DnBP like the U.S. In Japan, production of 37,478,585 pounds was reported during 1994 (ECHA, 2009). Korea reported 15,432,400 pounds produced in 2010 (Lee et al., 2014). The largest application of DnBP is as plasticizer in resins and polymers such as polyvinyl chloride (PVC). DnBP is added to hard plastics to make them softer, such as cellulose and some PVC plastics. Furthermore, DnBP is applied in many consumer products including cosmetics, perfume diluents and fixatives, suspension agents for solids in aerosols, grease for aerosol valves, antifoamer, skin soothing and as plasticizer in nail polish, fingernail elongators and hair sprays. It is also used in products like adhesives, dyes, lacquers and personal care, adhesives, printing ink, sealants, paints, film coatings, glass fibers, insect repellants, safety glass, and cosmetics (ECHA, 2009).

2.2.2 Production and application of BBP

Production of BBP, is generally through a two-step reaction process. Phthalic anhydride is first converted to monobutyl phthalate by alcoholysis with n-butyl alcohol in the presence of an acid catalyst. The monobutyl phthalate is then converted to BBP either by esterification with benzyl alcohol or by reaction with benzyl chloride in the presence of an acid catalyst (ECHA, 2009). BBP is used in a widespread variety of consumer and non-consumer products, together with children's products, household products and personal use products (Wee and Aris 2017). BBP is also applied as a plasticizer in PVC to soften the material and to add flexibility (ECHA, 2009). In addition, BBP is also formulated as a component in printing inks, paints, epoxy resin, sealants, conveyor belts, automotive trims, carpet, climate stripping and traffic cones (Wee and Aris 2017).

2.2.3 Production and application of DEHP

DEHP has been manufactured for over eight decades. Commercial production of DEHP began in Japan in 1933 and in the U.S in 1939 (ECHA, 2009). DEHP is produced when 2-ethylhexanol reacts with phthalic anhydride. DEHP is widely manufactured and used throughout the world. According to Toxics Use Reduction Institute, DEHP was the most commonly used phthalate plasticizer with an estimated global production ranging from 2,205 to 8,818 billion pounds per year. In 1993, the production volume of DEHP in Japan was 770,000,000 pounds (ECHA, 2012). In 1995, production in Taiwan and China was 460,000,000 pounds (ECHA, 2012). DEHP is used as a general-purpose plasticizer to impart flexibility in PVC, rubber, adhesives, PVA emulsion paints, and lacquers. As a plasticizers, DEHP, are extensively applied in a wide variety of consumer and industrial products. They are also useful in large quantities as a plasticizers for PVC products in numerous other products together with building materials, clothings, car parts, food packaging materials, and medicinal items (ECHA, 2010). Industrial uses of DEHP include the process of producing adhesives, binding agents and sealants, aerosol propellants, cleaning/washing agents, coloring agents, construction materials (such as flooring, roofing, wires, cables), fillers, flame retardants and extinguishing agents, heat transferring agents, non-agricultural pesticides and preservatives, paints, lacquers, and varnishes, agricultural pesticides, process regulators, reprographic agents, softeners, solvents, surface treatments, surface-active agents and others (ECHA, 2010).

2.2.4 Production and application of DnOP

There is inconsistency in the technical literature regarding the chemical name di-n-octyl phthalate and associated chemical identity. The literature has on occasion referred to dioctylphthalate, DEHP, DIOP and DnOP as the same chemical (ECHA, 2012). This report addresses the linear (i.e., not branched-chain) di-n-octyl phthalate (CASRN 117-84-0), with the structure (ECHA, 2012). DnOP is considered a high molecular weight phthalate. DnOP is produced through simple chemical synthesis by the reaction of n-octylbromide or n-octanol with phthalic anhydride in the presence of a catalyst like sulfuric acids or p-toluenesulfonic acids, or at high temperatures noncatalytically (ECHA, 2012). A total of 270 million pounds of total DnOP were produced in 1992. In US, DnOP was considered a high-production volume chemical in 2005 with estimated production ranging between 10 to fewer 50 million pounds. DnOP is used as a plasticizer in plastics, cellulose ester, polystyrene and vinyl resins (ECHA, 2012). It is also used as a chemical intermediate in the production of adhesives and lacquer coatings. It is a dye carrier in PVCs, a carrier for catalysts or initiators, and a substitute for electrical capacitor fluid (ECHA, 2012).

2.2.5 Production and application of DiNP

There are different production processes for DiNP leading to isomeric mixtures of eight to ten carbon alkyl ester chains in different proportions. DiNP can be produced by the ‘polygas’ technique (CASRN 68515-48-0) and from n-butene (CASRN 28553-12-0). In both processes, DiNP is made through esterification of phthalic anhydride and alcohol (either an octene- or n-butene-based alcohol) in a closed system (ECHA, 2010). Global production of DiNP has increased consistently since 1994, with an assumed growth rate of 2.5% annually. U.S production of DINP has been estimated at 356,000,000 pounds (178,000 tons) per year (ECHA, 2010). In the EU, total production volume was 408,000,000 pounds per year (204,000 tonnes) in 1994 (ECHA, 2010). DiNP has a wide range of applications as a plasticizer in PVC products, including toys, construction, and additional consumer products. DiNP is not used in medical products and is not heavily utilized in food packaging materials. Recently, DiNP are applied or utilized as a auxiliary for DEHP, to mitigate the potential risk of DEHP in human and the environment (ECHA, 2010).

2.2.6 Production and application of DIDP

DIDP are produced by reacting phthalic anhydride with isodecanol using an acid catalyst (ECHA, 2010). The Production of DIDP in the U.S was estimated to be approximately 616,000.000 pounds in 1994 (ECHA, 2010). In 2002, DIDP annual production is approximately 270,000,000 pounds in the U.S (ECHA, 2012). In 2012, the EPA reported U.S production to be 500,000–1,000,000 lb/yr. DIDP is mainly used in PVC as well as PVC/polyvinyl acetate co-polymers due to its high affinity to polymer materials, good solvation during processing and the ability to maintain low temperature flexibility. ECHA (2012) has indicated that DIDP is characteristically applied and useful as a plasticizer for heat-resistant electrical cords, leather for car interiors, and PVC flooring materials because of DIDP’s volatility resistance, heat stability and electrical insulating properties. DIDP is also preferentially used in car interior trims in order to meet the low fogging thresholds set by car manufacturers. Furthermore, DIDP is preferably used in cables and wires (ECHA, 2012).

2.3 Fate and distribution of PAEs in River ecosystems

An understanding of the biogeochemical behavior of PAEs in riverine environment can play a significant role in the mitigation, strategic and sustainable control and management of these synthetic organic contaminant (Staples et al., 1997). The fate of PAEs in the riverine ecosystems depends on a wide range of processes including abiotic effects such as hydrolysis and photolysis; biotic effects like biodegradation and bioaccumulation in biota and physical processes (Staples et al., 1997; Net et al., 2015).

Organic chemical pollutants usually enter the riverine ecosystems via numerous processes and pathways. Once, these organic pollutants are introduced they are subject to biogeochemical cycling, sinks as well as bio-accumulation processes. Their inputs can be due to direct discharge of untreated or semi-treated municipal and industrial wastewater, effluent from aquaculture and agriculture, urban runoff, as well as additional anthropogenic activities, or from unintended inputs from rivers and run-off in addition to atmospheric deposition (Gao et al., 2016).

The ubiquity, slow hydrolysis and photolytic rates of PAEs influences their possible accumulation in aquatic environment. Hydrolysis of PAEs is insignificant at neutral pH with aqueous hydrolysis half-lives in order of quite a lot of years, for instances the half-life of 22 years, 107 years and 2000 years for DnBP, DnOP and DEHP respectively, in aquatic environment have been observed and documented (Net et al., 2015). However, Okamoto et al. (2006) reported that on exposure to light irradiation, PAEs react with photogenerated hydroxyl ions (OH•) to form 4-hydroxy phthalate esters that present potential toxicity.

Volatilization in addition to deposition process of PAEs in air-water interface hinge on the Henry's law (H). Henry's law can be used to classify the rate of volatilization of phthalates esters from water. PAEs with low H values such as DnBP and BBzP were preferentially control by deposition into river surface, whereas DEHP with high H was more influenced by volatilization. Moreover, for DEHP, deposition plays a major significant role in the air-surface water gas exchange, whereas volatilization from seawater occurred in the near-coast environment (Net et al., 2015).

Biodegradation are considered to be the most significant process for the removal or elimination of PAEs from aquatic media (Net et al., 2015). Certainly, PAEs can be accumulated and biodegraded rapidly by microorganisms including bacteria and fungi, under both aerobic and anaerobic conditions. In water phase of river ecosystem, under aerobic environment, apart from low temperatures (<5 °C) and poor nutrition, the half-lives of primary biodegradation differs in less than 1 day to 2 weeks, and the half-lives for complete mineralization takes about 10 times longer (Staples et al., 1997). In water phase half-life of DEHP and DiNP have been estimated as 360 hours and 900 hours respectively (Cousins and Palm, 2003). The degradation of PAEs differs depending on the density as well as type of species of organisms. Several PAEs congeners have been detected in aquatic biota with a modest amount and were not likely to biomagnify up the food chain since it is degraded by organisms (Mackintosh et al. 2006). The biodegradation of PAEs in aquatic biota followed the order of fish > crustacean > molluscs > cnidarians > algae (Staples et al., 1997). Few works have focused on the biodegradation of PAEs in riverine and marine sediment. The potential kinetics of anaerobic biodegradation of PAEs in riverine sediment hinge on on numerous factors such as pH, temperature, surfactants, contaminants or pollutants, or chemical compounds that inhibit microbial activity. In sediments, under aerobic condition, the degradation half-lives of DnBP and DEHP were estimated range from 1.6 to 2.9 days and 5.0 to 8.3 days respectively (Yuan et al. 2002). Similar half-lives of DEP, DnBP, and DEHP for river sediment under anaerobic conditions at temperature of 30 °C with pH 7 were estimated at 16 days, 10 day, and 26 days respectively. For river sediment under anaerobic environments, DnBP, DPhP, and BBP might be degraded rapidly while DEP and DEHP degradation rates might be very low (Yuan et al., 2002; 2010). Primary biodegradation rates in sediments samples collected from aquatic environment were estimated at 3–4 weeks and 3 months, respectively, for DnBP and DEHP (Chen et al., 2017).

2.3.1 Bioaccumulation of Phthalate Esters in Aquatic Food-Web

Bioconcentration refers to the process in which an aquatic biota attains a concentration level of chemical pollutants that exceeds the level in the surrounding water due to exposure of the aquatic biota through the respiratory surface and the skin (Gobas et al. 2003). In addition, bioconcentration are usually achieved under laboratory conditions, in which the aquatic biota is exposed to a chemical substance in the water, but not in its diet. Bioaccumulation is referred to as the process by which the chemical concentration in an aquatic biota attains a concentration that surpasses the level in the water due to chemical uptake through all exposure routes or pathways of the chemical pollutants including dietary absorption, transportation of the pollutants across the respiratory surface and dermal absorption. Bioaccumulation are usually evaluated via field conditions or studies (Staples et al., 1997; Gobas et al., 2003; Mackintosh et al., 2006). Biomagnification is defined as the process by which the chemical level in the predator surpasses that in the prey biota it consumes (Gobas et al. 2003).

2.4 PAEs in Riverine system

Riverine systems can act as a sink and the primary means of environmental dispersal for a variety of hazardous chemical substances that arises in discharges, drainages, runoffs and other diffuse sources, mostly of anthropogenic origin (Teil et al., 2013; Liu et al., 2014; Selvaraji et al., 2015). Figure 1 shows possible pathway that PAEs can be released into aquatic environment. Consequently, chemical pollution status of a river ecosystem is highly influenced by the level of urbanization, industrialization and agricultural activities along the riverbanks (Zeng et al. 2008; Sun et al. 2013; Net et al. 2015). The river systems are also influenced by some river-based activities such as aquaculture, festivals held on riverbanks, tourist activities, transportation, constructions, waves, sedimentation rate, water flow rate. All the above-mentioned river activities directly or indirectly affect the fate, transport and contamination status of chemical pollutants such as PAEs in the riverine ecosystem (Li et al., 2015). Moreover, PAEs present in the atmosphere may precipitate into the river by wet or dry deposition mechanism and influence their occurrence and distribution in the riverine environment. Upon entering the river ecosystem, PAEs hydrolyze at slow rate with half-lives which ranges from roughly 3 years for dimethyl phthalate (DMP) to 2000 years for DEHP (Net et al., 2015). The PAE photo-oxidation process are relatively slow as well, with half-lives that ranges from 2.4 to 12 years for DEP and DnBP and 0.12 to 1.5 years for DEHP (Net et al., 2015). Nonetheless, biodegradation plays a major role in the fate and transport of PAEs in the aquatic environment. Research works have showed that aerobic degradation rates occurs up to 10 times faster than they occure during anaerobic degradation rates (Yuan et al., 2002). PAEs interact with many types of materials and undergo several changes between various media of the river such as water, suspended solid matter, sediments and aquatic biota, and can induce endocrine disrupting effects in aquatic organisms and human health via these media

River contamination by PAEs impacts several trophic levels, from primary producers to apex predators, and thus interferes with the structure of riverine communities and consequently ecosystem functioning (Gobas et al. 2003; Oehlmann et al. 2009; Net et al. 2015). Most of the river systems worldwide have been reported to be damaged from organic chemical pollution, significantly affecting drinking water sources, ecological balancing, agricultural productions and commercial fisheries. Therefore, control and prevention of the pollution of aquatic ecosystems has been identified as an immediate need for sustainable management and conservations of the existing drinking water sources, fisheries and aquatic resources (Islam et al., 2001). Apart from the ecosystems approach, ingesting contaminated water and aquatic biota are significant pathway through which humans gain exposure to these pollutants (He et al. 2013; Liu et al. 2013; Insuan et al. 2016). Therefore, investigating organic pollutants in water and sediment phase is an essential indicator in determining the pollution status, accumulation characteristic is very significant in assessing the potential ecological and human health risk of PAEs in river ecosystems. However, acknowledgement that both human life and wildlife can be more effectively protected by more integrated approaches to research, risk assessment, and decision making is on the increase (Dong et al. 2015).

Due to their physicochemical properties, fate and behavior, PAEs are detected in various media of the river ecosystems. The water phase is very significant in aquatic ecosystems and several studies on the distribution and contamination levels of PAEs in water phase have been reported globally including China (Li et al. 2017a), India (Selvaraj et al. 2014), Malaysia (Tan 1995), South Africa(Fatoki et al. 2010b), Nigeria (Adeniyi et al., 2011), France (Paluselli et al. 2017), Spain (Domínguez-Morueco et al., 2014) and Netherland (Peijnenburg and Struijs 2006). According to the review by Bergé et al. (2013), the median concentration of total PAEs contamination in water phase of North America (0.29 µg/l) are notably lower than median values of 1.24 µg/l and 1.18

µg/l reported for China and Europe respectively. Moreover, median contamination levels of DEHP for Europe (1.05 µg/l) and China (1.11 µg/l) are very similar, but lower than that of North America (0.27 µg/l). It is worthy of note that altogether, geographical areas exhibited a limited high outlier. In China, Sha et al. (2007), detected levels above 28µg/l which were 20-fold higher than the average levels in United Kingdom.

Water phase or dissolved phase is a significant medium that influences the fate, transport in addition to bioavailability of hydrophobic organic pollutants in riverine ecosystems(Zeng et al., 2008; Oehlmann et al., 2009). Furthermore, freely dissolved phase concentration (level in water phase) are more appropriate for ecotoxicology studies, as this represent the bioavailability to aquatic biota, whereas particulate bounded concentration (concentration in suspended solid matter and sediments) are more useful for fate and transport evaluations (Oehlmann et al., 2008; Sirivithayapakorn and Limtrakul, 2008; Net et al., 2015). In addition, sediments can also be used for evaluation of ecological risks in aquatic biota or benthic organisms (MacDonald et al., 1996; Wang et al., 2014; Arfaeinia et al., 2019).

Sediment in various water environments is a valuable research matrix for many disciplines. In environmental research, numerous studies have involved the collection and analyses of sediment samples. Compared with air and water, sediments accumulate higher concentrations of hydrophobic chemicals, facilitating their detection. Sediments are also much less mobile than water and air, and thus provide information on the spatial distribution of chemical accumulation over time (Butt et al., 2008; Li et al. 2015). Sediment can not only reflect all events happening in the water layer but also integrate the impact of events over long periods of time. Sediment cores can be used to retrieve the geochronology of the chemical input, which is valuable in identifying emission sources, examining post-depositional in situ degradation, and investigating the link between chemical pollution and changes in the ecosystem and human society. Benthic organisms, such as mussels and bottom-dwelling fish, accumulate PAEs from contaminated sediment, which causes concerns on human exposure to the chemicals (Wang et al., 2017).

River sediment are significant sources and sinks for dispersal and bioaccumulation of PAEs congeners in water phase and have been extensively utilized as an effective and efficient environmental indicator for the evaluation of PAEs pollution in the aquatic environment (Gobas et al. 2003). In the aquatic environment, sediments act as sink and deposition sources for PAEs congeners which possess low values of water solubility, volatilization rate, in addition to melting point (Mitsunobu and Takahashi 2006). Reversibility of chemical pollutants, usually occurs in the aquatic environment as a result exchange between sediment and the water phase resulting in sediments playing a major role as secondary sources of exposure to pollutants for the benthic and pelagic water ecosystem, effectively influencing biota exposure (Sirivithayapakorn and Limtrakul 2008). Through the interaction between sediments and water phase, the transfer of PAEs from sediments to aquatic biota is now regarded as a major route of exposure for many species of aquatic organisms in the river ecosystems (Staples et al. 1997). River sediments, thus, are significant sources for the evaluation of chemical compound pollution in aquatic environment as they have a long residence period for the organic chemical pollutants like PAEs (Sun et al. 2013b; Wang et al. 2014b).

Furthermore, river sediments are significant vectors in transporting organic chemicals like PAEs to the ocean (Mi et al. 2019). Clear determination of the amount of PAEs transported by riverine sediments can shed light into the cross-boundary transfer and help in the estimation of regional contribution of PAEs in the global inventory (Mi et al. 2019). This cross-boundary transport of organic chemical from one aquatic environment to the other are usually assessed by mass inventory and burden. There have been more studies on the mass inventory of organic chemicals including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic hydrocarbon (PAH), nonylphenol (NP), octylphenol (OP), bisphenol A (BPA) amongst others in river estuary (Gao et al., 2018) and bays (Shi et al.,2016). However, Mi et al. (2019) estimated the mass inventory of PAEs in Bohai and Yellow sea, which is one of the few studies that inventoried PAEs in aquatic environment. None of these studies focused on the mass inventory of PAEs in riverine system. Therefore, this work seeks to explore the estimation of mass inventory of PAEs in a river system.

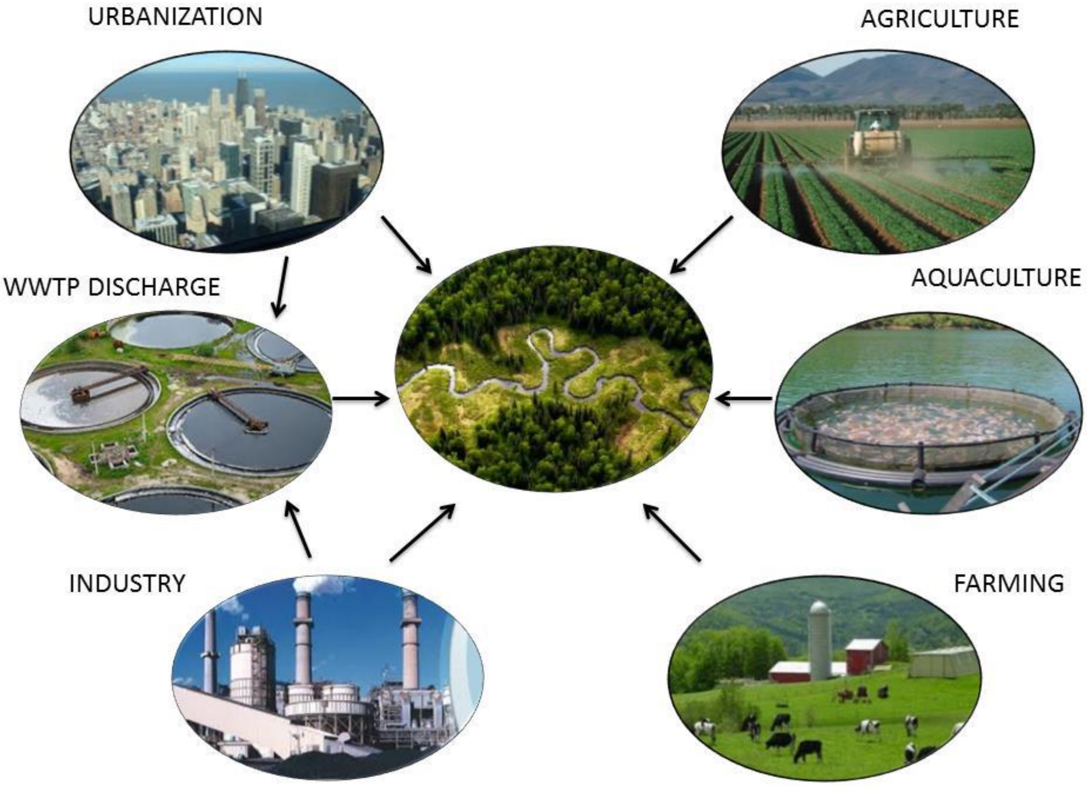

Figure 2.8 Possible pathways PAEs can be released into the aquatic environment

Source: Li et al. (2009)

2.4.1 Physicochemical parameters influencing PAEs in River systems

Several physicochemical factors are involved in influencing the occurrence and distribution of organic pollutants in the riverine sediments together with composition of sediments such as grain size fractions of sediments samples including sand, silt, and clay, water content, organic matter content, organic carbon, total organic carbon (TOC), salinity, pH, electrical conductivity (EC), total phosphorus (TP), partitioning processes and pattern of deposition of chemical pollutants in the sediments (Sanchez-Prado et al., 2010).

Hydrophobic organic chemicals are prone to combine with particles which influence their biogeochemical characteristic in sediments and aquatic ecosystem (Staples et al. 1997; Bergé et al. 2013). The grain size of sediments is one of the factors that influences the distribution of organic chemical pollutants in aquatic environment. It is generally accepted that fine-grained sediment that possess a high adhesion as well as cohesion has a high affinity or tendency to get attached to many organic chemical pollutants in aquatic ecosystems (Droppo et al., 2015)

Organic matter (OM) comparatively homogenous, lipophilic as well as gel like matrix is one of the principal factors influencing the absorption of organic contaminants in riverine sediments (Hu et al. 2006). In addition, particle size is significant for the adsorbing of OM. OM are easily adsorbed by small suspended solid particles (SSP) due to their large specific surface areas. This explains why PAEs of low molecular weight, such as DiBP/ DnBP, are easily adsorbed by larger suspended solid particles and specially deposited to sediments close to the sources of PAEs as compared to the longer alkyl- PAEs, such as DEHP/DiNP.

In addition to the physicochemical characteristics of PAEs, other physical parameters can affect the behaviour of these chemicals in the environment. Temperature affects the vapour pressure and therefore the volatility of these chemicals (Staples et al., 1997). Salinity also could affect the biodegradation and sorptive behavior of the phthalate esters.

Organic carbon (OC) content of sediment is also expected to have a significant effect on the bioavailability of hydrophobic chemicals. Since hydrophobic organic chemicals have a high tendency to bind to organic matter, the presence of high concentrations of sediment OC is expected to result in low free fractions of the chemical. Therefore, for highly sorbed chemicals, there is only a small portion of the chemical that is available for biodegradation reactions or uptake into organisms. In the case of PAEs, this was recently demonstrated by Kickham and colleagues (2012) who showed that highly hydrophobic PAEs were not biodegraded by microbes in natural sediments obtained from False Creek likely because they were predominantly bound to sediment OC. Less hydrophobic PAEs (e.g. DMP) were not bound to sediment OC and were biodegraded at approximately the same rate as the more hydrophilic metabolites of phthalate esters (MPEs) (Kickham, et al., 2012).

Biodegradation rates of PAE also can be affected by the temperature, nutrient addition, and their concentration (Staples et al. 1997). Environmental conditions such as temperature, pH, the fraction of OC dissolved or suspended in the water column could also affect the overall fate of PAEs (Staples et al. 1997).

2.4.2 Potential ecological risk of PAEs in a river ecosystem

Ultimately, some of the PAEs which will end up in the riverine system are taken up by the aquatic biota together with phytoplankton, algaes, microbes, as well as plants. These species are usually consumed or prediatored upon by fish and crustaceans, consequential in their bioaccumulation within food chains. PAEs pose severe threat to aquatic ecosystem because they bioaccumulate and recalcitrance in aquatic organisms or biota. Ecotoxicological studies shows that at low levels (ng/L or µg/L), PAEs may pose potential ecological threats to aquatic biota, in addition adversely affect the overall aquatic ecosystems. For example, eggs of Medaka fish exposed to DEHP level ranging from 0.01 to 10.0µg/L, resulted in reduced body weight, distortion of sex ratio in embryos and amplified mortality rate (Chikae et al. 2004). A recent study reported that DnBP and DEP caused neurotoxicity to embryos of zebra fish by hindering the activity of acetyl cholinesterase (He et al., 2013). Therefore, a comprehensive understanding of the ecological risk of PAEs in aquatic ecosystem, including microorganisms, seaweeds, fish, and invertebrates in riverine ecosystem or limnetic zones is a significant issue in the protection of aquatic life (Staples et al., 1997). The acute toxic effects of some PAEs congeners such as DMP, DEP, DnBP, and BBP for variety of aquatic biota have been evaluated as 29,000,000 ng/L to 337,000,0000; 10,300,000 ng/L to 1,310,000,000 ng/L; 350,000 ng/L to 6,290,000 and 210, 000 to 5,300,000 ng/L, respectively (He et al. 2013). Because of the numerous potential risks of PAE exposure, an all-inclusive assessment of the ecological risks of PAEs is mandatory.

Ecological or environmental risk assessment (ERA) is referred to as the way by which the likelihood or real adverse/negative effects of chemical contaminants and other man-made activities on aquatic ecosystems as well as their components are evaluated with a known degree of certainty by applying scientific techniques or procedures. ERA has become progressively imperative, since environmental scientists and researchers, risk assessors in addition to the public have learned that PAEs are ubiquitous environmental pollutants that can pose endocrine disrupting and toxic effects on both human and wildlife. Risk assessment procedure can be divided into a scientifically based risk analysis as well as politically founded risk management. Risk analysis involves or include, identification of hazards, toxicological effect assessments, exposure assessments and risk classification (Van Leeuwen and Hermens, 1995). Environmental risk management deals with regulatory dealings constructed on the basis of risk assessment as well as remediation (Van Leeuwen and Hermens, 1995). Ecological risks assessment is largely concerned with establishing the potential relationship between a contaminant source and an ecological effect triggered by exposure of organisms to the contaminant.

2.4.3 Potential human health risk of PAEs via aquatic media

It is common knowledge that humans are exposed to adverse effects of PAEs from aquatic contamination through consumption of contaminated water, edible aquatic biota and agricultural produce irrigated with the contaminated river water (Liu et al. 2016; Tang et al. 2012). Prolonged exposure to PAEs may cause adverse health effects such as birth defects, altered semen quality, hormonal abnormality and endocrine disruptions which may cause premature breast development, shortened gestation, infertility, testicular dysgenesis, lost of pregnancy, childhood social impairment, obesity and asthma (Colón et al. 2000).

Exposure to PAEs in source water and drinking water is an emerging area of public health concern. Studies suggest ingestion of water, as well as food, are important routes of exposure for phthalates (Liu et al. 2015; Sulentic et al. 2018). PAEs may occur in surface waters serving as municipal source waters due to industrial discharge or solid plastic waste; phthalates may also leach into municipal drinking water in distribution systems built with high-density polyethylene (HDPE) or polyvinyl chloride (PVC) pipes. Drinking water ingestion and absorption has been found to be a major source of human exposure to some PAEs species such as DBP, DEHP and DnOP in China (Wang et al., 2014). In France, drinking water has been identified as a major source of PAEs exposure in humans (Martine et al., 2013). Previous studies observed that PAEs in municipal drinking water supply is generating serious health effects in human (Shi et al., 2011; Tan et al., 2012). PAEs that are present in source water and drinking water are constantly ingested in daily life, exposing human to adverse effects of these hazardous chemical compounds (Kong et al., 2017). Treatment of PAEs in drinking water supply systems is the final security step to protect humans from exposure to adverse effects of these organic pollutants. Unfortunately, treatment plants, especially the conventional and traditional treatment plants are not efficiently designed to remove PAEs contaminated source water (Liu et al., 2013; Kong et al., 2017). Moreover, studies have observed higher concentration of PAEs in treated water as compared to source water (Yang et al., 2014). The evaluation of PAEs, removal characteristic and human health risk assessment will be a useful tool to risk assessors, decision makers and water industries.

The incorporation of human and ecological risk assessments may improve all stakeholder’s perception and ability to manage the designs, manufacturing, usage and final disposal of chemicals in a safe plus efficient manner. Integrating human health and ecological risk assessments represent a new way for describing the risks which anthropogenic related chemical contaminants present to the environment, within which humans make up a fundamental part. Recent studies on distribution and potential ecotoxicological risk of PAEs everywhere in the world submit that developing nations are at higher risk of exposure to PAEs as the PAEs emission sources have shifted from developed countries to developing nations (Bergé et al. 2013b). Nevertheless, in Asian developing countries, there is paucity of information on PAEs contamination status in aquatic environment as well as ecological and human health risk from exposure to PAEs via aquatic media.

2.5 Environmental occurrence of PAEs in surface water.

Surface water is one of the main environmental components that is mostly impacted by anthropogenic activities. The occurrence and distribution of PAEs in surface water has been measured or determined in aquatic environment all over the world, including in rivers, tap water and sediments. Table 2.3 shows the level of PAEs in surface water of different rivers in Thailand and other locations around the world. In China, the level and distribution of PAEs in surface water has been monitored more widely in the south than in the northern cities, with the highest levels, 41 μg/L DnBP and 101 μg/L DEHP, being measured and reported in the Haihe River. The total trend of PAEs occurrence and distribution in investigated aquatic environment in China indicated that, the average levels of DnBP and DEHP were higher than others PAEs congeners, which agrees with the widespread use of plasticizers. For instance, 134,000 and 394,000 tons of DnBP and DEHP were produced and consumed globally (Xu et al., 2008). Concentration of PAEs in surface water in China are comparable with other areas of the world such as Europe, US, Canada and Malaysia (Net et al., 2015), the US (Solis et al., 2007), Canada (Mackintosh et al., 2006) and Malaysia (Tan 1995), where concentrations in water ranges from 0.1ng/L to 300,000 ng/L. However, studies have documented that the concentration of PAEs in surface water of Nigeria and South Africa indicated higher PAEs contamination status, with a concentration of DEHP exceeding 2300 000 ng/L being reported, which was much higher than in any other published data (Fatoki and Noma, 2002; Adeniyi et al., 2011). In addition, PAEs level in surface water and tap waterare being regulated in China as previously mentioned. Moreover, more studies have been conducted in China than other countries in Asia region, thus, studies on the contamination status of PAEs in aquatic environment are generally limited in other Asian countries as compared to China, irrespective of the facts that other Asian countries put together are the second largest region that consumes PAEs all over the world (Gao et al., 2018; Wang et al., 2018). The necessity to routinely monitor PAEs as well as regulate the discharge of PAEs into aquatic environment cannot be overemphasis, considering their ubiquitous occurrence, resistant to degradation and potential adverse effects to both aquatic life and human life, especially, its endocrine disrupting effects and toxic effects on wildlife and human life.

Many studies have indicated that the occurrence and distribution of PAEs in aquatic environment are influence by seasonal variation (Sha et al., 2007; Wang et al., 2008; Liu et al., 2014; Sirivithayapakorn et al., 2014; Zhang et al., 2018; Arfeania et al., 2019). For instance, the variations in the levels of PAEs congeners in the water phase of the Yangtze River was attributed to seasonal variation, for both tributaries and the mainstream. PAEs levels in water samples collected during winter periods were higher than those measured during summer, the result indicated that the PAEs level ranged from 35.73 µg/L to 91.22 µg/L in water and 0.03–0.46 µg/L in summer, which may be attributed to the amount of rainfalls and seasonal variation (Wang et al., 2008b). Rains happened in summer period, and the high surface runoff in addition to high flow rate in riverine ecosystems may have acted as diluents which lead to a higher selfpurification capacity for the PAEs than during the winter, which was dry season. However, significant levels of DnBP and DEHP were detected in freshwater in Netherland during spring, summer and autumn. In addition, the result indicated that the DnBP and DEHP levels are influenced by varying seasons, and the highest concentrations of PAEswere reported during the summer (Peijnenburg and Struijs, 2006).

However, in Thailand, studies on the occurrence and distribution of PAEs in aquatic environment are lacking (Sirivithayapakorn and Thyvuiang, 2010; Sirivithayapakorn et al., 2014). Moreover, few available studies were conducted in the northern part of the country, majorly in Chao Phraya river basin. A study in 2010, detected PAEs concentration in water ranging from <LOD to 8.64 µg/L in Chao Phraya river. Four years later a similar study reported elevated PAEs concentration ranging from <LOD to 25.6 µg/L in Chao Phraya river basin. This result indicates that the later PAEs level is 3-fold in magnitude higher than the previous studies, necessitating the

need for more studies on the occurrence and distribution of PAEs in Thailand as well as necessary action to mitigate the effects of this hazardous chemical compound on human and aquatic environment. Nevertheless, based on extensive search of published literatures, there is no study on the occurrence and distribution of PAEs in several aquatic environment in Thailand, especially in southern Thailand. However, a current study reported on the occurrence of PAEs in dust generated from electronic waste disposal site (E-waste) in southern Thailand (Muenhor et al., 2017).

2.5.1 Occurrence of PAES in source water and tap water

Exposure to phthalates in source and tap water is an emerging area of environmental and public health concern. Studies have suggested that ingestion of water and aquatic food, are important routes of exposure for phthalates esters in human (Shi et al., 2011; Liu et al., 2013). Phthalates esters have been detected in surface waters serving as municipal source waters which were attributed to industrial discharge or dumping of plastic waste; PAEs congeners may also migrate into municipal tap water in distribution systems from plastic pipes manufactured using high-density polyethylene (HDPE) or polyvinyl chloride (PVC). The occurrence of PAEs in tap water hinge on on the sources, seasonal variation, type of storage systems, temperature as well as the removal efficiency of the tap water treatment plant (Domínguez-Morueco et al. 2014). Liu et al. (2014) evaluated the occurrence of PAEs in several tap water sources in china and reported the ubiquitous pollution of PAEs in all investigated tap water sources in China. Higher concentration of PAEs in treated tap water as compared to raw or source water was documented in Zhejiang Province in China (Wang et al., 2015). Many studies have observed elevated level of DEHP in potable water sources (Hashizume et al. 2002; Shi et al. 2012; Li et al. 2013; Das et al. 2014; Liou et al. 2014). Li et al. (2013) reported PAEs concentration ranging from ND to 6.6 μg/L in the Mopanshan Reservoir which serves as the source of tap waterfor Harbin city. The higher concentration of DEHP may be due to its wide application in several industrial, consumer, personal care products and household items. Currently, a review article evaluated the global trend of PAEs in drinking water**.** The result indicated that the top five countries ranked in the order of high to low for elevated concentration of DEHP in tap water were Thailand, Croatia, Czech Republic, Saudi Arabia and China, with the average levels of 61.1, 8.8, 6.3, 6.2 and 6.1 µg/L, respectively. These average values were all above the recommended limit of 6 µg/L by U.S FDA. The highest concentration of DEHP of 500µg/L in drinking water, in all the studies included in the review was 500 µg/L, which was reported in a potable water in Thailand (Kanchanamayoon et al. 2012). Table 2.2 shows the level of PAEs in tap water in Thailand and other location.

Table 2.2 Concentrations of PAEs in drinking water in Thailand and other locations

Country	PAEs level(µg/l)	Reference
Thailand	ND-500	Kanchanamayoon et al. (2012)
China	ND-6.57	Liu et al. (2013)
China	ND-0.28	Shi et al. (2013)
China	1.18-15.28	Wang et al. (2015)
Japan	ND-5.22	Hashizume et al. (2002)
Spain	ND-0.633	Dominguez-Morueco et al. (2014)
India	ND-0.633	Kumar et al. (2015)
Taiwan	ND-172	Liou et al. (2014)

2.5.2 Occurrence of PAEs in riverine Sediment

In aquatic systems PAEs partition strongly to suspended solid maters and sediments, particularly organic matter, avoiding the aqueous phase or water phase. Table 2.4 shows the level of PAEs in sediments in different locations all over the world. Sediment samples collected from riverine ecosystems in U.S and EU were evaluated for the occurrence and regional comparison of PAEs including BBP, DnBP, DIDP, DEHP, and DnOP. The result indicated DnBP had the highest detected level at 2,100 mg/kg in a sediment samples collected from a riverine ecosystem in the Netherlands. In several other study, sediment samples have been collected and investigated for the presence of PAEs, from riverine ecosystems in Europe, North America and developing countries, particularly China, India, Thailand and Nigeria (Yuan et al. 2002; Sha et al.

2007; Zeng et al. 2008; Liu et al. 2010; Adeogun et al., 2015; Net et al., 2015). The amount of DnBP and DEHP measured in these samples varied from 0.01 to 300 µg/kg.dw. Nevertheless, sediments collected and evaluated from the North Sea in the Netherlands recorded the highest concentration of PAEs ranging from 92.7–727.5 µg/g. PAEs levels in river sediments also varied expressively between urban and rural samples (Teil et al., 2014). The evaluation of PAEs in sediments samples collected from the Qiantang River, China, revealed that the PAEs level in urban areas were expressively higher than their levels in rural areas and the geometric mean value of PAEs level in urban sediment samples was appromixmately 3 times higher than the values in rural sites (Sun et al. 2013**c**)

Table 2.3 Concentrations of PAEs in river water in Thailand and other countries in the world (µg/l)

Country	Name of river	Media	PAEs level (µg/L)	Reference
Thailand	Chao Phraya river	Water	0.64- 27,.550	Sirivithayapakorn et al. (2014)
Thailand	Gulf of Thailand	water	0.042- 8.640	(Sirivithayapakorn and Thuviang, (2010)
United State of America	Eleven Point, White river	water	0.04-4,140	Net et al. (2015)
China	Jiangshu-Yangtze River	River water	0.178-1.4740	He et al. (2011)
China	Yangtze river delta	Tap watersource	3.00-3.800	Shi et al., (2012)
Malaysia	Khlang River	River water	0.004-0.389	Tan, (1995)
France	France-Seine river	River water	0.464- 0.771	Dargnat et al. (2009)
India	Kaveri river, India	water	0.313-1.640	Selvaraj et al. (2015)
Netherland	Freshwater	water	0.540-26.200	Peijnenburg and Struijs, (2006)
Nigeria	Ogun river	River water	3950-4,775	Adeniyi et al. (2011)

Table*2.4* Concentrations of PAEs Levels in sediments in different locations (µg/kg)

Country	Name of river	PAEs level (µg/kg)	Reference
China	Kaohsiung harbor	430-3320	Chen et al. (2017)
China	Yangtze river-Wuhan	76,300-450,000	Wang et al. (20080
Malaysia	Klang river	5.00-637	Tan, (1995)
India	Kaveri river, India	2.00-1,438	Selvaraj et al. (2015)
India	Gomti river	0.00-364	Srivastava et al. (2010)
Nigeria	Ogun river	325-2880	Adeniyi et al. (2011)
South Africa	Freshwater systems	0.2-3660	Fatoki et al. (2010)

2.6 Removal efficiency of PAEs in tap watersources

Potentially there are several sources of organic chemical contaminants in tap watersupply systems starting from the source water and continue through water treatment process to bottling facility. Phthalate esters in source water are the major contributors of PAEs in potable or drinking water. Moreover, plastic pipes and slats used in distribution of water supply systems are potentially, dischargers of PAEs into water. PAEs have detected in several stages of water treatment plants, even in treated water (Shi et al., 2011). Studies on the removal efficiency of PAEs in contaminated tap watersources by water treatment plants are lacking (Liu et al., 2013). Apparently, researches have shown that conventional or traditional water treatments process in waterworks could not efficiently and effectively eliminate these chemical compounds. Liu et al. (2013) observed removal efficiency of PAEs of 25.8% to 76.5% from contaminated source water after traditional tap watertreatment plants in Mophanshan waterworks in Northeast China. The removal efficiency of PAEs in finished water varied from 12.8% to 64.5% by Jiubin conventional water treatment plant in Eastern China (Kong et al., 2017). Yang et al. (2014) reported 42 to 78% removal efficiencies of phthalates in these processes. Conventional or traditional water treatment process are known for not being efficient in the removing of PAEs from contaminated source water. Consequently, the frequent detection and wide distribution of PAEs in rivers, especially tap watersources, are highly concerning. However, advanced water purification methods and tap watertreatment plants can reduce the concentration in drinking water.

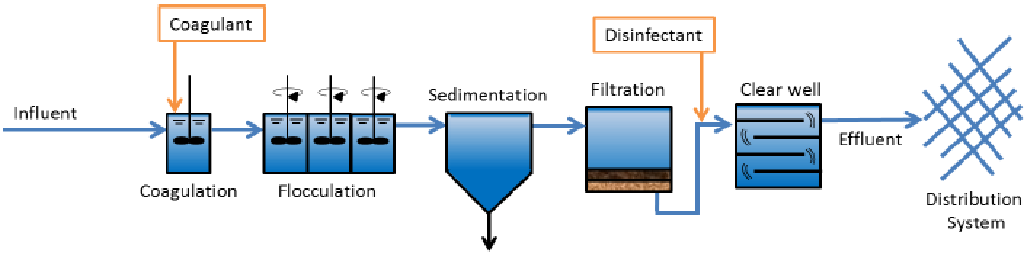

Figure 2.9 Schematic of conventional water treatment plant
Source: Li et al. (2011)

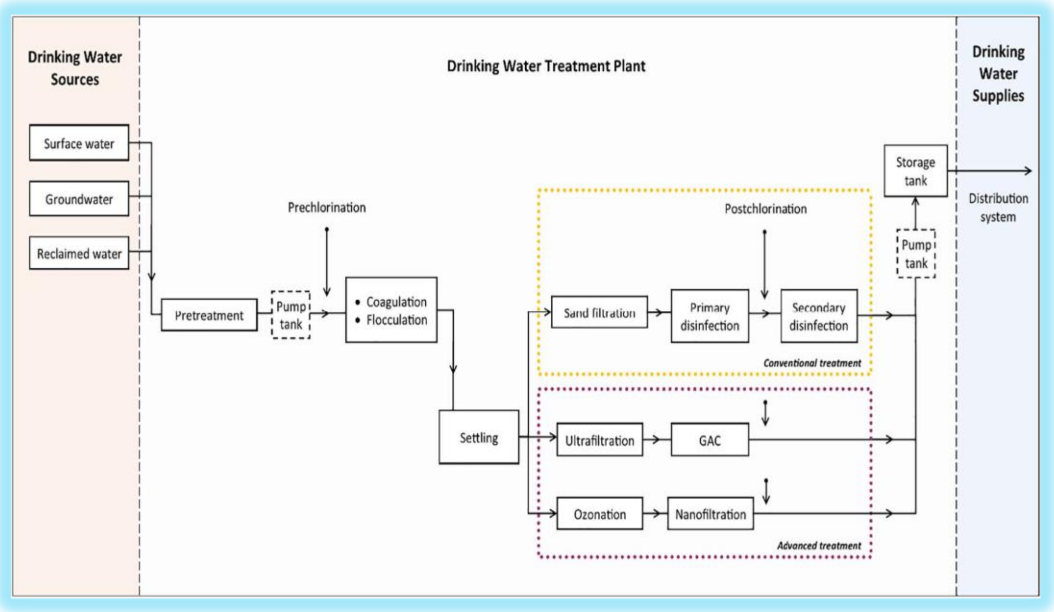

Figure 2.10 Schematic of advance water treatment plant
Source: Wee and Aris, (2017)

2.7 Influence of land use pattern on PAEs contamination of river ecosystem

Due to the close interconnections with the land use, River ecosystems are extremely susceptible to land-disturbing activities including industrialization, urbanization and agricultural activities (Gyawali et al., 2012). Industrialization, urbanization and agricultural activities have brought prosperity, alongside with several environmental problems, including chemical pollution of aquatic environment. It has been reported by several researcher that the quality of receiving water bodies are affected by anthropogenic actions via point source, such as wastewater treatment plants, and non-point source, such as runoff from urbanized area as well as agricultural land (Fatoki et al. 2010a; Olujimi et al. 2017). Increasing population growth, developmental pressures, lack of proper land use pattern, and competition for water resources, incessantly contribute to the degradation of water resources. Urbanization causes extensive modification to surface runoff timing and volume into aquatic environment, including riverine system. Agricultural areas occupying larger portion of landscape are major contributors of chemical pollution, when rainfall, surface runoffs carries sediment, nutrients, or chemicals to the river. These anthropogenic activities in rivers can increase organic chemical loading including phthalate acid esters posing serious risk on the aquatic ecosystems and public health. Several studies have reported link or association between PAE concentrations in river system and anthropogenic activities, urbanization as well as industrialization (Zeng et al. 2008; Zheng et al., 2014). In addition, PAEs concentration was found to be influenced by branch inflow and land use pattern in Songhua river, in China (Wen et al., 2018). Classification of land use pattern around river bodies may vary from place to place, they generally land use type include urbanization, industrialization, forest, grass land, water body, agricultural and waste management. Previous studies have considered the effects of land use pattern on the water quality of U-Tapao Canal. Findings of these studies indicated that the land use pattern around the river basin was impacting negatively on the water quality of the basin. For instance, Gywali etal. (2013), in a study assessed the influence of land uses of riparian zone on water quality of U-Tapao Canal, by using water parameters such BOD, DO, SS, FCB, DS, and Temp alongside GIS data of 100 meter Riparian zone together with analysis of variance, correlation of variance and stepwise multiple regression. Reported that the various land use types around the canal shows both negative and positive correlation. However, there is no study that looked at the impact of land use and chemical pollution; not to mention PAEs pollution of the canal. Information from GIS shows that the land use type sourrounding U-Tapao Canal basin include agricultural, residential and tourism, industrial and commercial, forest and water bodies. The various classification of land use pattern in U-Tapao Canal are indicated in Figure 2.10, 2.11, 2.12, 2.13, 2.14 and 2.15. Understanding the relationships between land use pattern and phthalate acid ester pollution of canal is important for watershed planning and management and beneficial for future strategies of PAEs pollution control and protection of river ecosystem (Lin et al. 2009).

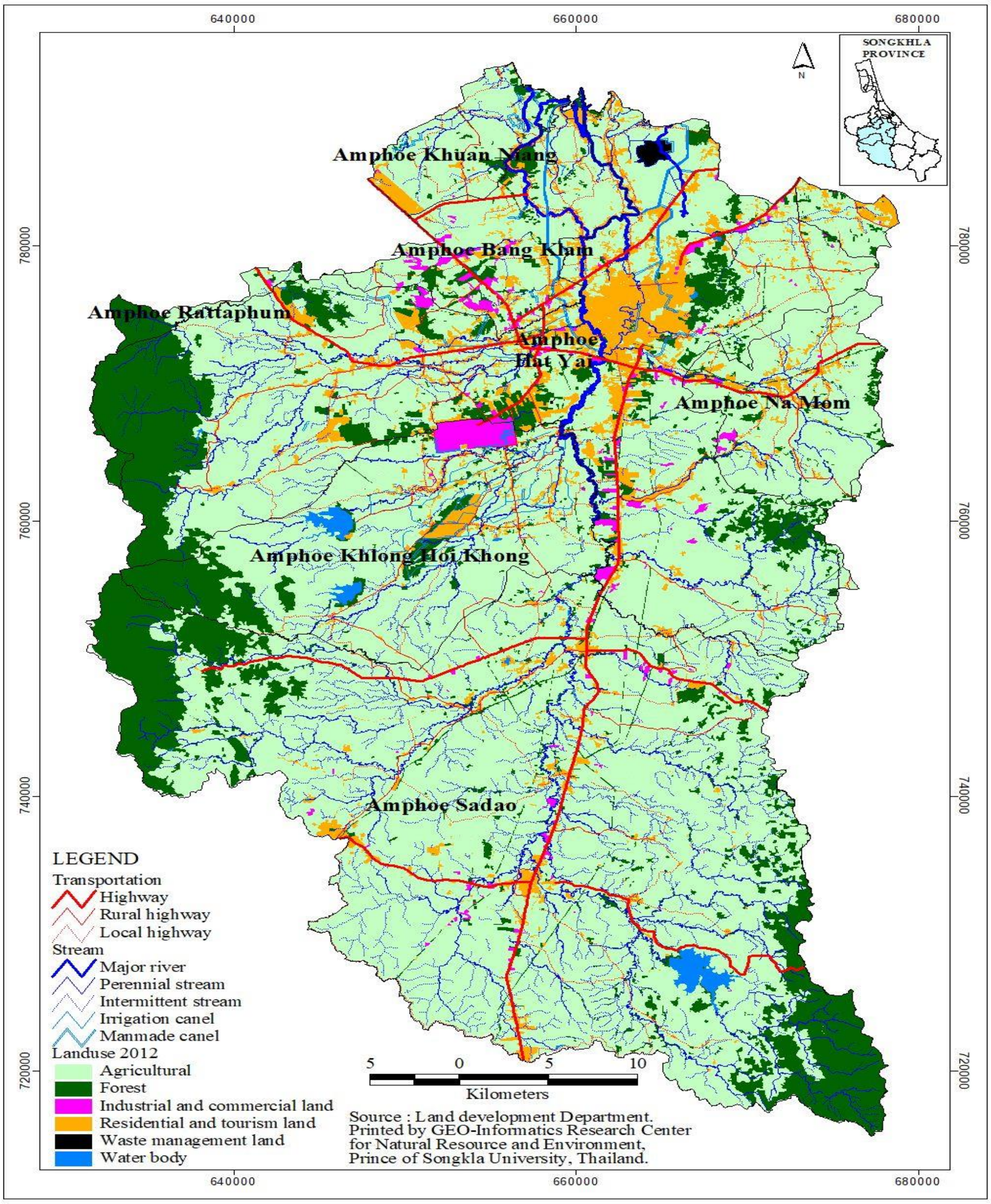

Figure 2.11 Map of land use pattern in U-Tapao Canal system

Source: Geo-informatic research center, Prince of Songkla University (2019)

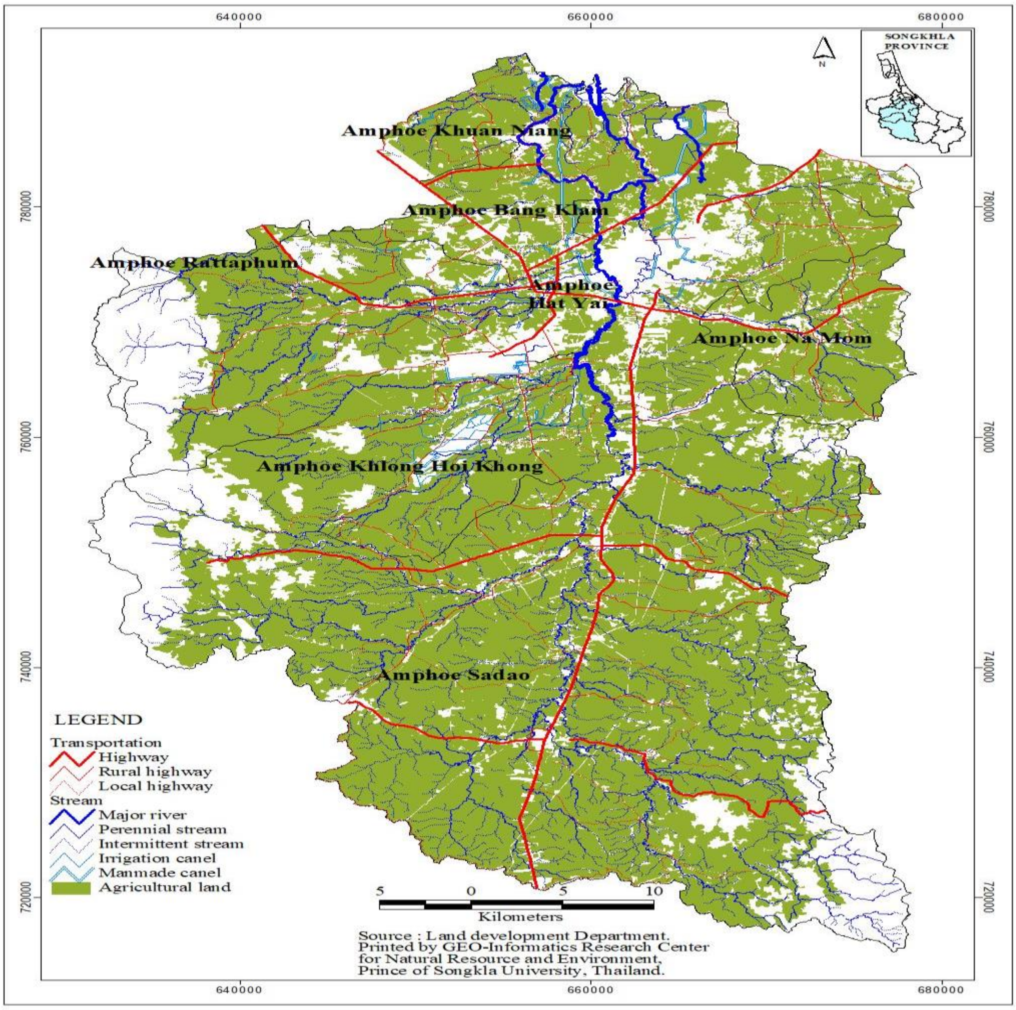

Figure 2.12 Map of agricultural land use pattern in U-Tapao Canal system

Source: Geo-informatic research center, Prince of Songkla University (2019)

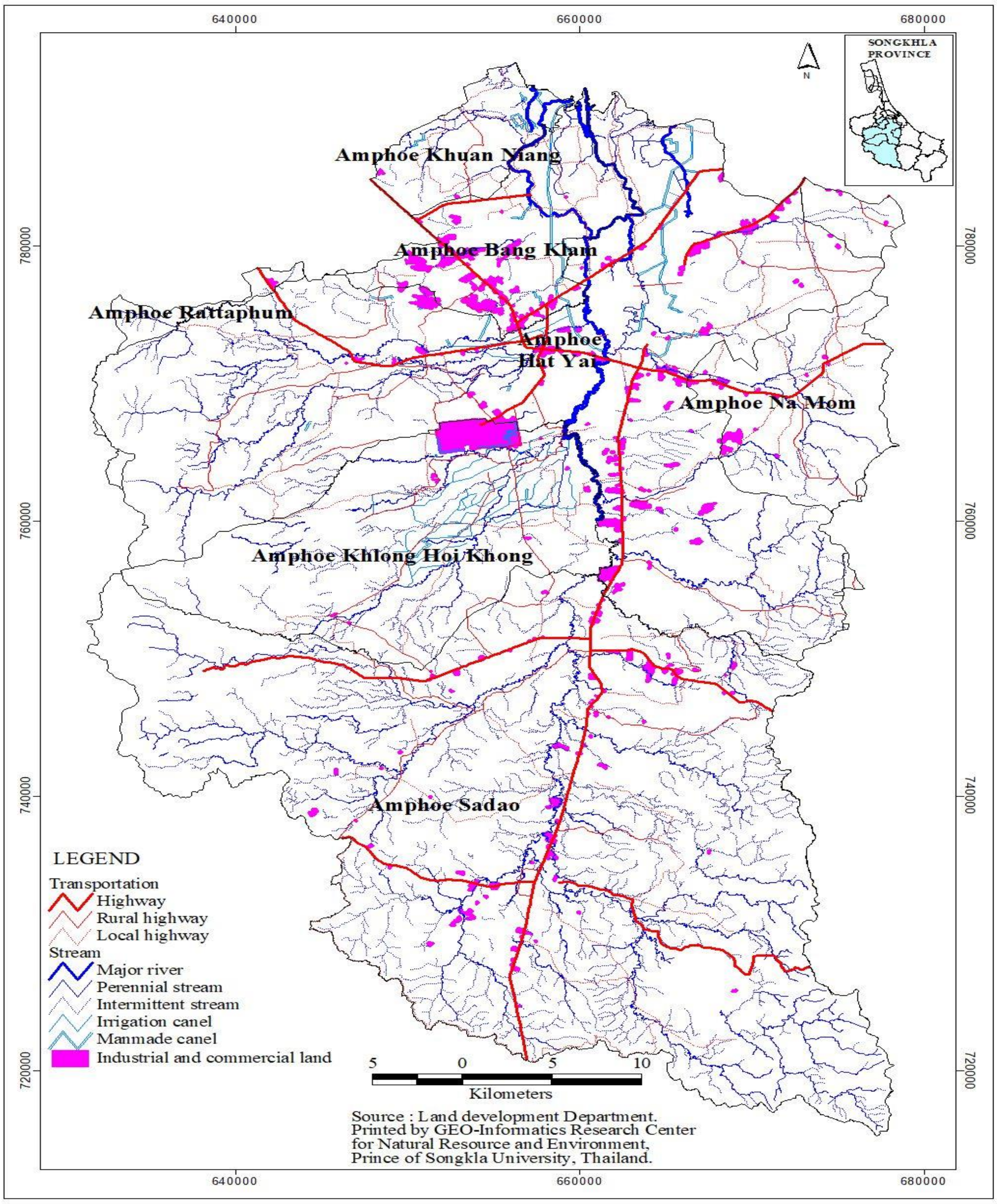

Figure 2.13 Map of industrial and commercial land use pattern in U-Tapao Canal

Source**:** Geo-informatic research center, Prince of Songkla University (2019)

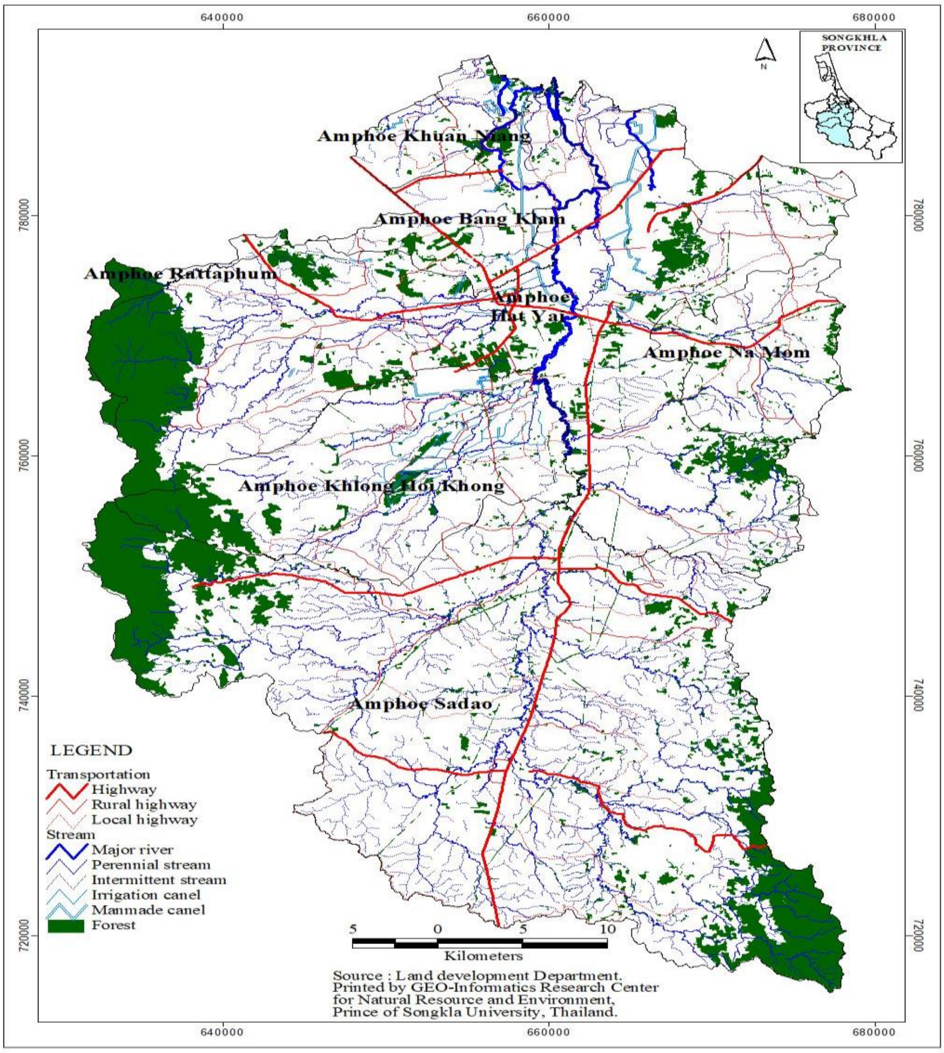

Figure 2.14 Map of forest land use pattern in U-Tapao Canal system

Source: Geo-informatic research center, Prince of Songkla University (2019)

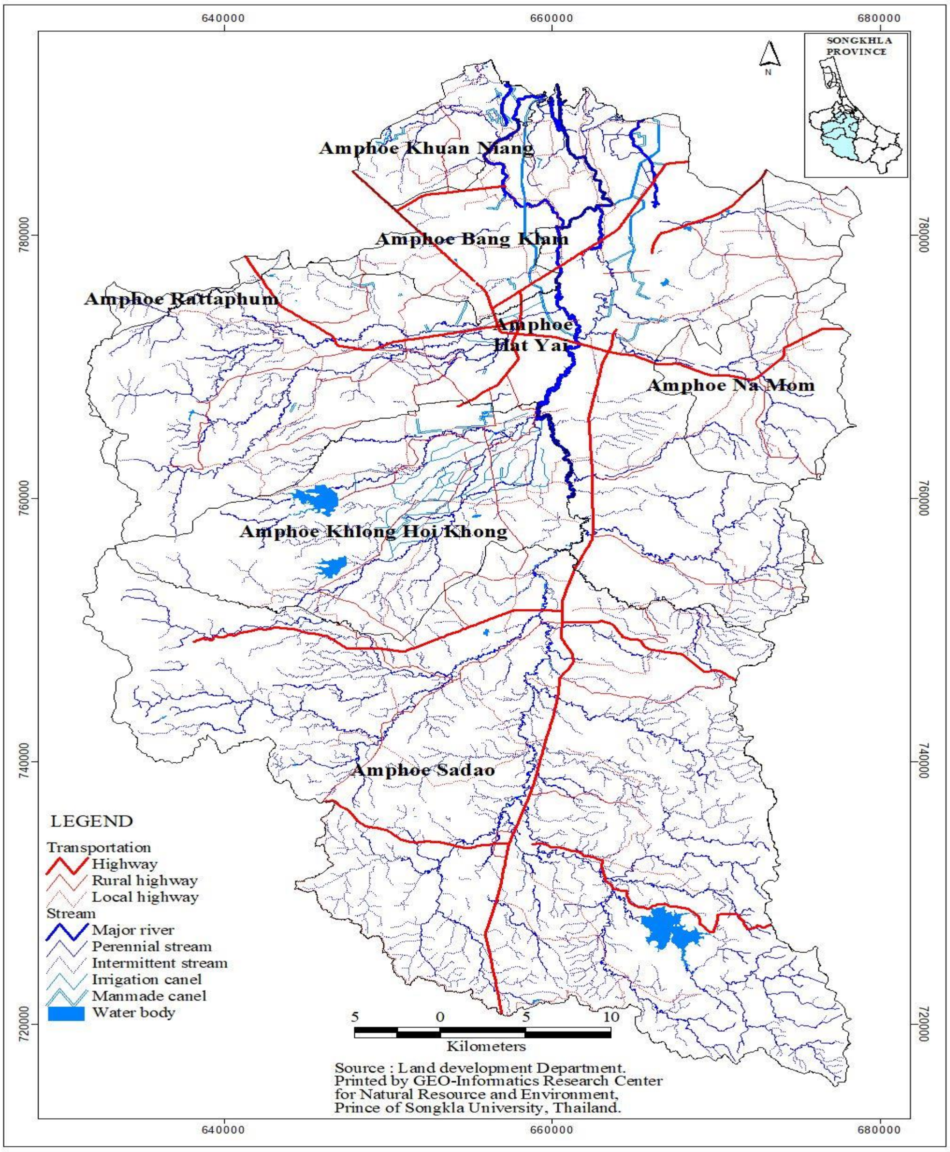

Figure 2.15 Map of water body of land use pattern in U-Tapao Canal system

Source: Geo-informatic research center, Prince of Songkla University (2019)

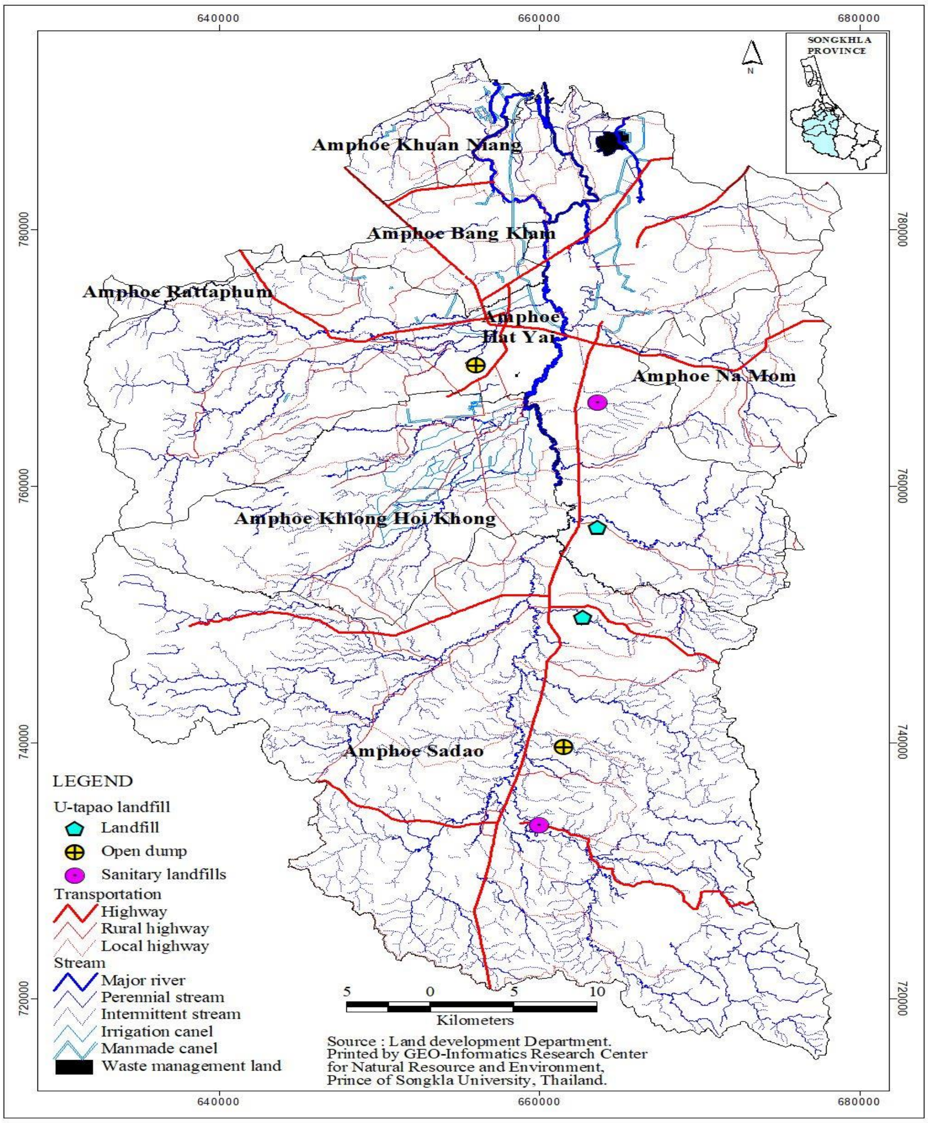

Figure 2.16 Map of waste management facilities in U-Tapao Canal

Source: Geo-informatic research center, Prince of Songkla University (2019)

2.8 Ecotoxicity of PAEs in aquatic biota

The ecotoxicity of PAEs in aquatic organisms have generated much concern in recent years, and this has led to the stipulation of environmental quality standards of PAEs in aquatic environment, with the intention to prevent contamination of the aquatic environment and protect the aquatic life from the adversative effects of PAEs. PAEs can trigger endocrine disrupting effects, specifically, reproductive physiological disruption in diverse species of fish and mammals (Staples et al., 1997). PAEs also poses adverse toxic effects on many other aquatic biotas. For instance, DEP have LC_{50}/EC_{50} values ranged from a concentration of 3 mg/L algae to 132 mg/L in protozoa, with the lowest NOECs for algae, invertebrates, and fish, ranging from 1.7 to 4 mg/L (Staples et al., 1997b). PAEs acquire unequivocal estrogenic activity in aquatic environment, because under light irradiation they form 4-hydroxy which are highly toxic to aquatic biota (Okamoto et al., 2006). A recent study evaluated the exposure of DEHP from hatching to adulthood in marine madaka. DEHP caused histological alterations in the testes and ovaries, as such the testes displayed a reduced number of sperm cells whereas the ovaries displayed an increased number of atretic follicles (Ye et al., 2014).

2.8.1 Ecological risk assessment

Ecological risk assessment (ERA) of chemical pollutants like PAEs is the practice of defining the likelihood or the actual adverse effects of PAEs on aquatic biota. It provides a framework for subsequent risk management and characteristically involves three tiers including identification of hazards, effects and exposure assessment and finally, risk characterization. ERA varies from health risk assessment since it usually considers a very large number of aquatic genera unike human health risk that considers a single species. Furthermore, human health risk assessment mainly aims to protect humans, whereas ERA is mainly concerned with protection of wildlife (Cura 1997; Schmitt-Jansen et al., 2008).

To date, toxicological risks that originate from PAEs contamination in aquatic environment have been commonly assessed by using predicted-no-effect-concentration

(PNEC) and measured environmental concentration (MEC) depending on the data available, matrix of study, and sensitivity of the species. For instance, the ecological risk assessment of chemical pollutants including PAEs are usually performed in accordance to the European Commission's Technical Guidance Document (European commission 2003). The risk quotient (RQ) approach based on this method uses the contaminant concentrations in surface waters and sediments to assess the potential ecological risk of PAEs on aquatic biota via these media. The RQs are usually calculated as the quotient of the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC). Sensitives organisms used in assess RQ include fish, crustacean and alagae. The RQs of PAEs are usually calculated as follows:

$$RQ = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \text{--} 1$$

In recent time, aquatic life criteria (ALC) for PAEs have been developed and used to evaluate ecological risk of DEHP and DnBP. For instance, Zheng et al. (2019) employed ALC to assess the preliminary ecological risk of the four PAEs congeners in Lao river basin in China. The method uses hazard quotient (HQ) to evaluate the potential ecological risk of PAEs on aquatic biota. HQ is referred to the ratio of measured exposure concentrations divided by a statistically derived effect concentration. Deterministic HQ was evaluated by equation 11

$$HQ = \frac{\mathrm{EEC}}{\mathrm{ALC}} \qquad 2$$

Where ALC stands for aquatic life criteria with ALC values for DBP = 0.62 µg/l and DEHP = 0.04µg/l. EEC stand for environmental exposures concentrations. The mathematical explanation of this method was listed below (Lemly, 1996):

$HQ \leq 0.1$, indicates that no risk exsts
HQ = 0.1 -1.0 indicates low risks
HQ = 1.1-10, indicates that risk is moderate
$HQ \geq 10$, reveals that risk is high

2.9 Human exposure to phthalates and possible health effects

Because of their widespread use, humans are extensively and continuously exposed to phthalates via different exposure routes. This section explains exposure of humans to PAEs via aquatic food and contaminated water. Health effects commonly associated with phthalate exposure are discussed below. Figure 2.17 shows the different route of PAEs exposure to human.

2.9.1 Oral ingestion

Oral ingestion is the principal exposure pathway for the entry of compounds that are present in foods and drinks. Specifically, for phthalates, numerous studies have indicated that, for the general population, dietary intake is the most important exposure route, especially for DEHP, DiBP and DnBP (Wormuth et al., 2006; Koch et al., 2011; Wittassek et al., 2011).

2.9.2 Human exposure via aquatic food and contaminated water

Humans can be exposed to potential risk via consumption of contaminated edible aquatic biota. For instance, in China, elevated levels of PAEs were reported in aquatic food in the eastern and southern regions, including Jiangsu, Shanghai, Zhejiang, and Guangdong of concentration ranging from 0.19 to 5.0 mg/g, 6.43 to 7.52 mg/g, 3.19 to 3.20 mg/g and 10.6 to 17.3 mg/g, respectively. In addition, high concentration of PAEs were also detected in edible aquatic biota collected from Pearl River Delta area with concentration ranging from 1.57 to 7.1 mg/g and varying fish species from Hong Kong market ranging from 25.4 to 52.4 mg/g, with DEHP as the highest contributor (Huang et al., 2008; He et al., 2015). In a recent study, He et al. (2015) reported the highest concentration of PAEs in edible aquatic biota as compared with other food groups including cereals, beverages, condiments, snacks and meat products sold in Yanji market in China, with geometric mean values and median levels of 1380 and 1210 ng/g ww, respectively. It was reported that PAEs levels detected in human body were positively correlated with the amount of fish consumption, which subjugated the total dietary PAEs intake (Chen et al. 2012). Aquatic products are a major dietary source of protein for most of Thailand residents (Insuan et al., 2016). In Thailand elevated concentration of PAEs in aquatic food ranging from ND to 385.2 ng/g have been documented (Insuan et al., 2016). Most of the aquatic products available in Thailand markets majorly come from the surrounding coastal and river ecosystem, suggesting the likelihood of significant exposure to PAEs via dietary intake of aquatic biota. In addition, human exposure to phthalate ester may also occur, due to unintended contamination of PAEs in various food materials during processing, storing, and transport (Cao 2010).

Moreover, human can be exposed to PAEs via drinking water, water is consistently and constantly ingested in daily life, suggesting that tap wateris an important source of human exposure to PAEs (Kong et al., 2017). Phthalate ester may occur in surface water serving as source water for public tap watersupply system as a result of industrial and municipal discharge or plastic pipes and slats. Tap wateringestion and absorption has been found to be a major source of exposure for some PAEs species including DnBP, DEHP and DnOP in China

Phthalates that are ingested, enter the body by absorption in the gastrointestinal tract. According to Wormuth et al. (2006), average absorption rates are about 55-82% depending on the phthalate compound. In principle, absorption of phthalates can take place anywhere along the digestive tract, i.e. from the mouth to the rectum. However, the major site for absorption is the small intestine because of its physiological function of absorbing nutrients.

2.9.3 Inhalation

The main lung function is to control the exchange of oxygen from air to blood and of carbon dioxide from blood to air. For this purpose, alveolar walls are very thin and do not only allow the passage of oxygen, but also of many other chemical substances. Once inhaled and absorbed through the lungs, phthalates may directly affect the respiratory as well as the cardiovascular system (WHO, 2003).

Inhalation is a dominant exposure pathway for volatile short alkyl chain phthalates. For instance, Wormuth et al. (2006) calculated for the general population that 70 to almost 100% of the total exposure to DMP originates from inhalation. In an

American study, DEP and DnBP were identified as the most abundant phthalate compounds in indoor air (Wormuth et al., 2006).

2.9.4 Dermal absorption

When a chemical penetrates the skin, its toxicity depends just like for oral ingestion and inhalation on the degree of absorption in the blood that takes (Sharpe, 2005). According to Wormuth et al. (2006), phthalates' dermal absorption rates are very low, i.e. 0.1-2.0% for adults and 1.3-4.1% for children. Once penetrated, phthalates enter the blood stream and are then carried to all parts of the human body (Sharpe 2005). Humans can be in dermal contact with phthalate via bathing and washing with contaminated water.

2.9.5 Metabolic fate of phthalates in the human body

Phthalates are usually metabolised in at least two steps, i.e. a phase I hydrolysis followed by a phase II conjugation step. Figure 2.16 shows the schematic diagram of the methabolic process of PAEs. Once entered in the human body, phthalate diesters are first rapidly hydrolysed into primary phthalate metabolite monoesters. This process is catalysed by lipases and esterases and occurs in the intestines (majorly the small intestine) and lung parenchyma. Unlike for most chemicals, this metabolic step is not a detoxification step, since studies have shown that phthalate monoesters are more bioactive than their parent compounds. In a second step, the remaining alkyl chain of the monoester can be metabolized via hydroxylation or oxidation to secondary metabolites. Both the hydrolytic monoester and the secondary metabolites can be conjugated with glucuronic acid to form hydrophilic phase II glucuronide conjugates. This last transformation step is often catalyzed by the enzyme uridine 5'-diphosphoglucuronyl transferase (Wittassek et al., 2011). Relatively polar and short alkyl chain phthalates are primarily metabolized into their hydrolytic monoesters, while the monoesters of long alkyl chain phthalates are usually further metabolized to more hydrophilic, oxidized products (Hauser and Calafat 2005) .

Phthalates are majorly excreted via urine; only a small amount is eliminated via faeces (Hauser and Calafat 2005). For instance, a German study figured out that about

67% of DEHP was excreted in the urine of a male volunteer after 24h of oral ingestion. On the second day, an additional 3.8% of the DEHP dose was excreted (Koch et al., 2005a). When monoesters and oxidative metabolites undergo phase II biotransformation to produce glucuronide conjugates, their water solubility increases and consequently, their urinary excretion also increases (Hauser and Calafat, 2005).

On entering the human body, PAEs are rapidly absorbed, metabolized by hydrolysis and followed oxidation and then excretion via in urine and stool or faeces (Hauser and Calfat, 2005). Although PAEs are rapidly excreted from human body, their endocrine-disrupting effects and toxicity to reproduction will already have been attained or happened.

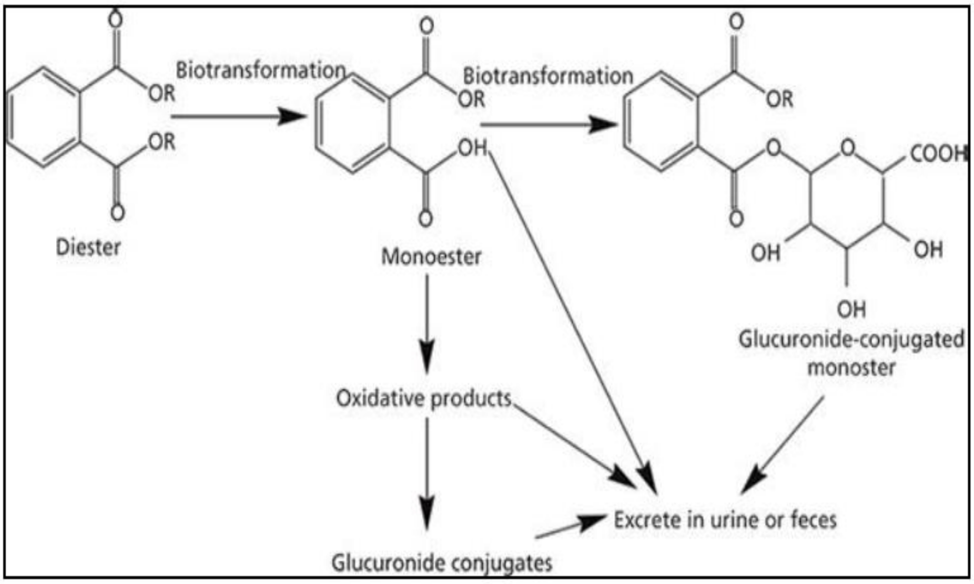

Figure 2.17 Schematic diagram of phthalate pathway

Source: Chen et al. (2014)

2.10 Health effects related to phthalate exposure

Some phthalates and their metabolites have been identified to be endocrine disrupting compounds (EDCs). EDCs are exogenous substances or mixtures that alter the functioning of the endocrine system and consequently cause adverse health effects in intact organisms, or their progeny, or (sub) populations. In Europe, a priority list was made of all chemicals with potentially endocrine disrupting activities. Based on the strength of evidence for endocrine disrupting organic chemicals have been classified into three categories: Category 1 include chemical pollutants that shows evidence of endocrine disrupting activity in at least one species of intact animals. Category 2 refers to those chemical contaminants that can generate some *in vitro* evidence of biological activity related to endocrine disruption; Category 3 refers to chemical compounds with no evidence of endocrine disrupting activity or no data available. PAEs congeners such as DEP, DnBP, BBP, DCHP and DEHP have been classified as Category 1 substances, DiBP, DiNP and DiDP as Category 2 and DnOP as Category 3 (European Commission 2014). In this section, an overview is given of potential adverse health effects of phthalates in humans. Most of the described effects are derived from epidemiological studies and unless mentioned otherwise are dealing with background exposure to PAEs. A distinction is made between effects observed in children and in adults.

2.10.1 Health outcomes in children

2.10.1.1 Gestational age and birth weight

The effects of phthalate exposure on gestational age (i.e. the estimated age of a fetus expressed in weeks, calculated from the first day of the last normal menstrual period) and birth weight were investigated by measuring serum levels of MEHP in cord blood of 84 Italian infants. Newborns having MEHP detected in their cord blood, had a significantly lower gestational age compared with other infants. No significant relationship was found between MEHP and birth weight (Latini et al. 2003). In a Taiwanese study, prenatal exposure to phthalates and its effect on birth weight and gestational age were also examined. MnBP, MEHP, MEP, MBzP and MMP levels were determined in the amniotic fluid of 64 pregnant women. For female newborns, a significant positive association was found between MnBP concentration in amniotic fluid and birth weight. The gestational age of the newborns was not influenced by prenatal exposure to any of the five considered phthalate compounds (Huang et al., 2009).

2.10.1.2 Anogenital distance

In humans, the anogenital distance (AGD; i.e. the physical distance between anus and the genitalia) in males is normally about twice that in females (Sharpe 2006). This variance is a direct reflection of growth stimulating actions of androgens, such as testosterone, on the perineum in foetal life. In other words, AGD is an indicator of the levels of androgen actions in the foetus and hence of the masculinisation process (Sharpe 2006).

Some epidemiological studies suggest that prenatal exposure to a number of phthalates at environmental levels might affect the AGD. For instance, Swan et al. (2005) examined AGD and other genital measurements in male infants in relation to their mothers' phthalate exposure. MEP, MnBP, MBzP and MiBP concentrations in prenatal maternal urine samples were associated with a shortened AGD. Of the three investigated DEHP metabolites, MEHP was not affecting the AGD while MEOHP and MEHHP were borderline significant in affecting the AGD. MMP was also not associated with a shortened AGD. A few years later, the results of this study were updated, i.e. more participants were included, and statistical analyses were improved (Swan 2008). In the new dataset, urinary concentrations of MEP, MnBP, MEHP, MEOHP and MEHHP in male infants were significantly and inversely related to AGD; MBzP was no longer associated with AGD. Furthermore, a significantly negative correlation between MnBP levels in amniotic fluid and the AGD in female newborns has been observed by Huang et al. (2009).

2.10.1.3 Cryptorchidism and hypospadias

Cryptorchidism (undescended testes) and hypospadias (abnormally placed urethra) are the two most common congenital malformations in male newborns (with 2-4% and 0.3-0.7% incidence, respectively). Both malformations are symptoms of the testicular dysgenic syndrome or "phthalate syndrome" and thus may be caused by phthalate exposure (Sharpe, 2005).

The difference in prevalence of congenital cryptorchidism in infants between Denmark and Finland was investigated. The result indicated the prevalence of cryptorchidism at birth was 9.0% in Denmark and 2.4% in Finland. Even after adjustment for confounding factors, significant geographic differences were still present. According to the authors, genetic factors could account for this geographic difference, but it would be more likely that this dissimilarity may be explained by environmental factors, including endocrine disruptors and lifestyle (Boisen et al**.** 2005). Main et al. (2006) investigated whether phthalate monoester (i.e. MMP, MEP, MnBP, MBzP, MEHP and mono-isononyl phthalate (MiNP), a metabolite of DiNP) contamination of human breast milk had any influence on the difference in prevalence of cryptorchidism in this Danish-Finnish cohort study. In contrast with rodent studies, no significant difference was observed between children with or without cryptorchidism with regard to any phthalate monoester concentration in breast milk, if analysed either separately for each country or together. In fact, levels of MnBP, MBzP and MEHP were higher in Finnish than in Danish breast milk, which is the inverse compared with the prevalence of cryptorchidism in the two countries. Main et al. (2006) concluded that their study groups may have been too small to detect subtle changes related to the presence or absence of cryptorchidism and that further research is urgently needed.

The risk of hypospadias in relation to phthalate exposure was investigated in a British case-control study. In that study, a two to threefold increased risk of hypospadias was found among children of mothers exposed to hair spray and phthalates in the workplace during pregnancy (Huang et al., 2009).

2.10.1.4 Hormone production

Main et al. (2006) determined phthalate monoester metabolites in human breast milk samples that were collected postnatally after one to three months. Additionally, serum samples of male newborns were analysed for gonadotropins (follicle-stimulating hormone (FSH) and luteinising hormone (LH)), sex-hormone binding globulin (SHBG), testosterone and inhibin B. The free testosterone index was calculated from testosterone and SHBG: [(testosterone x 100)/SHBG]. MEP and MnBP were positively correlated with SHBG and MMP, MEP and MnBP with the ratio of LH to free testosterone. Besides, MnBP was inversely related with free testosterone.

2.10.1.5 Thelarche

Thelarche or premature breast development is the growth of mammary tissue in girls younger than eight years without any other manifestations of puberty. In a Puerto Rican case-control study, Colon et al. (2000) investigated whether exposure to phthalate compounds may be responsible for more cases of thelarche in Puerto Rican girls during the last two decades. For this purpose, they measured several phthalates and monoester metabolites in blood serum samples of 41 thelarche patients and 35 controls. Significantly higher levels of DMP, DEP, DnBP, DEHP and MEHP were analysed in thelarche patients than in controls suggesting a possible association between phthalate exposure and the cause of premature breast development in Puerto Rican girls. Although this study was noteworthy since the effect of phthalate exposure on thelarche was an understudied area, a few years after the results of this study were published, questions have been raised about the analytical procedures used in this study to analyse phthalate diesters in blood serum (Hauser and Calafat, 2005). DEHP substitutes may also be injurious such as DiNP. Frederiksen et al. (2012) linked 12 PAEs metabolites including DiNP with delayed pubarche in girls.

In a multi-ethnic longitudinal study, associations between phthalate exposure and the development of breasts and pubic hair was investigated in 6-8 years old American girls. Breast and pubic hair development were present in 30% and 22% of the girls, respectively. Small inverse associations were seen for high molecular mass phthalate metabolites (sum of MBzP, 3cx-MPP, mono-2-ethyl-5-carboxypentyl phthalate, MEHP, MEHHP and MEOHP) and the stage of pubic hair development. For low molecular mass phthalate metabolites (sum of MEP, MnBP and MiBP), a positive trend was observed for both breast and pubic hair development (Wolff et al., 2010).

2.10.1.6 Respiratory function, allergic symptoms and diseases

Various studies have examined respiratory function, asthma and allergy and their relation to phthalate exposure. In a Swedish case-control study, dust samples from the houses of 400 children were examined for the presence of phthalates. Of the 400 participants, 198 children suffered from persistent allergic symptoms and the 202 other children showed no allergic symptoms. Analysing the case group by symptoms revealed that BBP was associated with rhinitis and eczema, whereas DEHP was related to asthma (Hoppin et al. 2013)

2.10.1.7 Childhood behavior

Children’s play behaviour was investigated in order to study possible links between prenatal phthalate exposure and neurodevelopmental outcomes. Play behaviour scores were examined in relation to prenatal maternal urinary concentrations of several phthalate metabolites for boys and girls separately. Urinary concentrations of MnBP, MiBP and their sum as well as levels of MEOHP, MEHHP and the sum of MEOHP, MEHHP and MEHP were associated with a less masculine score in boys. Although based on a small sample size (74 boys and 71 girls), these results suggest that prenatal exposure to phthalates may be associated with less male-typical play behaviour in boys and that phthalates have the potential to alter androgen-responsive brain development in humans (Swan et al., 2010).

The role of prenatal phthalate exposure on child behaviour and executing functioning was tested among a multi-ethnic population in New York. Phthalate metabolites were analysed in third-trimester maternal urine samples and children were assessed three times for cognitive and behavioural development between the ages of 6 and 11 years. Several behavioural domains (e.g. aggression, conduct problems and attention problems), which are commonly found to be affected in children clinically diagnosed with conduct or attention deficit hyperactivity disorders (ADHD), were found to be positively associated with prenatal exposure to MMP, MEP, MiBP and MnBP (Engel et al. 2009).

2.10.2 Health outcomes in adults

2.10.2.1 Semen quality

Hauser et al. (2006; 2007). In a follow-up study, more participants were included and the effect of the metabolites of DEHP on human sperm quality was also considered. Besides confirming the previous results, relation between MEHP and sperm DNA damage was observed. Noteworthy is that the latter association was found after adjustment for the oxidative metabolites of DEHP, suggesting that the oxidation of MEHP to MEHHP and MEOHP may actually be “protective” against sperm DNA damage.

2.10.2.2 Anogenital distance

In a cross-sectional study, the relationship between the AGD and adult female reproductive characteristics was investigated in 100 college-age volunteers. One of the outcomes of this study was that the AGD was positively associated with the number of ovarian follicles (Sharpe 2006).

2.10.2.3 Endometriosis

DEHP and MEHP levels were analysed in serum and peritoneal fluid of 24 healthy women and 35 women with endometriosis. Endometriotic women showed significantly higher plasma concentrations of DEHP than women in the control group while plasma MEHP levels were comparable between the two groups. Cases and controls had similar levels of peritoneal DEHP and MEHP concentrations (Hauser and Calafat 2005). However, the correlation between serum DEHP and MEHP concentrations was weak (r=0.16), which raised questions regarding the quality of the DEHP measurements. Peritoneal fluid may contain esterases capable of hydrolysing DEHP to MEHP, further investigation into why the relationships between DEHP and MEHP with endometriosis varied acceptable (Hauser and Calafat, 2005).

2.10.2.4 Respiratory function, allergic symptoms and diseases s

Bertelsen et al. (2013)studied the relationship between exposure to the primary metabolites of DnBP, BBP, DEP and DEHP in 240 American adults and four pulmonary function (forced vital capacity (FVC), forced expiratory volume at 1 sec (FEV1), peak expiratory flow (PEF) and maximum mid-expiratory flow). After adjusting for race, age, height, body mass index and smoking, they found inverse associations between male urinary concentrations of MnBP and FVC, FEV1 and PEF and between urinary MEP levels and FVC and FEV1. No consistent associations were observed in women.

Recently, the association between urinary phthalate metabolites and allergic symptoms and sensitization was investigated among the American population. MBzP was the only metabolite that was positively associated with ongoing allergic symptoms in adults (wheeze, asthma, hay fever and rhinitis). Furthermore, 3cx-MPP and the sum of DEHP metabolites were positively associated with allergic sensitization in adults whereas MEP was inversely related to sensitization (Hoppin et al. 2013).

2.10.2.5 Obesity and diabetes

Phthalate exposure and its relation to abdominal obesity and insulin resistance was examined in American adult men. Urinary concentrations of the metabolites MBzP, MEP, MEHHP and MEOHP were significantly associated with increased waist circumference. Three phthalate metabolites (MEP, MnBP and MBzP) were significantly related to the Homeostasis Model Assessment (HOMA) index2, which is often used in epidemiological studies as a measure of insulin resistance (IR). Although these findings have to be confirmed by longitudinal studies, this study provides preliminary evidence that exposure to phthalate esters plays a major to the population burden of obesity, insulin resistance and associated clinical disorders (Stahlhut et al., 2007).

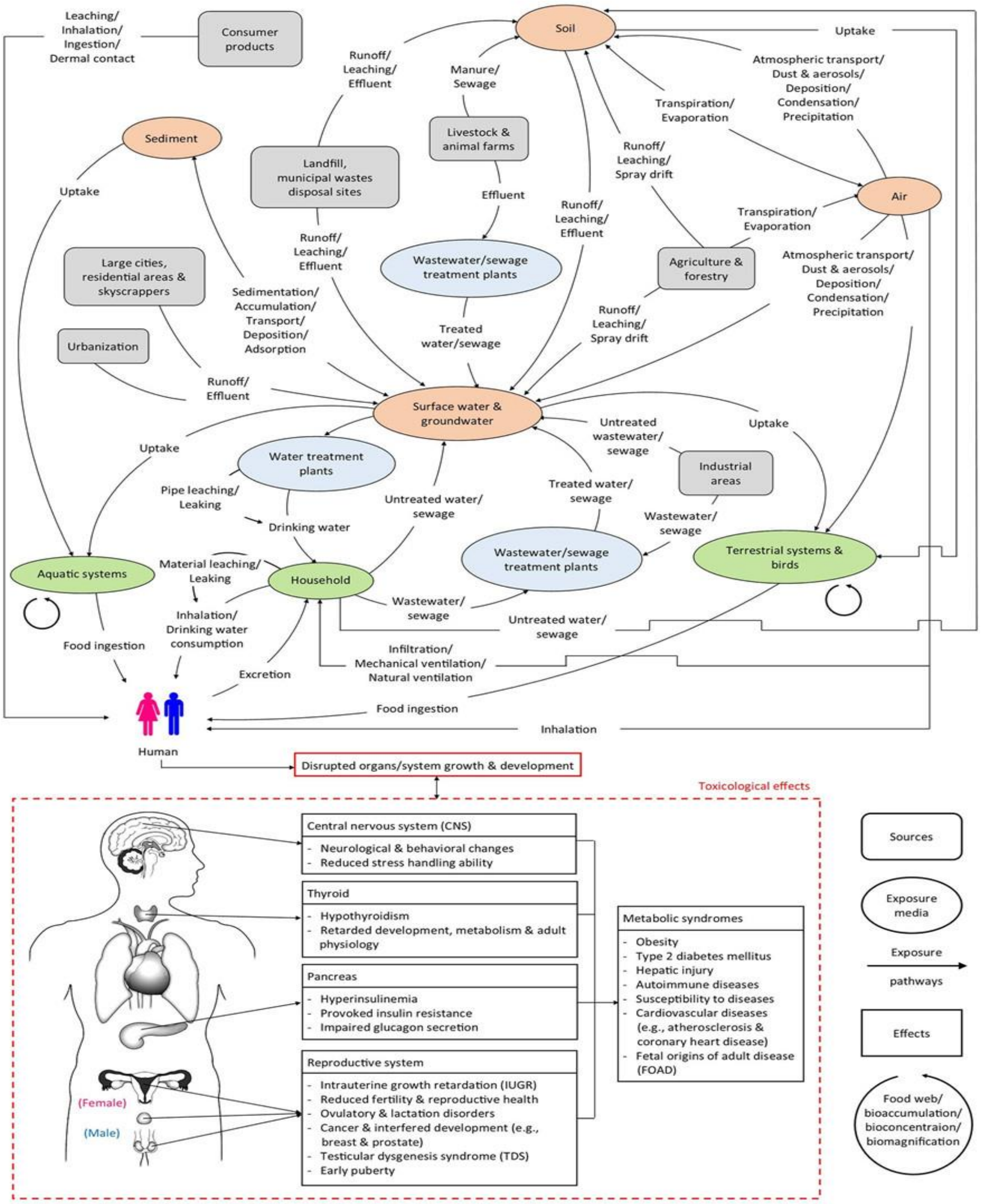

Figure 2.18 Environmental and Human exposure to PAEs

Source: adapted from Wee and Aris, (2017**)**

Table 2.5 Health effects of PAEs congeners on mother-infant pair

Country/study population	Matrix	PAEs congeners	Health effects	References
USA/295 mother/infant pairs	Maternal urine	MMP, MEP, MnBP, MiBP, MBzP, MEHP MEHHP, MEOHP, MCPP, MECPP	Neurological toxicity, Sex-specific effects	Engel et al. (2009)
CHINA/201 mother/infant pairs	Cord blood, maternal blood	DEP, DBP, DEHP, MEHP, MnBP	Developmental toxicity	Zhang et al. (2009)
CHINA/207 mother/infant pairs	Cord blood	DMP, DEP, DMEP, DBP, DEEP, DiBP, DPP, DMPP, DBEP DCHP, DnHP, BBzP, DEHP, DnOP, DiNP	Duration of human pregnancy and developmental toxicity	Huang et al. (2014)

Table ***2.6*** Health effects of PAEs congener on Children

Country/study population	Matrix	PAEs congeners	Health effects	References
USA/1619 children (6-19)	urine	MEP, MnBP, MiBP MMP, MBzP, MCPP, MEHP, MEOHP, MECPP, MEHHP, MCOP, MCNP, MiNP	Risk of hypertension	Trasnde and Attina. (2015)
Canada/1044 children (6-11)	urine	MBzP, MnBP, MCHP, MEHP, MEHHP, MEP, MnOP, MMP, MCPP, MiNP	Learning and behavior problems and poor attentional performance	Arbuckel et al. (2016)
CHINA/430 children (6-14)	Urine	MnBP, MMP, MEP, MEHP, MEHHP, MEOHP (Majorly-MEHP)	Speed and delayed puberty in girls and boys respectively. Sex specific toxicity	Zhang et al. (2015)
CHINA/167 boys (11)	Urine	MnBP, MMP, MEOHP, MEP, MEHP, MEHHP,	Anti-androgen effects and delayed growth and puberty	Xie et al. (2015)

Table *2.7* Reproductive and Health effects in Adults

Country/study population	Matrix	PAEs congeners	Health effects	References
China/687 men	Semen	MMP, MEP, MnBP MBzP MEHP, MnOP MEHHP, MEOHP	Impaired semen quality and altered reproductive hormone level	Wang et al. (2016)
USA/1546	urine	MiBP, MnBP, MEP, MMP, MCNP, MBzP MCiOP, MCCP	Allergic symptoms and sensitization	Hoppin et al. (2013)
Canada/1597 Pregnant women	Urine 1st trimester	MnBP, MEP, MMP, MBzP, MCHP, MiNP MCPP, MEHP MEOHP, MEHHP	Potential anti-androgen effects	Velez et al. (2015)
USA/369	Urine (2nd trimester)	MEP, MBzP MCPP, MnBP MEHP, MiBP MEHHP, MEOHP, MECPP	Risk of pregnancy-induced hypertension	Werner et al. (2015)

2.11 Potential risk of PAEs and health risk assessment

Phthalates acid esters are characteristic endocrine disrupting compounds (EDCs) which can stimulate reproductive effects, thyroid-disrupting effects, insulin-like growth factor I -disrupting effects in addition to children growth-disrupting effects, alongside several other toxic effects (Boas et al., 2010; Li et al., 2010). PAEs and their metabolites are generally detected in human bodies, for instance, Chen et al. (2008), Boas et al. (2010) with Toft et al. (2012) detected PAEs' metabolites in children's urine samples, in pregnant women's urine, as well as in serum blood in addition to breast milk of women undergoing parturition, respectively. According to Bertelsen et al. (2013), phthalates have been implicated to be associated with diseases such as rhinitis, eczema with asthma. Recently, fourteen phthalate acids ester metabolites were evaluated in human urine samples collected from some Asian countries, and phthalate metabolites were found in all samples (Boas et al., 2010**;** L. Chen et al., 2012; Katsikantami et al., 2016). PAEs are a main concern on the growing list of endocrine disrupting compounds (EDCs), with several million tons of PAEs produced worldwide annually. DEHP is classified as group 2B, probably human carcinogen and confirmed to have 2.4 times higher risk of causing female breast cancer (Net et al., 2015).

2.12 Legislation

As elaborated earlier, several studies have reported that PAEs are associated with adverse health effects in human life and wildlife. Therefore, national and international authorities have established regulations regarding the use of PAEs in a wide range of applications and environment, including aquatic environment. This section describes the regulation of PAEs under the European REACH regulation and legislations concerning their use in plastic products, toys, childcare articles, cosmetic and personal care products, medical devices and food contact materials. This is because PAEs will leach or migrate from these products during production, usage and disposal and discharged into aquatic environment. Additionally, exposure limit values are summarized that will be used to assess the risks related to aquatic wildlife and human exposure to PAEs.

2.12.1 The REACH regulation

The acronym ‘REACH’ stands for Registration, Evaluation, Authorization and Restriction of Chemicals and enacted into law on June 1st, 2007. It is a regulation, adopted to improve the protection of human health and the environment compartment from the exposure to hazardous chemicals and subsequent risks that can be posed by such chemicals, while enhancing the competitiveness of the European chemicals industry (Austin et al. 2015).

REACH specifies that industry must register all chemical substances that are either produced in or imported into the European Union in annual quantities of more than or equal to one tonne. So far, 25 different phthalates have already been registered, and more phthalates (with an annual production volume between 1 and 100 tonnes) are expected to get registered in the years to come. Several phthalates registered in the European Union are included in the Candidate List of substances of very high concern (SVHCs) because they are toxic to reproduction. SVHCs are carcinogens (category 1a or 1b), mutagens (category 1a or 1b), toxic to reproduction (category 1 or 2), persistent and/or bioaccumulative toxicants, or substances of equal concern (e.g. having endocrine disruption properties) (Saillenfait 2015).

The authorization process aims to guarantee that the risks from SVHCs are properly controlled and that these chemical compounds are progressively replaced by suitable alternatives while still ensuring the good functioning of the European internal chemical market. After a two-step regulatory process, SVHCs may be included in the Authorization List and become subject to authorization (Saillenfait 2015). After a given cut-off date, the so-called sunset date, substances on the Authorization List may not be placed on the market anymore, unless a company has obtained authorization for this purpose. Now, all uses of DEHP, DiBP, DnBP and BBP are subjected to authorization except for the use of DEHP, BBP and DnBP in the immediate packaging of medicinal products. Irrespective of the facts that high concentration of PAEs have been reported for developing countries, such regulations and authorization of PAEs are lacking.

2.12.2 Water Framework Directive

The European Water Framework Directive (WFD) is the short name of Directive 2000/60/EC of the European Parliament and the Council, establishing a framework for the Community action in the field of water policy. This Directive was published on December 22nd, 2000 and entered directly into force. It requires that all inland and coastal waters achieve a good qualitative and quantitative ecological status by 2015. According to Article 16 of the WFD, environmental quality standards (EQSs) should be developed for pollutants that present a significant risk to water and/or the aquatic biosphere. Furthermore, these pollutants should be identified by the European Commission and classified as priority substances (WFD 2000).

In Directive 2008/105/EC, EQS limits were established for 33 priority substances in surface waters. This Directive also stated that Member States should assess and monitor water, suspended particles, sediment and biota, as suitable, at an satisfactory frequency in oder to provide adequate data for a reliable long-term trend investigation of those priority substances, including PAEs congeners that tend to be insoluable in water and futher accumulate in sediment and/or biota. Regarding phthalates, EQS limits have only been imposed for DEHP. In both inland and other surface waters, the annual average EQS limit for DEHP amounts 1300 ng/L(European Commission 2000**;** Hecker and Hollert 2011).

2.12.3 Exposure limit values

To assess risks associated with PAEs exposure, estimated PAEs intake values can be compared with exposure limit values. These values are estimates of the daily intake of a chemical which can occur over a lifetime without appreciable risk for human health and are established by authorities like EFSA, the WHO or the American Environmental Protection Agency (US EPA). Examples of exposure limit values are tolerable daily intake (TDI) values and reference dose (RfD) values. Since there are, in most cases, inadequate data from humans to permit calculation of TDI or RfD values, exposure limit values are mostly based on endpoints observed in animal studies. In such toxicological experiments, animals are exposed to chemical substances at certain dose ranges. After the experiment, a dose-response relationship is made and the “no observed adverse effect level” (NOAEL) is determined. The NOAEL is the highest dose of a substance that causes no detectable adverse alteration of morphology, functional capacity, growth, development, or life span of the target organism. By considering a safety or uncertainty factor, NOAELs are extrapolated to exposure limit values applicable to humans. When a NOAEL cannot be determined, the “lowest observed adverse effect level” or LOAEL may be used to derive exposure limit values for humans (Katsikantami et al., 2016; Net et al., 2015).

2.12.4 Legislations of PAEs in aquatic environment

Due to the adverse potential risk of PAEs contamination on the environment and human health, especially the endocrine disrupting effects, standards and regulations of environmental risks assessment and management for PAEs have been established, including the Environmental Quality Standards (EQS) for freshwater and seawater protection, Environmental Risks Limits (ERLs) for aquatic sediment and soil, Minor Adverse Effect Concentration (MAEC) for aquatic sediment, Maximum Contaminant Level (MCL) for potable water (Net et al., 2015). In addition, six congeners of PAEs including DBP, BBP, DEHP, DnOP, DMP and DEP have been blacklisted as priority pollutants and endocrine disrupting chemicals by USEPA. In China, DEHP, DBP, DMP, DEP and DnOP have been listed as priority pollutants by the China National Environmental Monitoring Center. Nevertheless, most rapidly developing countries in Asia region including Thailand do not have specific regulations of PAEs in water bodies and hence they are not included in their lists of routinely-monitored organic chemicals in waterbodies (Sirivithayapakorn et al., 2014; Selvaraji et al.,, 2015).

The reduction of the release of these toxic, hazardous, persistent and bioaccumulating chemicals is an agreed goal for a number of international organizations and this has in turn, been incorporated in the policy for many countries. The main purpose of such policy is to protect the aquatic ecosystems and humans, which may be exposed directly or more frequently, indirectly to such toxic and harmful chemical substances. Because of their ubiquitous occurrence in the environment, the

European Commission considered some PAEs congeners including di-n-butyl phthalate (DnBP); di-2-ethylhexyl phthalate (DEHP); di-isodecyl phthalate (DIDP) and di-isononyl phthalate (DINP) in the list of priority substances (Oehlmann et al., 2008). Like other priority chemical substances in the European Union, these synthetic anthropogenic chemicals are subject to an ERA which are usually conducted in accordance to the stipulations in the Technical Guidance Document(European commission 2003).

Furthermore, many existing national environmental regulations and environmental management practices are based on conditions in developed countries, under conditions that are totally different from those existing in developing countries. Lack of robust studies of occurrence and risk assessment of phthalate esters in aquatic environment in developing countries, might explain why PAEs are being left out of policy and monitoring programs. The protection of aquatic environment such as lakes, rivers systems, provision of safe water for usage and consumption is one of the major priorities of the Thai Government. Numerous Thai government agencies play foremost roles in environmental management of aquatic ecosystems in Thailand. The Ministry of Natural Resources and Environment (MONRE) is the major Thai government agency bestow with the responsibility of environmental quality and management at the national level. Under the Ministry, three major parastatals are responsible for different aspects of environmental management: The Office of Natural Resources and Environmental Policy and Planning (ONEP) is majorly bestow with the role to establish or formulate of environmental policy and planning for the enhancement and conservation of national environmental quality. The core responsibility of the Department of Environmental Quality Promotion (DEQP) is to preserve and improve environmental quality by providing quality environmental research and development courses, for staff of concerned authorities and the general public. The core role of PCD of is to establish national environmental pollution management plans as well as set and recommend standards for environmental parameters and pollution discharges.

The contamination of water resources by endocrine disrupting organic chemicals like phthalate acid esters, which can cause severe acute and possibly chronic health problems to citizens and wildlife should be a matter of priority. Superficially, it does not appear that there could be serious health risks associated with consumption of PAEs contaminated water and aquatic organisms, considering their low presence and concentration in water and aquatic biota. However, chronic problems especially endocrine disrupting effects has been associated with low concentration of some congeners of PAEs via contaminated water, edible vegetable and aquatic biota(Adeniyi et al., 2011; Fatoki et al., 2010a). For these government agencies to develop policies and regulations that will facilitate the protection, prevention and control of water pollution and mitigate public health exposure to PAEs species via aquatic environment in the country, robust scientific studies of PAEs pollution and risk assessment in aquatic environment are necessary. Due to lack of data about PAEs in aquatic environment in developing countries, it is difficult for the concerned agencies to set intervention standards. Because intervention standards are decided upon after risk assessment based on dose-response relationship. Lack of risk assessments for anthropogenic chemical pollutants like PAEs in aquatic environment, might explain why such compounds are being left out of policy and monitoring program (Shao et al. 2013). This will be useful to the responsible agencies who are deeply concerned over pollution, (Chuvanich et al. 2017; Gyawali et al., 2011) including organic and inorganic chemical pollutants in all aquatic environment in the country and ensure minimum concentration-based discharge requirements are strictly enforced.

Table *2*.8 Regulation of PAEs in surface water in different countries/International organization (µg/L)

Country/INT	DEHP	DMP	DEP	DBP	BBP	DIBP	Reference
EU							
EQS in surface water	1.3						Net et al. (2015)
EQS in wastewater	20-40	800-4000	200-1000		20-1000	8- 40	Net et al. (2015)
Denmark				2.3/0.23	7.5/0.75		DMOE (2010)
EQS in surface water							
Canada							
EQS	16.0						Net et al. (2015)
WHO	8.0						Net et al. (2015)
Australia and New Zealand		900	3000				Net et al. (2015)
CHINA	8.0			3.0			Liu et al. (2014)
KOREA							KMOE (2014)
Surface water	8.0						KMOE (2014)
Wastewater [a]	20.0						KMOE (2014)
Wastewater [b]	200.0						KMOE (2014)
Wastewater [c]	800.0						KMOE (2014)

[a]clean area [b]general area [c]exceptional area

Table *2*.9 Regulation of PAEs in tap water(µg/L)

Country/INT	DEHP	DMP	DEP	BBP	DBP	Reference
USA	6.0					USEPA (2012)
WHO	8.0					Net et al. (2015)
Australia	9.0					Maycock et al. (2008)
New Zealand	10					Maycock et al. (2008)
CHINA	8.0		300		3.0	Liu et al. (2014)
JAPAN	100			500	200	Net et al. (2015)

2.13 Analysis of Phthalates

The endocrine disrupting and toxic effects of PAEs in human via environmental media has generated serious concerns, as a result, the need for sensitive and reliable procedures to correctly screen and determine the occurrence of these chemical compounds in different environmental matrices have become a critical subject. Analytical procedures for PAEs assessment in environmental samples commonly involves the extraction of PAEs from environmental media followed by the isolations, separations and instrumental detection of the PAEs. The choice of instruments and procedures used for such investigation are majorly reliant on the type and complexity of the environmental media surveyed (Cao 2010). The extraction of PAEs is a critical stage in the detection and monitoring of these chemical compounds in environmental media. The extraction of PAEs in aquatic media including water, sediments and aquatic biota are mainly carried via liquid-liquid extractions (LLE) and solid phase extractions (SPE) (Cao 2010).

2.13.1 Liquid-liquid extraction (LLE)

LLE comprises the partitioning of analytes of PAEs between two immiscible solvents. For PAEs extraction, non-polar organic diluents, including acentone, methanol, dichloromethane and n-hexane are used. The extraction is characteristically conducted in numerous steps, then drying by using anhydrous sodium sulfate and subsequently by evaporation to concentrate the sample (Net et al, 2015). LLE has the advantage of being very easy and cheap, in addition, this technique offers high reproducibility and recovery values for the most frequently occurring PAEs. On the other hand, the disadvantage of LLE include time consuming, usage of large amount of solvents, and brings about a high risk for sample pollution by the solvents and materials used (Net et al., 2015; David et al., 2003). Despite this, LLE is still considered very useful and is extensively used in PAEs extraction.

2.13.2 Solid Phase Extraction (SPE)

SPE is an extraction system that is based on the partition of PAEs analytes between a liquid (solvents) and a solid phase (sorbent) packed in a cartridge or a disk. Usually, analytes are retained on the sorbent and are later eluted from the sorbent using an organic solvent or diluent (David et al., 2003; Net et al., 2015). The different sorbents used in SPE technique of PAEs include silica-based C-18 and cross-linked polystyrene-divinylbenzene (PS-DVB). The advantage of SPE include using less solvents as compared to LLE, reduction potential health risks, and allowing the extraction of numerous samples simultaneously. However, the disadvantage of SPE include risk of sample contamination from solvents and cartridges used (David et al., 2003; Net et al., 2015).

Figure 2.19 Vacuum manifold for solid-phase extraction
Source: Gao et al. (2015)

2.13.3 Instrumental Procedures

There are numerous varying types of instrumental systems that can be used to separate, identify and quantify PAES, including gas chromatography combined with mass spectrometric detection (GC-MS), gas chromatography linked with flame ionization detection (GC-FID), and gas chromatography fixed to electron capture detection (GC-ECD). ECD and FID are largely less selective as well as less sensitive for PAEs as compared with those based on MS detection, and consequently are less frequently used in the determination of PAEs (David et al. 2003; Net et al., 2015). Liquid chromatography joined to mass spectrometry detection (LC/MS/MS) can also been utilized for the separation and determination of PAEs, predominantly for PAEs monoester metabolites (Net et al. 2015).

GC-MS is the main and most commonly used instrument for the detection of PAEs in water because it is very sensitive and specific for PAEs compounds(Cao, 2010). This technique employs a gas chromatograph for separation and a mass spectrometer for identification and quantification of chemical compounds. The sample solution is inoculated into the GC inlet where it is heated and vaporized and flows via a chromatograph in column by an inert carrier gas. The sample flows through the chromatograph column and the compounds are separated based on their volatility and their relative interaction with the coating of stationary phase as well as mobile phase, which is the carrier gas (mobile phase)(Net et al., 2015). The separated compounds are then transported via an interface to the MS ionization source, where they are usually converted under high vacuum into ionized fragments. These fragments are focused, sieved and distinguished by the mass detector.

CHAPTER THREE

MATERIALS AND METHODS

3.1.1 Study Site and Design

To assess the extent of phthalate acid ester contamination and potential risk in a riverine ecosystem, a cross-sectional study was conducted in U-Tapao canal in Songkhla Province, southern Thailand. U-Tapao canal, the mainstream river and one of the most important riverine system in southern Thailand, 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 canal ranges between <6 and 90 m^3 in dry and raining seasons respectively. The tropical monsoon climate of the canal is strongly influenced by two monsoons; the northeast and southwest monsoon with average rainfall estimated to range from 1600 mm to 2400 mm annually. The northeast monsoon causes a heavy rainfall in the area from mid of October to mid-February. Temperature within and around the canal ecosystem varies between 24 ºC and 32 ºC all through the year. The canal flows through the center of numerous agricultural fields, industries and urbanized areas and discharges into Songkla Lake, which is connected to Gulf of Thailand.

The canal is highly exploited for several uses such as irrigation, aquaculture, tap watersource and industrial activities. This very important water resource is currently facing serious pollution as a result of rapid increase of urbanization, industrialization, aquaculture and agricultural activities as well as deforestation in areas surrounding the canal. Untreated and semi-treated municipal and industrial wastewater are still be discharged into the canal. Major sources of industrial waste discharged into U-Tapao canal include plastic, rubber, parawood, aquaculture, agriculture and food processing industries at the rate of 4,100 m^3 per day. Development and accumulation of chemical pollutants in the aquatic environment and movement of the canal sediments into Songkla Lake have been reported to cause adverse effects on the biodiversity cycle of the lake. Along its course, the U-Tapao Canal passes through major urban centers such as Sadao, Ban Pru, and Hat Yai city, with large number of urban settlements and rural areas as well as domestic and industrial wastewater, agriculture and aquaculture effluent discharge.

3.1.2 Sampling sites selection criteria and sample collection

In this study seventeen sampling sites for both water and sediments were selected along the canal respectively, from the upstream to downstream, and the selection criteria of the sampling locations were based on the population of residents, number of industries, land use pattern, agricultural and aquaculture activities along the river. Based on these selection criteria, the 17 sampling sites were classified into two different group viz: urban and rural areas. Urban areas n = 9 and rural areas n = 8. In this study urban areas are referred to areas with large number of populations, factories and commercials places. Sampling sites selected from vicinities in urban areas were selected based on the large number of populations, factories and commercial areas. Sampling sites in urban areas include ST1, ST2, ST 3, ST4, ST6, ST7, ST9, ST10, ST12 and ST13. Sampling sites selected as rural areas were mainly dominated with natural, agricultural fields and aquaculture ponds. Sites located in the vicinity of rural area were ST5, ST8, ST11, ST14, ST15, ST16 and ST17. See Appendix 6 for details. For surface water and sediments, four samples were collected and analyzed for each site, given n=4 per sites. Figure 3.1 shows the map of the sampling sites of U-Tapao canal.

Raw and tap water samples were also collected from each of 4 waterworks that get their source water supply from U-Tapao Canal. These waterworks include Sadao waterworks, Phang La waterworks, Prik waterworks and Hat Yai waterworks. For raw water and tap water, four samples were collected and analyzed per waterwork, given n=4 for raw water and n=4 for tap water for each of the waterworks. All the water and sediment samples were collected during August 2018 to March 2019.

The sample collection points for surface water and sediments were always set away from convergence of wastewater or effluent outlet. The sampling locations include urban, suburban and rural areas, which were in the proximity to cities, factories, agricultural fields and aquaculture ponds.

Surface water samples were collected from 17 sampling sites, by using glass water sampler and transferred to pretreated brown glass bottles, which were immediately placed in ice and transferred to the laboratory and kept at 4^{o}C in a refrigerator in the laboratory until analysis. All samples were analyzed within 3 days.

Sediment samples were collected from 17 sampling sites by using a grab sampler and transferred onto pretreated 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.

Raw and tap water were drawn from the four waterworks in the study areas. Raw water or influent was collected at 0.5 m below the water surface of each site, which is the representative of the mixed water columns. The raw water was collected in pretreated brown bottles. Tap water were taken from distribution points of each waterwork. Water samples were collected in triplicates in 1liter pretreated bottles, placed in an ice box and transferred to the laboratory and stored at 4 ^{o}C refrigerator in the laboratory until analysis. An aliquot of 120 µL of 0.75g/ml sodium thiosulfate solution was placed in 1 L of tap water to block the chlorine content of tap water and prevent it from forming interference and affect the analysis. All samples were extracted within 2 days and analyzed within 3 days.

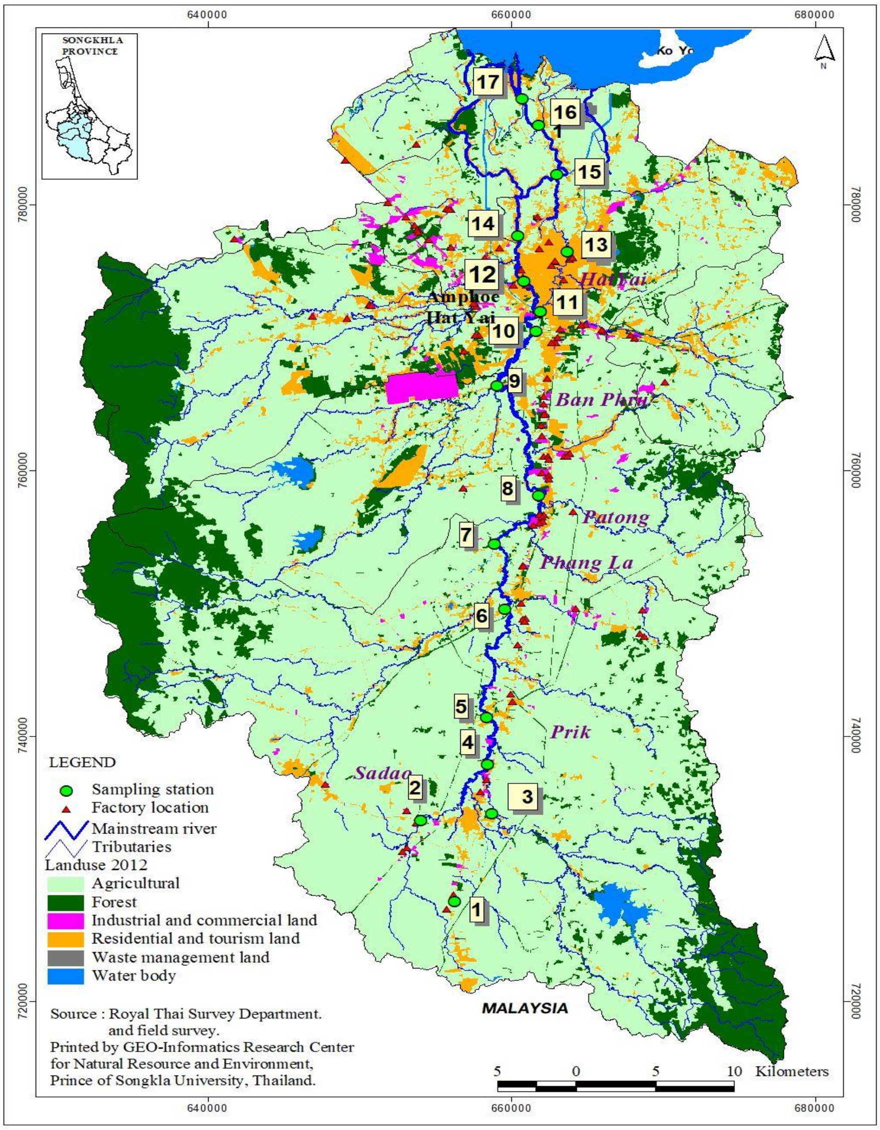

Figure 3.1 Map showing sampling sites for water and sediments of U-Tapao Canal

Source**:** Geo**-**informatic research center, Prince of Songkla University (2019)

3.2 Chemical analysis

The chemical analysis of phthalate acid esters was conducted at Central Laboratory Company of Agricultural Research Center Thailand. Nevertheless, for completeness and because of their significance, we have included descriptions of the methods related to the chemical analysis in this PhD thesis report.

3.2.1 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, methanol, hexane, and dichloromethane, and 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 ^{o}C for 10 h.

3.2.2 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), di-iso=nonyl phthalate (DiNP), diisodecyl phthalate (DIDP) (AccuStandard, U.S.A). Solid phase extraction cartridge containing Florisil (1g 6cc, Chrom and Sep, U.S.A).

3.2.3 PAEs Pretreatment in water and sediments

Water samples collected from U-Tapao canal were pretreated in accordance to EPA method 3535 and EPA method 8061a with slight modifications. Each water sample (250 mL) was filtered via a 0.45 μm Millipore membrane, and then pre-concentrated by solid-phase extraction (SPE). The SPE cartridge with florisil (1g 6cc, Chrom and Sep), was consecutively activated by 5 mL Hexane, 1 mL acetone, 2 mL methanol and 2 mL pure water, respectively. After loading of water samples, SPE cartridge was air-dried for a period 3 min. The eluent was filtered via the dried chrom and sep cartridge at a speed of 1 mL/min. The eluate was partially dried by evaporation, using a gentle flow of nitrogen gas. The residue was redissolved with an extraction solvent, 2 ml of n- hexane as well as adding the isotope surrogate standard prior to GC–MS analysis.

The freeze-dried sediment samples collected from U-Tapao canal were pretreated based on Wang et al., 2014 with slight modification. Each 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 (10.0 g) were placed into glass centrifuge tubes, mixed with 10 mL acetone/hexane (1:1 v/v), left overnight and extracted by using ultrasonic technique for 30 min. The process was repeated twice, and each extract was then filtered into a round bottom flask. Subsequently, the filtrates were concentrated to 1–2 mL with a rotary evaporator, solvent exchanged with n-hexane and dichloromethane and cleaned by using solid phase extraction techniques. The SPE cartridge with florisil, was successively activated by 15 mL n-hexane followed by 15 mL acetone/n-hexane (1:1, v/v), and the eluents were properly disposed off. The PAEs extract was moved to the extraction cartridge and eluted with 10 mL acetone/n-hexane (1:4, v/v), the final eluent was collected into sample containers. The portion containing PAEs was concentrated to 2 mL. At this stage, the isotope surrogate standard was added, and the portion was adjusted to a constant volume of 1 mL and filtered via a 0.25 μm membrane filter into a brown vial bottles for sample injection prior to GC-MS.

3.2.4 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.

3.2.5 Quality control and quality assurance

Quality control and quality assurance used in this work include procedural blank, samples of matrix-spiked, duplicate in addition to solvent blank were treated with each batch of 5 water and sediments samples to evaluate the matrix effects in these procedures. Isotope surrogate standards were mixed to all the water and sediment samples at a constant amount before GC–MS analysis, and the instruments were calibrated on daily basis with calibration standards prior to analysis. The obtained mean recovery was satisfactory for water and sediments. The recoveries of the six target PAEs ranged from 92. 8% to 97.6% in the spiked water samples and from 89.0% to 96% in spiked sediment samples. The 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). The LOD values for DnBP, BBP, DEHP, DnOP, DiNP and DIDP in water were 0.4 µg/L, 0.2 µg/L, 0.4 µg/L, 1.0 µg/L, 0.5 µg/L and 0.5 µg/L respectively. The LOQ concentration of DnBP, BBP, DEHP, DnOP, DiNP and DIDP in water were 1.0 µg/L, 0.5 µg/L, 1.0 µg/L, 3.0 µg/L, 1.4 µg/L and 1.4 µg/L, respectively. In sediments the LOD levels of 5 ng/g was used for each of the six targeted PAEs congeners, whereas LOQ was 10 ng/g. The determinattions of limits of detections (LOD), limit of quantifications (LOQ), accuracy and precision of each individual PAEs was calculated by using the formula below.

$$LOD = 3SD \tag{1}$$

Where SD is standard deviation of the calculated concentration values

$$LOQ = 10SD \tag{2}$$

$$Precision = \frac{\mathrm{SD}}{\bar{X}}\ x\ 100 \tag{3}$$

Where $\bar{X}$ is mean is the calculated concentration values

$$Accuracy = \frac{\mathrm{Cs-Cu}}{\mathrm{C}}\ x\ 100 \tag{4}$$

Where Cs is concentration of spike sample, Cu is concentration of test sample and C is spike concentration.

3.3 Measurements of physicochemical parameters in water and sediments

3.3.1 Analysis of physicochemical properties of PAEs in water

Data of five physicochemical parameters of water in the 17 sampling sites were reported officially from Environmental office-region 16 Songkhla in 2018. This Thai government agency is responsible for assessing, collating and maintaining water quality data for southern areas of Thailand. Water quality index data collected include pH, temperature, salinity, dissolved oxygen (DO) and biological oxygen demand (BOD). The parameters were analyzed in the laboratory using standard methods for the examination of water and wastewater.

3.3.2 Analysis of physicochemical properties of sediments

The physicochemical parameters of sediments were performed by Analytical Research Center of Prince of Songkla University. As stated earlier, for completeness and due to their significance, we deem it necessary to include the description of the measurement techniques employed. The sediment parameters evaluated include pH, organic matter (OM), organic carbon (OC), electrical conductivity (EC), total phosphorus (TP), moisture contents (MC or WC) and sediment texture including clay, silt and sand (Walkeley and Black, 1998). Details of the procedures were shown in appendix 1.

3.4 Risk assessment

3.4.1 Ecological risk assessment in water

3.4.1.1 Preliminary ecological risk assessment

The aquatic life criteria (ALC) for PAEs developed and used to evaluate ecological risk of DEHP and DnBP in Lao river in China (Zheng et al., 2019) was employed to assess the preliminary ecological risk of the two PAEs congeners in U-Tapao Canal. The method uses equation 5 to evaluate the potential ecological risk

$$HQ = \frac{\mathrm{EEC}}{\mathrm{ALC}} \tag{5}$$

Where, HQ is hazard quotient, ALC stands for aquatic life criteria with values for DBP = 0.62 µg/l, DEHP = 0.04 µg/l. EEC is environmental exposure concentration. The mathematical explanation of this technique was listed below (Lemly, 1996):

$HQ \leq 0.1$, reveals that there is no risk existing

HQ = 0.1 -1.0, indicates that low risk is existing

HQ = 1.1-10, reveals that moderate risk is existing

$HQ \geq 10$, shows that high risk is existing

Moreover, the ecological risk of PAEs in water phase were also considered by the application of the risk quotient method (RQ). In accordance to the European technical guidance document (TGD) on risk assessment of chemical pollutants (European commission 2003), RQ for PAE congeners was evaluated by dividing the measured environmental concentration (MEC) with the predicted no effect concentration (PNEC), as indicated in equation 6. RQ was used to evaluate the ecological risk for the three sensitive aquatic species, including algae, crusteacean and fish as indicated in Table 3.1. MEC was the concentration of Individual PAEs measured in water and sediment samples. Whereas, PNEC was obtained from no observed effect concentration (NOEC) or median effective concentrations (EC_{50}), which were divided by an assessment factor (AF) (Gros et al. 2010).

The estimated environmental risk could be considered insignificant if RQ < 0.1, low when the RQ value ranges from 0.1–1, moderate if RQ values lies from 1 to 10, and high if RQ >10 (Li et al., 2017). The RQs of PAEs were estimated by using the formula below:

$$RQ = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \qquad (6)$$

3.4.1.2 Ecological risk assessment of PAEs in sediment

The sediment quality guidelines (SQGs) were used to evaluate the ecological risk of DEHP, DBP and total PAEs by comparing their original concentration, 10% organic matter (OM) normalized levels with values of sediment quality guidelines. The SQGs used include the threshold effect level (TEL), the probable effect level (PEL), the maximum permissible concentrations (MPCs), the ecotoxicological serious risk concentrations (SRC_{eco}), the environmental risk limits (ERLs) the sediment quality criteria low level (SQC-Low), the SQC upper level (SQC-Up), the no observed effect concentration (NOEC), and the predicted environmental concentration (PEC) were also applied to compare the measured DEHP and DBP (where applicable) concentrations in this study. Since the values of MPCs, SRC_{eco} and ERLs have been set on a 10% OM-normalized basis, the original DEHP concentrations and DnBP levels where applicable were divided by the OM content (%) and multiplied by 10 to compare it with the SQG (MPCs, SRC_{eco}, and ERLs). Table 3.2 indicated the SQGs value used in the evaluation of the ecological risk of PAEs in this study.

Similarly, as in water, risk quotient (RQ) technique was also used to assess the ecotoxicological risk of PAEs congeners measured in sediment in this work. RQ for PAE congeners were estimated by dividing PAEs concentration measured in the sediment samples the predicted no effect concentration (PNEC), as indicated in Equation 7

$$RQ = \frac{\mathrm{MEC}}{\mathrm{PNEC}} \qquad (7)$$

Table 3.1 shows the values used in the RQ calculation of the three PAEs congeners (DnBP, DEHP and DiNP) detected in sediments.

Table 3.1 Toxicity of PAEs in some sensitive aquatic organisms

PAEs	Species group	Species scientific name	Toxicity data (µg/L)	Assessment factors (AF)	PNEC$_{water}$ (µg/L)	PNEC$_{sediment}$ (µg/g)
DnBP	Algae	*Pseudokichneriella subcapitata*	96h, population, NOEC=210	10	21	2.33
	Crustaceans	*Americamysis bahia*	21d, mortality, NOEC= 260	10	26	2.88
	Fish	*Oncorhyncus mykis*	99d.growth, NOEC=100	10	10	1.11
DEHP	Algae	*Pseudokrichneriella subcapitata*	96h, population, EC_{50} = 100	1000	0.1	3.25
	Crustacean	*Mytilus edulis*	21d, mortality NOEC=42	50	0.84	13.6
	Fish	*Gasterosteus aculeatus*	28d, mortality NOEC= 300	50	6	32.5
DiNP	Crustaceans	*Daphina magna*	21d, mortality, NOEC=34	100	0.34	181.4

Source: Li et al. (2017)

Table3.2 Sediment quality standards values for PAEs

PAEs	TEL (ng/g)[a]	PEL (ng/g)[a]	MPC (ng/g 10% OM)[b]	SRC_{eco} (ng/g at 10% OM) [b]	ERLs (ng/g at10% OM)[c]
DnBP			2,100	36,000	700
DEHP	182	2,647	1,000	10000	1,000
BBP	-	-	1,400	4,800	
DnOP	-	-	-	-	
DiNP	-	-	-	-	
DIDP	-	-	-	-	
∑PAE			1,400	57,000	

[a]McDonald et al**.** (1996), [b]Verbrugggen et al**.** (2001), [c]Van Wezel et al. (2000)

3.4.2 Human health risk assessment:

A human health risk assessment (HHRA) was conducted to provide an indication of whether the level of phthalate esters detected in tap water samples may cause adverse health effects to human. HHRA was done with the assumption that Thai residents may be exposed to PAEs in tap water via two ways including ingestion through drinking of water and dermal absorption due to daily washing/bathing with the tap water. For the calculation of health risk, the target population are children and adults who are Thai residents and are users of water from the river system and waterworks. The exposure routes to human considered are the following: (i) ingestion through drinking of tap water and (ii) dermal absorption during bathing and washing with tap water. Approaches as described by Fatoki et al. (2010), Hu et al. (2012) and United States Environmental Protection Agency (USEPA) (2012) were implemented with slight modification for human health risk assessment (Tables 3.3, 3.4 and 3.5). The potential human health risk assessment of PAEs in tap water was computed as the mean concentration of PAEs to which humans are exposed to on daily basis over a specific exposure time. A USEPA exposure and risk assessment model named EXPOFIRST was used in the estimation of the human health risk assessment

The average daily exposure concentration, in this regard is refered to as average daily dose (ADD) and were computed using Eq. 8

$$ADD = \frac{\text{Cmean x IR x ED x Fc}}{BW\ x\ AT} \tag{8}$$

Cmean is the concentration of PAEs in the polluted tap water samples collected from four waterworks in the study area; IR represents the average daily consumption rate; ED is referred to the exposure period (in years); Fc simply means the fraction contaminated; BW simply means the average body weight; AT represents the average lifetime of exposure (mg/kg/day).

Carcinogenic risk assessment as a result of lifetime exposure was evaluated by using the following formula:

$$LADD\ ingestion = ADDingestion\ \times\ (\frac{ED}{Lft}) \tag{9}$$

Where, LADD is referred to as the average daily dose of lifetime exposure; Lft means lifetime

Dermal absorption dose (DAD) was evaluated by using, formula 10:

$$DAD\text{dermal} = \frac{\text{Cmean x SA x SL x ABS x EF x ED}}{\text{BW x AT}} \tag{10}$$

SA simply represent the skin surface area; SL is skin adherence factor = 0.7 mg cm^{-2} day^{-1}; ABS is referred to as, the dermal absorption factor; EF is exposure frequency

Risk characterization

The risk of cancer development as a result of human exposure to DEHP detected in tap water was estimated based on the assumption that humans are exposed to DEHP concentration in tap water via ingestion and bathing on regular basis. In addition, chronic exposure of PAEs via these pathways have been obsevred to be injurious to humans. For DEHP that have the potential for causing cancer, carcenogenic risk was calculated using the following equation:

$$Risk\ ingestion = \beta \times\ LADD\ ingestion \tag{11}$$

Where $Risk_{ingestion}$ is the potential risk due to ingestion of contaminated water; LADD is lifetime average daily dose; β is oral potency factor/slope**.**

Children are the most vulnerable group that are susceptible to potential risk of PAEs mainly because they are in the developmental stage of their lives. In addition, their immune systems are not fully developed to combat disease or disorder causing agents which include environmental pollutants like PAEs.

Moreover, children have a larger body surface area to volume ratio as compared to adults and are therefore exposed to a higher internal dose of chemicals (Sathyanarayana 2008). The major route of childhood exposure to PAEs have been reported to be via ingestion of dietary sources which include food and water, mouthing/sucking of dust and phthalate-containing products, body care products (Sathyanarayana, 2008; Koniecki et al. 2011). However recent evidence indicates that dermal exposure may also be major source of PAEs exposure in children (Schettler et al. 2006**;** Wormuth et al. 2006).

In this work, an exposure and risk assessment tool were applied to estimate the exposure and risk of PAEs to children, adolescents and adult via ingestion and dermal contact of contaminated tap water. The model is named Exposure Factors Interactive Resource for Scenarios Tool (ExpoFIRST). This is a free EPA exposure scenario and human health risk assessment model which permit users to apply data from the 2011 ExpoFIRST Handbook (EFH) to develop user-defined scenarios for exposure and risk assessment of chemical pollutants on the basis of route of exposure, medium, receptor (s), timeframe, and dose matrix for a chemical pollutants of concerns. This USEPA model help risk assessors and researchers to evaluate exposure, dose, and risk of chemical pollutants. Generally, exposure and risk assessment procedure include facts, data, assumptions, inferences, and sometimes professional judgment about how the exposure takes place. ExpoFIRST model are available for free download from the EPA-Expo-Box website. However, it worth of note that the tool was designed for exposure assessors who understand the overall ideas of exposure assessment.

3.5 Removal efficiency of conventional or traditional water treatment plant

A major step in reducing the potential effects of endocrine disrupting organic chemical in humans is by efficient treatment or elimination from contaminated source water. Therefore, in this research we intend to assess the removal efficiency of the four water filtration plants in southern Thailand that uses water from U-Tapao Canal system as their source or raw water. Removal efficiency of the conventional water treatment plants was calculated using equation 12

Calculation of Phthalate esters in treated water
The equation below (12) was used

$$C_{treated}=C_{source} \text{ x } (100\% \text{ -Res}) \qquad (12)$$

where $C_{treated}$ and C_{source} represent PAEs in treated and source water in the water treatment plant, RE represents the removal efficiency of PAEs by the water treatment plant.

3.6 Inventory and sedimentary transfer of PAEs

Sediments serves as sinks and transfer agents of chemicals. Studies on inventory and burden have revealed that riverine sediments do not only acts as sinks to organic pollutants but can also serves as vectors to transfer organic contaminants form riverine ecosystems to coastal environment. In this study, the inventory of sedimentary transfer of PAEs from U-Tapao Canal to Songkla Lake was evaluated using equations 13 (Zhao et al., 2011):

$$Inventory = C \times p \times A \times D \times a \text{ -- } (13)$$

where C (ng/g) is referred to as the mean concentration of PAEs in investigated sediment in this present work and ρ (g/cm^3), simply means the dry density of the sediment. A (cm^2) is referred to as the area of the river basin, D (cm/y) is the sedimentation rate, and a (y) represents the number of years or durations considered in the inventory.

Table 3.3 Exposure parameters used for noncarcinogenic risk and carcinogenic risk

Parameter		Value
Reference dose (RfD)	BBP	0.2 mg/kg/day
	DEHP	0.02 mg/kg/dy
	DnOP	0.02 mg/kg/day
	DnBP	0.1 mg/kg/day
	DiNP	0.115 [b] mg/kg/day
Concentration of PAEs (C)	Mean value of PAEs	See Table 4.11-4.22
Intake rates (IR)	Adults	1.5
Exposure frequency (EF)	Adults	365 years
Exposure duration (ED)	Adults	30 years
Exposure duration (ED)	Adolscents	10 years
Exposure duration (ED)	Children	6 years
Body weight (BW)	Adults	60 kg
	Adolscent	30 kg
	Children	15kg
Average time (AT)	Noncancer risk	365 x ED
	Cancer risk	365x 70
Slope factor (SF)	DEHP	0.014 mg/kg/day

Source: USEPA (2012), [b] EFSA (2005)

Table 3.4 Exposure parameters used to generate exposure estimate of PAEs

Exposure parameter	Unit
Drinking water	365 events/year, 2L/event (adult), 1L/event (children); 100**%** portion of contaminated tap water
Dermal absorption	365 events/year; 12 min/event, 6 min/event; 5700cm^2 skin surface (adult), 2800 cm^{2}skin surface (children); Skin adherence factor = 0.7 mg/cm^2/day; ABS is dermal absorption factor = 0.1 for all PAEs congeners

Source: Fatoki et al. (2010) Olujimi et al. (2017)

Table 3.5 Established health limit of daily intake of PAEs, TDI and RfD

PAEs compound	TDI µg/kg/day	RfD mg/kg/day	References
DnBP	10	100	USEPA (1989)
DEHP	50	20	USEPA (1989)
DiNP	150	-	ESFA (2005)
DIDP	150	-	ESFA (2005)
BBP	500	200	USEPA (1989)

Table 3.6 Parameters of PAEs used as input in the ExpoFIRSTmodel

PAEs compound	Molecular weight (g/mol)[a]	Permeability coefficient K_{p-g} (m/h)[b]
DnBP	278	4.8
DEHP	391	5.8
DiNP	419	5. 9
DIDP	446	6.1
BBP	312	5.9

[a] Net et al. (2015)

[b] USEPA (2012)

3.7 Statistical analysis

Statistical analysis method was employed for the data analysis, including the spearman correlation matrix (SCM) and hierarchical cluster analysis (HCA) using SPSS 20.0 for window (IBM SPSS Inc, Chicago, IL). The spearman correlation coefficient was used to obtain the correlation between PAEs in sediments and sediment parameters including OM, OC and pH. Spearman correlation coefficient was also used to test the relationship between PAEs concentration in water and sediments samples. HCA was used for sampling sites discrimination of water and sediments samples. The level of significance was set at $p \leq 0.05$ and $p < 0.01$. Figures, maps were plotted as well as calculations using SPSS and Microsoft Excel, version 2010.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Occurrence, distribution and ecological risk of phthalate acid esters in surface water

4.1.1 Occurrence of PAEs in water

The concentrations of the six targeted PAE congeners, including DnBP, BBP, DEHP, DnOP, DiNP and DIDP, in surface water samples of U-Tapao canal are shown in Table 4.1. Some PAEs congeners were detected in all the water samples analyzed including DnBP, DEHP and DiNP, suggesting that PAEs are ubiquitous priority pollutants in the river system. The total concentration of PAEs in water ranged from non-detectable (ND) to 12.08±0.09 µg/L with mean value of 5.23±0.04 µg/L and median level of 4.92±0.03µg/L. The mean concentration of DEHP, DiNP and DnBP were 2.54±0.02µg/L, 1.46±0.01µg/L and 0.98±0.04 µg/L, respectively. The distribution of PAEs are shown in Figure 4.1. The distribution patterns of PAEs in the water phases of U-Tapao canal are mainly controlled by various factors including the hydrodynamic state of the canal, the properties of the suspended solid particles, the physicochemical properties of the PAEs themselves and the level of urbanization (Sun et al., 2013; Li et al., 2017). The differences in distribution patterns of PAEs in urban and rural area of the canal suggested that there might be variation of pollution sources along the canal network. Among the sampling sites in the canal, ST 13 had the highest total concentration of PAEs (12.08±0.09 µg/L) in water. This site is in Hat Yai city, the most populated, industrialized and urbanized city in southern Thailand, housing many residential, industrial and commercial hubs. This was followed by site 1 which is also located near an urbanized area in Dan Nok, close to Thailand and Malaysia boader. In addition, site 1 is also located near a rubber glove industry; thus, the elevated concentration may be due to high concentration of PAEs used in the manufacturing of rubber gloves and contaminations caused by commercial activities such as plastic waste disposal. High concentration of total PAEs were also detected in sites ST2 (7.00±0.17µg/L), ST4 (7.02±0.30µg/L) and ST10 (7.30±0.12µg/L), these sites were also located in urbanized areas, in addition, sites 2 and 4 were also located near rubber gloves factories. ST 10 recieves wastewater from Banpru and Khuan Lung subdristrict.

This finding is consistent with previous studies that reported that urbazition influences the pollution status of PAEs in aquatic environment (Sun et al., 2013; Wang et al., 2014). Relatively high concentration of PAEs were detected in sites ST3 (4.16±0.25 µg/L), ST6 (4.92±0.02 µg/L), ST7 (5.85±0.04 µg/L), ST9 (4.36±0.05 µg/L) and ST12 (4.80±0.23µg/L). Sites 7 is located near rubber glove factory, while sites 3 and 9 recieves wastewater from Sadao and Banpru. In addition, these sites are in urban region of the canal.

Low concentration of PAEs were detected at sampling sites that are mainly located at rural region of the river including ST5 (3.48±0.06 µg/L),ST 8 (2.89±0.08 µg/L), ST11 (1.60±0.02 µg/L), ST14(3.14±0.14 µg/L), ST15 (1.44±0.11 µg/L), ST16 (1.92±0.07 µg/L) and ST17 (2.24±0.04 µg/L). These sites are mainly dominated by agricultural and aquaculture activities, which may be the main contributor of PAEs pollution in these areas. In addition, most of these sites are located at the downstream of the canal, thus higher river flow may have caused better dilution of local discharge as well as the fact that there may be fewer or no actual municipal and industrial discharge wastewater in these regions of the canal. Studies have confirmed that PAEs may enter the aquatic environment via agricultural and aquaculture activities as well as atmospheric depositions (Niu, et al., 2014; Net al., 2015; Cheng et al., 2018). Previous studies in U-Tapao canal reported that land use pattern in ST8, ST11, ST14 and ST15, ST16, ST17, which are located at the upstream and downstream of the river respectively, are dominated by agricultural and aquaculture land use type (Gyawali et al., 2011; Gyawalietal., 2012).

Table 4.1 Water concentration of PAEs in U-Tapao Canal (n=4) (µg/L)

SITES	DnBP	DEHP	DiNP	BBP	DnOP	DIDP	∑PAEs	Area
ST 1	3.00±0.18	2.80±0.09	2.08±0.11	ND	ND	ND	7.88±0.41	Urban
ST 2	1.84±0.03	2.88±0.07	2.28±0.08	ND	ND	ND	7.00±0.17	Urban
ST 3	1.04±0.07	1.68±0.12	1.44±0.06	ND	ND	ND	4.16±0.25	Urban
ST 4	1.34±0.04	3.28±0.16	2.40±0.13	ND	ND	ND	7.02±0.30	Urban
ST 5	ND	1.68±0.01	1.60±0.10	ND	ND	ND	3.48±0.06	Rural
ST 6	ND	2.72±0.19	2.00±0.07	ND	ND	ND	4.92±0.20	Urban
ST 7	1.28±0.02	4.32±0.08	ND	ND	ND	ND	5.85±0.04	Urban
ST 8	1.36±0.05	1.28±0.15	ND	ND	ND	ND	2.89±0.08	Rural
ST 9	ND	2.16±0.09	2.00±0.04	ND	ND	ND	4.36±0.05	Urban
ST 10	1.72±0.07	3.14±0.16	2.44±0.07	ND	ND	ND	7.30±0.12	Urban
ST 11	ND	1.60±0.02	ND	ND	ND	ND	1.60±0.02	Rural
ST 12	ND	2.64± 0.01	2.16±0.19	ND	ND	ND	4.80±0.23	Urban
ST 13	3.36±0.22	5.28±0.38	3.44±0.27	ND	ND	ND	12.08±0.90	Urban
ST 14	ND	1.68±0.06	1.46±0.08	ND	ND	ND	3.14±0.14	Rural
ST 15	ND	1.44±0.11	ND	ND	ND	ND	1.44±0.11	Rural
ST 16	ND	1.92±0.07	ND	ND	ND	ND	1.92±0.07	Rural
ST 17	ND	2.24±0.04	ND	ND	ND	ND	2.24±0.04	Rural

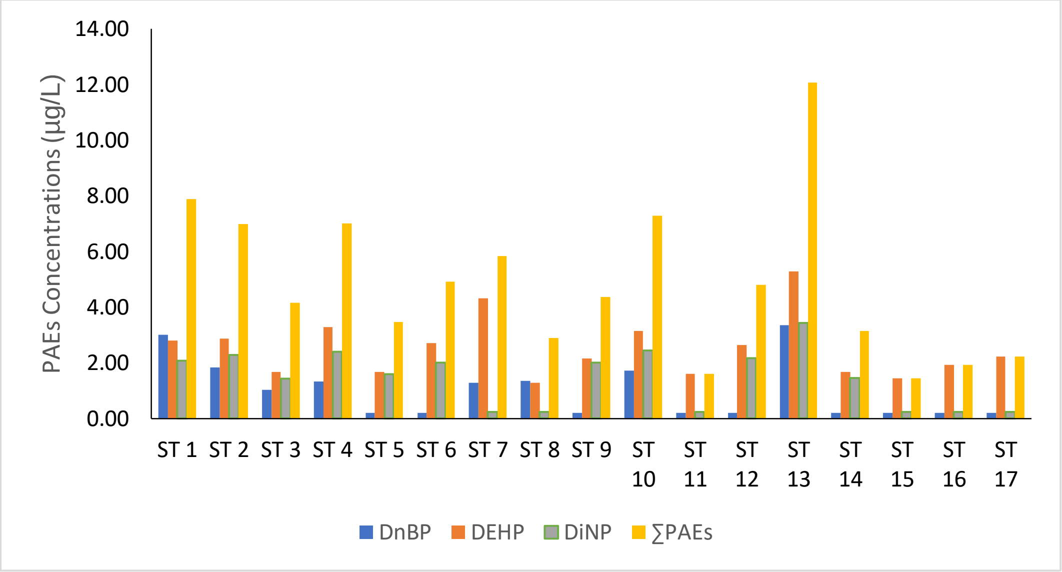

Figure 4.1: Distribution of PAEs in surface water of U-Tapao Canal (µg/L)

The results of hierarchal cluster analysis (Fig 4.2) classify the study sites into two groups, group1 and group 2 according to their contamination degree and physiochemical parameters. All group 1 were in suburban and rural area with relatively low pollution status, these sites include ST 12, ST 15, ST 11, ST 17, ST 16, ST 8, ST 6, and ST 14. Sampling sites in group 2 include ST 1, ST 2, ST 13, ST 10, ST4, ST 7, ST 9, and ST 3, were majorly located in urban area and few suburban areas with moderate to high pollution status.

Untreated and semi treated industrial wastewater effluents are still being discharged directly into the U-Tapao Canal, because, the legislation regulating the discharge of industrial waste into aquatic environment in Thailand, does not specify PAEs (Kevin et al., 2004; Sirivithayapakorn et al., 2014; Chuvanich et al.,, 2017). This might be the most significant source of PAEs pollution of the investigated canal. The major sources of industrial pollutants into U-Tapao Canal, include plastic, rubber, Para wood, and food processing industries at a rate of 41000 m^3per day (Sirinawin, & Sompongchaiyakul, 2005; Gyawali et al., 2012). Industrial pollutants, like PAEs enter the aquatic environment mainly through industrial discharges of contaminated wastewater effluent. In addition, urban runoff, municipal effluents, domestic garbage, surface runoff from municipal solid waste sites, effluent from aquaculture and agricultural activities are also principal transport pathway PAEs into aquatic environment (Zeng et al., 2008; Clara et al., 2010; Sun et al., 2013; Adeogun et al., 2015; Gao & Wen, 2016; Arfaeinia et al., 2019). The variability in the level and geographical distributional characteristic of PAEs indicates that industrial discharge and municipal runoff may be the major source of PAEs in river ecosystem in this area.

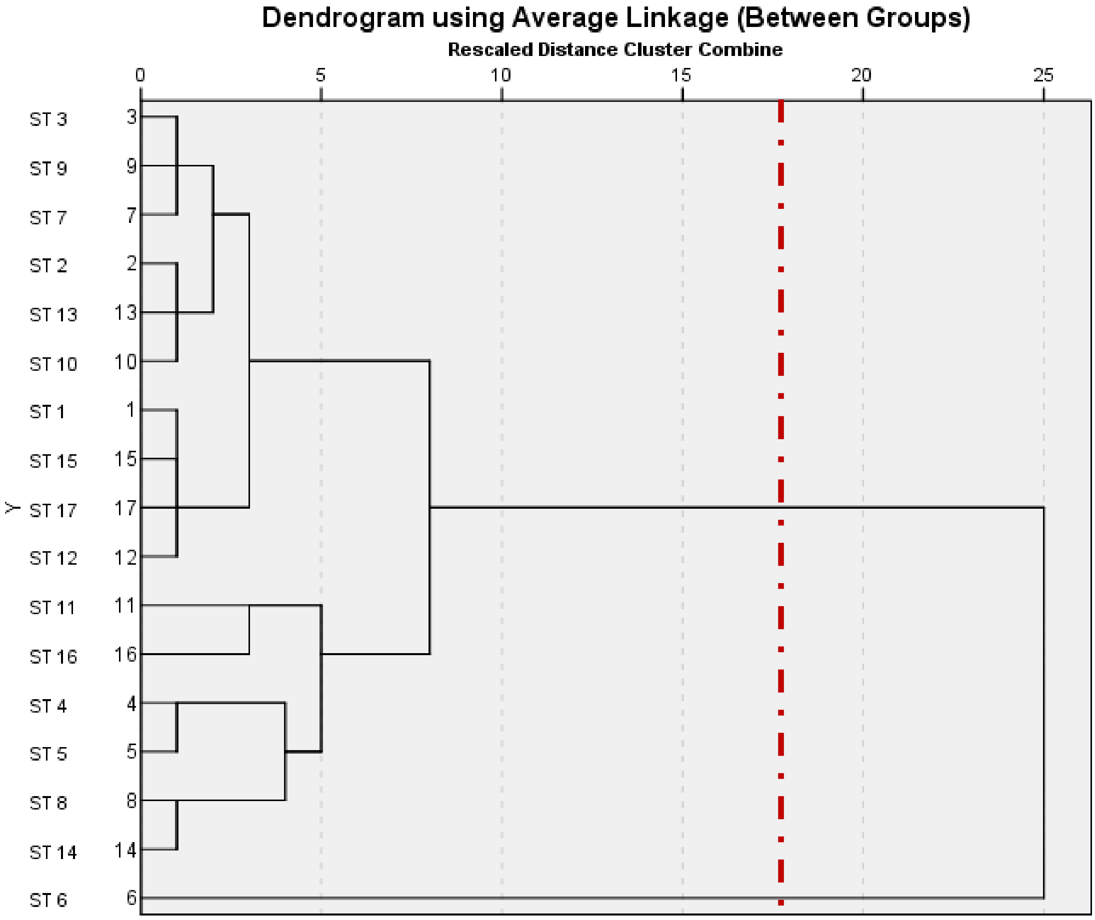

Figure 4.2 Cluster analysis of water distribution of PAEs in U-Tapao Canal

4.1.2 PAE congener profiles in water

Many researchers have recommended the use of analysis of the individual PAEs composition or PAEs congener profile to track the contaminant source as well as illustrate the biogeochemical characteristic of PAEs in multimedia environment; thus, different PAEs profile or compositions may indicate different sources of PAEs (Zeng et al., 2008; Sun et al., 2013; Arfaeinia et al., 2019).

Of all the PAEs, DEHP was presence in all the water samples analyzed. The detected concentrations for DEHP ranged from 1.28 to 5.28µg/L in the water samples. For DiNP and DnBP the detected concentrations ranged from non-detectable (ND) to 3.44 and ND to 3.36 µg/L respectively. DiNP was detected in 65% of the water samples, while DnBP was detected in 41.2% of the samples. Giving, an individual PAEs congener frequency of detection (FOD) order of DEHP>DiNP and DnBP. The relative contribution presented in Figure 4.3 shows that DEHP has the highest contribution ranging from 35.5% to 71.3 %, followed by DiNP which ranged from 15.9 % to 43.8 % and then DnBP, ranging from 7.7 % to 43.3%. The relative contribution pattern followed the order of DEHP>DiNP>DnBP. By contrast, BBP, DnOP and DIDP were below their detection limits (LOD) of 0.2 µg/L, 1 µg/L and 0.50 µg/L. It is clear, that DEHP was predominant in water samples analyzed in this work. This result is consistent with previous studies that reported that DEHP are dominant components of PAEs in water (Zeng et al., 2008; He et al., 2013; Selvaraji et al., 2015; Li et al., 2017;; Zhang et al., 2018). In addition, this observation reflects the usual pattern of plastic or rubber industry productions being dominated by DEHP documented in published literature (Gómez-Hens & Aguilar-Caballos, 2003; Zeng et al., 2008; Wang et al., 2014). Moreover, prevailing DEHP values have been reported for India, Korea, Malaysia,Taiwan, China, Canada, Nigeria and South Africa (Tan, 1995; Fatoki & Noma, 2002; Gobas et al., 2003; Adeniyi et al., 2011; He et al., 2013; Kumar & Gomathy, 2015; Lee et al., 2019).

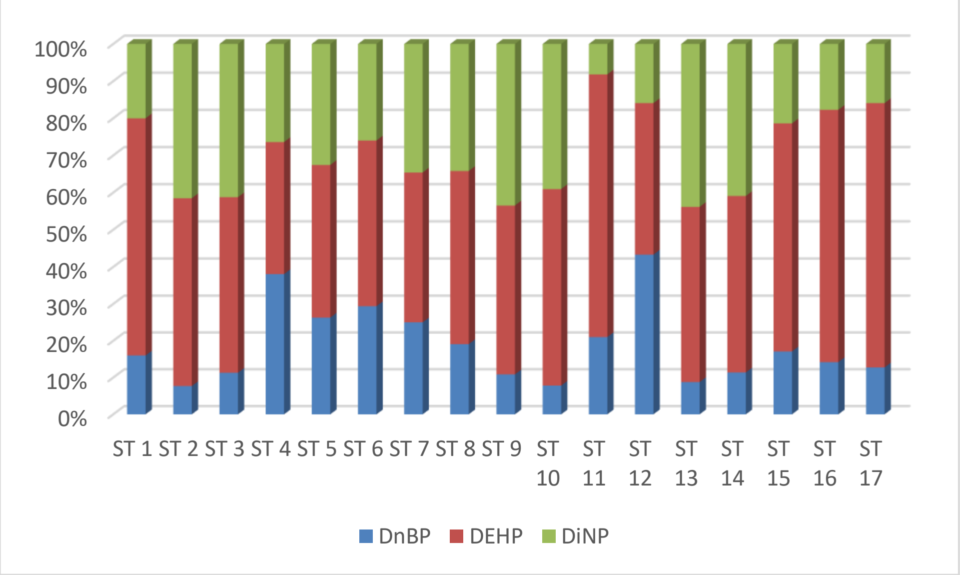

Figure 4.3 Relative proportion of PAEs in surface water of U-Tapao Canal

Spearman correlation of 3PAEs congeners in water of U-Tapao Canal were examined. The result indicated that significant correlation existed among DEHP and DiNP (Spearman r>0.565, P<0.05), suggesting that DEHP and DiNP may have the same source. However, there was no correlation between DEHP or DiNP and DnBP, indicating that they are of different sources. Furthermore, this present study shows that DEHP, DiNP and DnBP were highly correlated to ∑PAEs concentration in water samples. Spearman correlation coefficient of 0.84 (P<0.01) between DEHP and ∑PAEs, 0.783 (P<0.01) between DiNP and PAEs and 0.675 (P<0.01) between DnBP and ∑PAEs, suggesting that DEHP may be used to predict the total concentration of PAEs in water samples collected from the investigated canal.

These pattern of PAEs congeners, in respects to the sampling sites are complex, indicating several factors controlling the occurrence and distribution of PAEs congeners in the canal systems including source composition, sedimentary transfer/dispersion/accumulation patterns, environmental degradation or metabolism by sedimentary communities.

4.1.3 Comparison with other studies in other location

Although the complete data on all 6 PAEs in water are limited; however, the concentration for DnBP, DEHP, BBP and DnOP are routinely available, but data for DiNP and DIDP are scarce. Nevertheless, the concentration of total ∑PAEs obtained in this study were compared with few data of DnBP, DEHP and DiNP in water, documented in published literature to evaluate the severity of the problem of these PAEs congeners in U-Tapao Canal. As indicated by the data listed in Table 4.2, the concentration of 3 PAEs present in water in U-Tapao Canal were at medium magnitude as compared to those measured in other locations (Gobas et al. 2003; Gustavsson et al. 2017; Li et al. 2017b; Wen et al., 2018; Zhang et al. 2018a).

The concentration of DEHP in water of U-Tapao Canal, were comparable with those reported for Bohai sea and Yellow sea in China (Zhang et al., 2018), and were estimated to be 3 fold in magnitude lower than those determined for Jiulong River and Jiulong river estuary (Li et al., 2017a; Li et al., 2017b), and were approximately 2-20 fold higher than the concentrations documented for False Creek Harbor in Canada, Coastal water of Sweden and Songhua river basin, China (Gobas et al. 2003; Gustavsson et al. 2017; Wen et al. 2018).

Although the data of DiNP are limited for comparison, however, the concentration of DiNP in this study was compared with few available studies. The concentration of DiNP was comparable with that of Songhua river basin in China and were approximately 5-450 fold higher to those present in Bohai sea and Yellow sea, coastal water bodies in Sweden, Jiulong River and Jiulong River estuary (Gobas et al., 2003; Gustavsson et al., 2017; Li et al., 2017). It is worthy of note that most of the available studies used for comparison of this grouping of PAEs congeners detected in the study are current studies, mainly 2017 and 2018, except the case of False Creek harbor in Canada, suggesting that detection of DiNP in water phase were limited and may be due to scarcity of DiNP in previous studies.

The concentration of DnBP detected in water samples from sampling sites of U-Tapao Canal were lower than the levels measured in Songhla river basin, and comparable with concentration determined for Jiulong River (Li, e et al., 2017; Wen et al., 2018), whereas DnBP levels detected in this work, were higher than those reported for other studies (Gobas et al., 2003; Gustavsson et al., 2017; Li et al., et al., 2017; Zhang et al., 2018). Individual PAEs congener's levels in water samples from U-Tapao Canal varies considerably at different sampling stations as well as locations. The highest concentration of DnBP (3.36 µg/L) in ST 13, is of serious concern as this is higher than the environmental quality standards of surface water of USEPA (3.0 µg/L) and China surface water quality standards of (3.0 µg/L) and exceeded the EU EQS of 1.3µg/L by approximately 2 fold higher. Moreover, DnBP is strongly linked to antagonistic effects of the thyroid hormone in source water (Fatoki et al., 2010;; Shi et al., 2012; Net et al., 2015). The difference in PAEs profiles determined in the water samples of U-Tapao Canal may reflect the predominant PAEs congeners being used in the area. The result of this work indicated DEHP is predominantly used, followed by DiNP. As no data were available on past level in southern region, no conclusion or comparison can be made on the changes of PAEs in the area.

Table 4.2 Comparison of the concentration of DEHP, DnBP and DiNP in surface water of other location

S/N	Location	DnBP (ng/L)	DEHP (ng/L)	DiNP(ng/L)	Refreence
1	Bohai and Yellow sea, China	266-1,239	61.6-4,352	ND-5.41	Zhang et al. (2018)
2	Jiulong River Estuary China	300 – 1,770	120 – 12,400	ND - 520	Li et al. (2017b)
3	Jiulong River, China	280 – 2,400	790 – 10,900	ND - 524	Li et al. (2017a)
4	Songhua river basin, China	190 – 4,762	364- 2,682	ND- 2,465	Wen et al. (2018)
5	Coastal waters, Sweden	<188 - 498	< 68 - 223	< 50 - 134	Gustavsson et al. (2017)
6	False Creek Harbour	50 - 244	170 - 444	61. 2 - 135	Mackintosh (2002)
7	U-Tapao Canal, southern Thailand	ND-3,000	1,280 – 5,280	ND- 3,440	This study

4.1.4 Evaluation of the potential ecotoxicological effects of PAEs in surface water of U-Tapao Canal

In this study, for better understanding of the ecological risk of PAEs on aquatic habitats in U-Tapao Canal, a comprehensive ecological risk assessment was conducted using several methods that have been used by many researchers. These include comparing PAEs concentrations with standards guidelines, using aquatic life criteria derived for PAEs in aquatic environment in China and calculating the risk quotients (RQ).

Standard guidelines for surface water have been useful in comparing, monitoring and regulating PAEs pollution of aquatic environment. For instance, Australian and New Zealand guiding principle for freshwater and sea water quality have introduced trigger levels for DEHP of 900 µg/ L, asserting that 99% of all aquatic species would likely experience adverse effects above these levels (Net et al., 2015). The concentrations of PAEs (DEHP 1.28 to 5.28µg/L) in the surface water of the U-Tapao Canal were well below these threshold values. According to the environmental quality standard for surface water by USEPA and EU = 3.0µg/L and =1.3 µg/L, respectively, for the protection of aquatic environment, especially freshwater (Fatoki et al., 2010b; Net et al., 2015). The concentration of PAEs in this present study exceed the USEPA and EU standards, except in site 8, which is in a rural area. In China, the stipulated standard limits specified for DEHP and DnBP in surface water are 8 and 3 µg/L, respectively. In this study, the DEHP and DnBP concentrations in surface water of U-Tapao canal ranged from 1.28 to 5.28 µg /L and ND to 3.36 µg/ L, respectively. Suggesting that the concentration of DEHP are lower than these regulating limits. However, the concentration of DnBP in ST13 and ST1 (3.36 and 3.00 µg/L), indicated that the level of DnBP in this sampling sites of the river may start posing ecological risk on the aquatic habitats. Moreover, contamination level of DEHP in surface water of U-Tapao canal was compared to NQE value set by EU, based on NQE (1.3 µg/L) in fresh and marine water, all the measured sites exceeded the standard guideline value. In addition, the environmental risk levels (ERLs) for DnBP and DEHP, based on their ecotoxicological and environmental chemistry, with concentration levels in water set at a standard of 10 µg/L and 0.19 µg/L, respectively, was also applied in the evalaution of the ERA (van Wezel et al. 2000, Wang et al. 2013). In this present research, the levels of DnBP measured in surface waters samples collected from all the sites in U-Tapao canal were found to be well below ERLs. However, the mean concentration of DEHP (5.23 µg/L) in the canal surface water samples were observed to be approximately 28 times higher than its ERLs, indicating that the canal surface waters are severely polluted with DEHP. DEHP are endocrine disrupting organic compounds, displaying adverse reproductive effects on organisms (Scholz 2003); therefore, there are possibilities that these levels of DEHP may be constituting adverse effects on the aquatic biota in the canal.

In addition, a preliminary ecological risk assessment was further conducted using derived aquatic life criteria (ALC) for DnBP and DEHP as reported by Zheng et al. (2019), which employed the hazard quotient (HQ) method. The calculated HQ values of DEHP and DnBP were above 1 in all the sites, execpt sites with measured DnBP and DEHP < LOD. Figure 4.4 shows HQ of DnBP and DEHP on aquatic biota. As indicated in Figure 4.4, DEHP poses higher ecological risk to sensitive algae, crustaceans and fish as compared to DnBP. Considering the endocrine disrupting effects of PAEs, there is need to redetermine the screening benchmark values of PAEs.

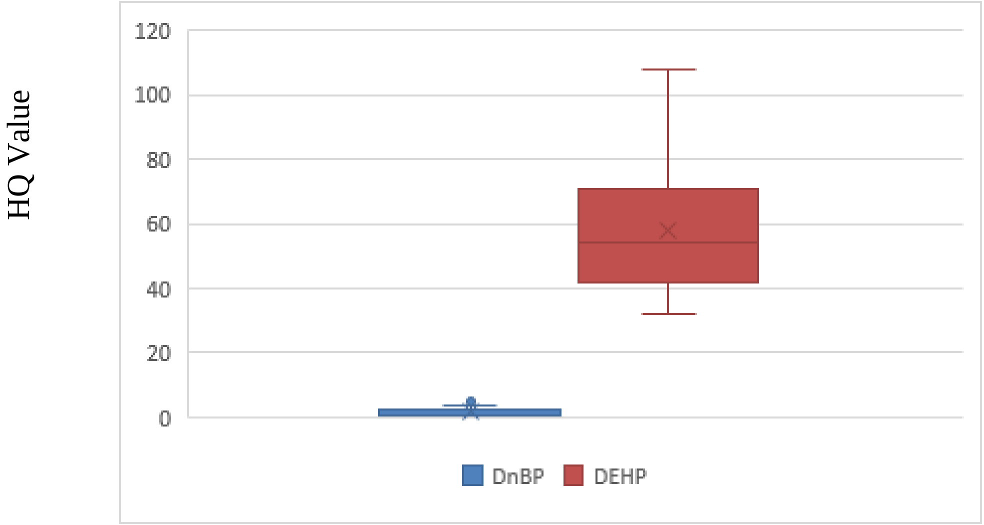

Figure 4.4: Box plot of HQ values of Ecological Risk Assessment of DnBP and DEHP using Aquatic Life Criteria (ALC)

Moreover, RQ method was used to further evaluate the potential ecological risk of the 3 PAEs congeners detected in water samples. As indicated in Figure 4.5, RQ values of the 3 PAE congeners in the water phase showed that the ecological risk of PAEs followed the order of DEHP >DiNP> DnBP. The RQ values of DEHP were above 10 (RQ>10) for algae, >1<10 for crustacean and > 1 for fish. Suggesting that DEHP level in water phase poses high ecological risk to algae, moderate risk to crustaceans and low risk to fish. Moreover, RQ values for DnBP in all investigated sites ranged from 0.049 to 0.143, showing low risk. For DiNP, RQ values ranged from 4.24 to 7.05 (RQ>1<10), indicated that DiNP poses moderate risk on sensitive crustaceans in the aquatic ecosystem.

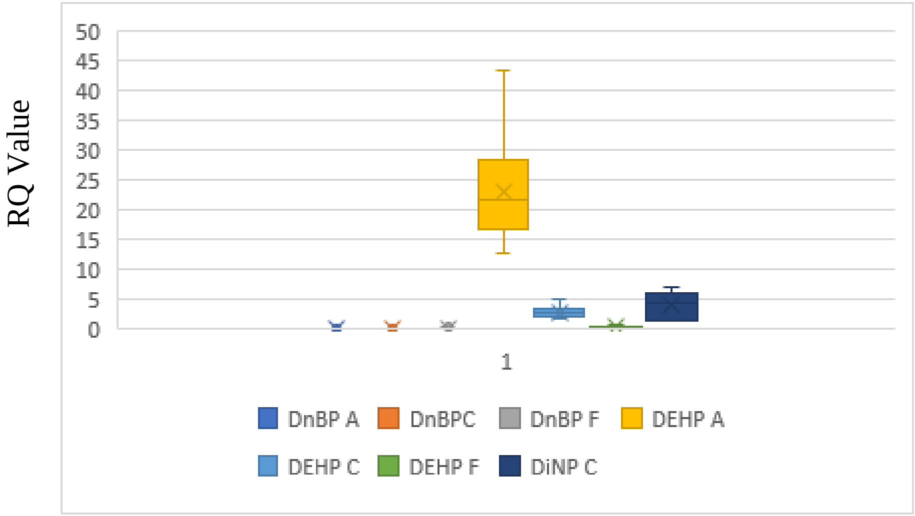

Figure 4.5: Box plot of RQ value of Ecological risk of PAEs in surface water using Risk Quotient (RQ). Symbols A: algae; C: crustacean F: fish

4.2 Occurrence, distribution and ecological risks of phthalate esters in sediments of U-Tapao Canal, Songkla Province, Southern Thailand

4.2.1 OM, pH, OC, and PAEs levels in the sediments

Table 4.3 showed the levels of OM, OC, pH and PAEs congeners (DnBP, DEHP and DiNP) contents in sediments analyzed from 17 sampling sites of U-Tapao Canal. As seen, the result indicated that the analyzed sediments samples contained OM contents that ranged from 1.0% to 4.0%. Mai et al. (2005) observed that organic matter (OM) in sediment is the major factor influencing the sorption of organic chemical compound in aquatic environment. Thus, PAEs concentration in river sediment in the U-Tapao Canal were expected to be correlated with the sediment OM values. In this study, Spearman correlation coefficient was conducted to evaluate the influence of OM on the distribution of PAEs in sediments of U-Tapao canal. As shown in Table 4.6, no significant correlation was observed between OM values and PAEs concentrations. This observation was due to different contamination of different sites. The differences of PAEs concentrations in the canal sediments are mainly influenced by different pollution sources including industries, residential areas, agricultural fields and aquaculture ponds. Furthermore, this result suggested that the distribution of PAEs in this present study was also influenced by other factors other than OM, such as transport, mixing, sedimentation/accumulation pattern, metabolic processes and pathways in sediments and characteristics of the investigated river systems, which is consistent with previous studies (Srivastava et al., 2010; Chen et al., 2013; Sun et al., 2013; Liu et al., 2014)

Table 4.3: Concentration of OM, OC and pH in sediment (n=4)

SITES	OM (%)	OC (%)	pH	Area
ST 1	2.56±0.65	1.91±0.47	6.00±0.73	Urban
ST 2	1.11±0.42	0.64±0.07	6.45±0.70	Urban
ST 3	1.41±0.13	0.82±0.09	6.64±0.17	Urban
ST 4	1.71±0.20	0.99±0.04	5.75±0.85	Urban
ST 5	1.00±0.30	0.58±0.05	5.43±0.57	Rural
ST 6	1.80±0.66	1.05±0.16	6.00±0.49	Urban
ST 7	1.20±0.17	0.70±0.02	5.94±0.71	Urban
ST 8	1.64±0.24	0.95±0.06	5.47±0.85	Rural
ST 9	2.86±0.71	1.66±0.14	5.32±0.45	Urban
ST 10	2.53±0.45	1.47±0.11	5.65±0.87	Urban
ST 11	4.00±0.66	2.32±0.34	5.20±0.74	Rural
ST 12	1.11±0.44	0.65±0.08	5.63±0.35	Urban
ST 13	3.72±0.55	2.17±0.13	5.30±0.78	Urban
ST 14	2.53±0.23	1.47±0.17	5.55±0.68	Rural
ST 15	1.00±0.07	0.58±0.02	5.20±0.57	Rural
ST 16	4.44±0.77	2.17±0.18	6.64±0.76	Rural
ST 17	2.01±0.08	1.17±0.12	5.73±0.54	Rural

Table 4.4: Concentration of PAEs in sediments of U-Tapao Canal (ng/g) (n=4)

SITES	DnBP	*DEHP*	*DiNP*	BBP	DnOP	DIDP	∑PAEs	Area
ST 1	130±0.41	*600±0.74*	*790±0.58*	ND	ND	ND	1520±1.78	Urban
ST 2	110±0.21	*560±0.88*	*640±0.84*	ND	ND	ND	1310±1.78	Urban
ST 3	50±0.32	*260±0.51*	*580±0.47*	ND	ND	ND	890±1.07	Urban
ST 4	120±0.50	*540±0.47*	*750±0.78*	ND	ND	ND	1419±1.09	Urban
ST 5	80±0.18	*290±0.28*	*480±0.87*	ND	ND	ND	850±0.52	Rural
ST 6	40±0.14	*430±0.42*	*520±0.53*	ND	ND	ND	990±0.84	Urban
ST 7	ND	*220±0.19*	*380±0.47*	ND	ND	ND	600±0.71	Urban
ST 8	ND	*80±0.47*	*230±0.52*	ND	ND	ND	310±0.58	Rural
ST 9	ND	*390±0.40*	*ND*	ND	ND	ND	390±0.62	Urban
ST 10	125±0.56	*540±0.47*	*660±0.54*	ND	ND	ND	1325±0.15	Urban
ST 11	80±0.57	*110±0.44*	*ND*	ND	ND	ND	190±0.24	Rural
ST 12	60±0.11	*220±0.47*	*ND*	ND	ND	ND	280±0.41	Urban
ST 13	140±0.78	*840±0.35*	*760±0.58*	ND	ND	ND	1740±1.94	Urban
ST 14	80±0.20	*360±0.18*	*160±0.48*	ND	ND	ND	600±0.87	Rural
ST 15	40±0.41	*90±0.41*	*140±0.75*	ND	ND	ND	270±0.57	Rural
ST 16	ND	*190±0.57*	*ND*	ND	ND	ND	190±0.14	Rural
ST 17	40±0.13	*120±0.59*	*60±0.37*	ND	ND	ND	220±0.41	Rural

SQGs values of PAEs in sediment TEL:DEPH= 182 ng/g, PEL:DEHP= 2,647 ng/g ERLs:DnBP= 700 ng/g, DEHP= 1,000ng/g

The results from Table 4.1 showed that the pH values of the investigated sediment samples lied between 5.20 and 6.64, indicating acidic characteristic of investigated riverine sediments. This acidic characteristic of sediment samples may be as a result of frequent discharge of effluents from wastewater plants containing large quantities of organic compounds (Zhao et al., 2004). In addition, human activities including discharge of acid-containing industrial wastewater, use of fertilizer/organic amendments in the agricultural fields and urban parks and gardens, usage of pesticides and aquaculture ponds (Jafari et al., 2018). However, no significant correlation was obtained between pH and PAEs, indicating that pH is not a determinant factor influencing the distribution of PAEs in the sediments of the investigated river (Sun et al., 2013; Wang et al., 2014). Our result is consistent with those of previous studies that reported no correlation between ∑PAEs and pH in sediments (Wang et al., 2014a; Arfaeinia et al., 2019).

As seen in Table 4.3. Organic carbon (OC) concentrations lied within the ranges of 0.58% to 2.32% in the riverine sediments. Previous studies have observed that the significance of the distribution patterns of PAEs such as DnBP, DEHP and DiNP may be associated to OC of sediments, which plays a significant role in the absorption of these compounds (Sha et al., 2007; Zeng et al., 2008, 2009; Lin et al., 2009). In addition, the relatively high log Koc values of PAEs congeners such as DEHP and DnBP (i.e. 7.50 for DEHP and 4.45 for DnBP) lead to their high attraction to OC in aquatic sediments. Subsequently, PAEs congeners are hydrophobic, the OC in aquatic sediments performs the role of a sink for PAEs in the aquatic sediments, leading to slow biotic degradation of DEHP and DnBP. Furthermore, their hydrophobic characteristics makes it easy to dissolve in macromolecular organic compound, such as humic compounds and finally deposit to sediments (Adeogun et al., 2015; Zhang et al., 2018a).

The result obtained from PAEs analysis in river sediments are shown in Table 4.4. Of the six PAEs (DnBP, BBP, DEHP, DnOP, DiNP and DIDP) targeted in this study, only 3 congeners were detected in sediments such as DEHP, DiNP and DnBP. The total PAEs concentrations in the canal sediments ranged from ND to 1740ng/g dw, with mean value of 824 ng/g, while the median value was 800 ng/g. Among the six PAEs, DEHP was detected in all investigated sediment samples (frequency of detection (FOD) of 100%), with measured concentrations ranging from 90 to 840 ng/g and mean level of 349.3 ng/g; indicating that DEHP is a ubiquitous organic pollutant in the riverine environment. For DiNP, FOD was 71.4%, with determined concentrations ranging from non-detectable (ND) to 790 ng/g and mean value of 422.1 ng/g. For DnBP, FOD was 64.3%, with measured concentration ranging from ND to 140ng/g, and mean concentrations of 57.5 ng/g. Frequency of detection for individual PAEs congeners in this study, followed the order of DEHP>DiNP > DnBP. However, the relative percentage contributions of the total level of PAE congeners detected in the sediments indicated that DiNP had the highest relative contribution percentage, followed by DEHP and then DnBP. These results are not consistent with the commonly documented findings published in literature, which indicated that DEHP and DnBP are the predominant congeners with the highest concentration in sediments (Chen et al., 2013; Hassanzadeh et al., 2014; Liu et al., 2014). The discrepancy between our result and previous research may be largely caused by the relatively scarce shortage of DiNP previously. In addition, 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 is 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.

4.2.2 Comparison with other studies in the world

Among most commonly used PAEs congeners such as DnBP, BBP, DEHP, DnOP, DiNP and DIDP; four of these congeners including DnBP, BBP, DEHP and DnOP have been widely studied in sediments, but studies of DiNP and DIDP in sediments are lacking all over the world, including Thailand. The concentrations of total PAEs found in this present work were compared with data obtained from previous work to understand how serious the problem is for total PAEs pollution in U-Tapao Canal.

As indicated by the data listed in Table 4.5, U-Tapao Canal has higher total PAEs concentration in its sediment than those of Cianjhen river in Taiwan (Yang et al., 2017) and Jiulong river estuary in China (Li et al., 2017), though it is lower than values reported elsewhere, Kaoshiung Harbor, Taiwan (Chiu et al., 2017), Shannon international river basin, Ireland (Kelly et al., 2010) and Garda Sedimentation facility in Sweden (Bjorklund et al., 2010), but comparable with PAEs levels reported for Jiulong river, China (Li et al., 2017) and False Creek Harbor, Canada (Mackintosh et al., 2002). According to Sha et al. (2007), the highest PAEs concentrations ranging from 30.52 to 85.16 mg/kg in a riverine in sediments was attributed to local industry's use of a high amount of PAEs as raw materials for production. Similarly, Wang et al. (2014) observed that discharge from the industrial areas the main cause of high concentrations of PAEs in the riverine sediment of Yangtze River, in Southern Jiangsu, China. Moreover, Chen et al. (2018) documented that the high concentration of PAEs in the sediments of Love River was mainly due to influx of industrial effluents, domestic sewage and surface runoffs along the riverbank. Furthermore, discharge from Urban and agricultural areas were indicated to be the main contributors for elevated concentration of PAEs in sediments of Persian Gulf, in Iran (Arfeania 2019). Therefore, the relatively high total PAEs levels in sediments of U-Tapao canal might be ascribed to the incessant discharging of wastewater from industries and residential areas, effluent from agricultural fields and aquaculture ponds as well as surface runoffs from nearby municipal solid waste sites, especially during flooding (Gywali et al., 2012; Na Phatthalung et al., 2016; Chuvanich et al., 2017).

Table 4.5 Comparison of DnBP, DEHP and DiNP levels in different countries (ng/g)

Location	DnBP	DEHP	DiNP	Reference
Kaoshiung Harbor Taiwan	0.0-34.6	152.6-14,646.6	0.00-67,495.9	Chen et al. (2017)
False Creek Vancouver, Canada	9320-63,900	7,350-136,00	14,700-50,400	Mackintosh et al. (2006)
Jiulong River Estuary, China	1.6 - 92.8	4.3-394.7	Nd-110	Li et al. (2017)
Dianbao River, Taiwan	400 - 1865	494-1947	361-1277	Yang et al. (2015)
Kaohsiung Harbor	38.3-259.0	574-21,559	392-26,500	Chen et al. (2017)
Jiulong River, China	3.0-230	7.00-1160	ND -470	Li et al. (2017)
ChangJiangRiver Estuary, China	340-7080	260-8550	NA	Zhang et al. (2018)
Cianjhen River, Taiwan	<1-1.00	217-445	189-398	Yang et al. (2016)
Kaoshiung Ocean, Taiwan	22.4-136	1031-4247	125-882	Chen et al. (2017)
Houjing River, Taiwan	1987	2144	934	Yang et al. (2015)
False Creek Harbor, Canada	57.5-182	1130-3870	259-900	Mackintosh et al. (2002)

Concentration of DEHP, DiNP, DnBP, OM, OC and pH in sediments samples collected from the canal that behave alike or similar in characteristic were identified or discriminated using Hierarchical Cluster Analysis (HCA). The cluster technique applied, maximized the between group linkage while minimizing the within group linkage. Generally, in a clustering method, all sample within a cluster are equally belonging to the cluster. The result of the cluster analysis revealed that the samples may be classified into two clusters (cluster 1 and 2). Cluster 1 consist of ST 13, ST 14, ST 1, ST 2, ST 3, ST 5 and ST 7. These stations were in relatively low to moderately polluted stations. Cluster 2 include ST 11, ST 10, ST 9, ST 8, ST 4 and ST 12. These sampling stations were in relatively high polluted areas. The result was not surprising as majority of these sampling sites were in industrial and urban areas of the U-Tapao canal.

Spearman's correlation analysis was carried out to identify the relationship between PAEs in sediments and physicochemical parameters of sediments. As indicated in Table 4.6, showed that there were some correlations among DnBP, DEHP, DiNP and ∑PAEs and no significant correlationship existed between PAEs congeners and the sediment parameters evaluated in this study.

Table 4.6 Spearman correlation matrix of PAEs and physicochemical parameters of sediments of U-Tapao Canal

	OM%	OC%	pH	DnBP	DEHP	DiNP	∑3PAEs
OM%	1						
OC%	.578**	1					
pH	-.534*	-.546*	1				
DnBP	-0.338	-0.351	0.164	1			
DEHP	0.158	0.165	-0.246	0.497	1		
DiNP	0.245	0.251	-0.319	0.559*	.414**	1	
∑PAEs	0.198	0.2	-0.216	0.545*	.552**	.677**	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Furthermore, we used Spearman correlation coefficient to compare the relationship between PAEs in water and sediments. As indicated in Table 4.7, there is some significant correlation between the concentrations of DnBP in surface water and DnBP in sediments ($r = 0.553$, $p < 0.05$), strong significant relationship between DEHP in surface water and DEHP in sediments (r = 737, $p < 0.01$) and DiNP in surface water and DiNP in sediment (r = 630, $p < 0.01$), suggesting that the concentration PAEs in water sample of the investigated canal may be used to predict the concentrations of PAEs in sediment vice versa.

Table 4.7: Spearman correlation matrix of PAEs concentration in water and sediment

PAEs	DNBPS	DEHPS	DiNPs	DnBPW	DEHPW	DiNPW
DNBPS	1					
DEHPS	.709**	1				
DiNPs	.688**	.750**	1			
DnBPW	.553*	.587*	.817**	1		
DEHPW	0.442	.737**	.578*	.569*	1	
DiNPW	.740**	.880**	.630**	.535*	.677**	1

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

4.2.3 Distribution of PAEs in sediments of U-Tapao Canal

The distribution of DnBP and DEHP in sediments of U-Tapao canal in 17 different sites of the canal which was classified to include urban and rural zones of the canal are shown in Figure 4.6. As seen, concentrations higher than standards for DEHP where mainly detected at urban sites (ST1, 4, 10 and 13) and site 3 which is located at suburban region of the river. The highest concentration of DEHP (840±0.35) was detected in Hat Yai city, in a site that is100meter away from the discharge point of the effluent from a municipal wastewater treatment plant in Hat Yai city. Previous studies reported that, to date, semi-treated and untreated wastewater are still frequently discharged into the canal (Gywali et al., 2012; Chuvanich et al., 2017).

Figure 4.6 shows the distribution of PAEs in sediments of U-Tapao canal. Generally, the distribution pattern of PAEs featured high concentration in the urban zones, relatively high levels in suburban areas and low concentration in rural regions. Obviously, the highest concentration of PAEs in the canal sediments in urbanized waterway were mainly related to the intensity of industrial and commercial activities as well as rapid population growth. Such contamination patterns have been observed by previous studies (Sun et al., 2013; Wang et al., 2014; Liu et al., 2014; Chen et al., 2018; Arfeania et al., 2019).

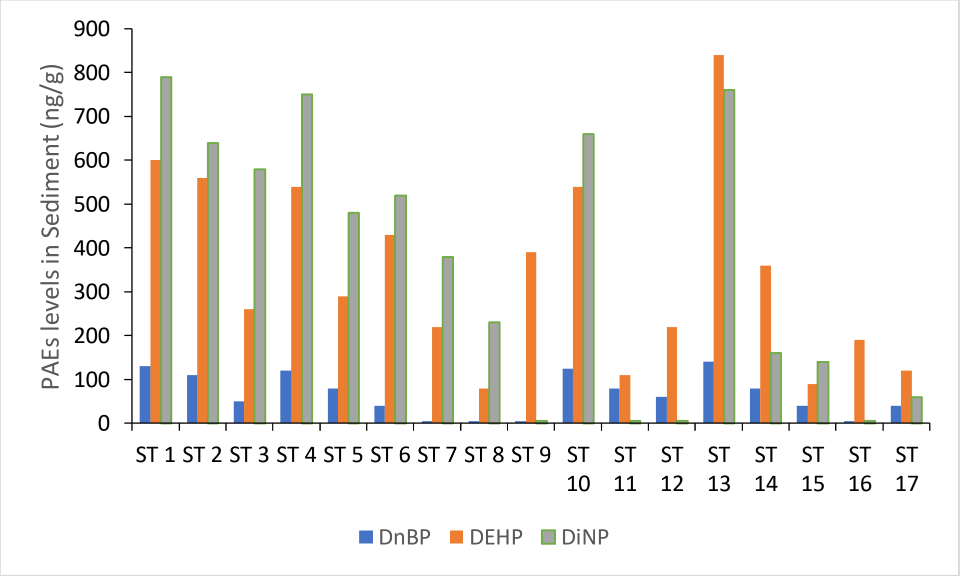

Figure 4.6 Distribution of PAEs in sediments of U-Tapao Canal (ng/g)

4.2.4 Evaluating the potential ecotoxicological effects.

Five methods of sediment quality guidelines (SQGs) were used to evaluate the ecological risk assessment (ERA) of PAEs on aquatic biota or benthic organisms in this study by comparing the level of PAEs in sediment samples for TEL and PEL, whereas the value of 10% OM normalization was used in the case of MPC, SRCeco and ERL. Table 4.8 showed the result of ERA evaluation. In addition, risk quotient method was also used in evaluating ERA of PAEs. DEHP concentrations, in sediments samples of U-Tapao Canal contained moderate level between TEL and PEL (182– 2647 ng/g), suggesting chances of generating occasional adverse ecological risk. Based on SQGs value of DEHP documented by Macdonald et al. (1996), the threshold effect level (TEL) for DEHP was obtained as 182 ng/g and the probable effect level was obtained as 2647 ng/g. Concentration below the TEL value do not pose adverse ecological effects on aquatic biota, while those between TEL and PEL can pose occasional adverse ecological effects and when DEHP level is greater than PEL, may cause severe ecological risk on aquatic biota. As at the time of this study, there was no TEL and PEL values for DnBP and other congeners.

Alternate method such as the equilibrium partitioning theory by Verbruggen et al. (2001) have been widely employed by many researchers to evaluate the ecological risk posed by PAEs (Zeng et al., 2008; Chen et al., 2017a; Arfaeinia et al., 2019). Application of these method on data obtained in this study shows that DnBP concentrations were < MPC and SRCeco in all the sampling sites, suggesting that the level of DnBP in sediments may not pose ecological risk on aquatic biota. For DEHP, 90% of the sampling sites were > MPC and < SRCeco in 100% of the sites, while for ∑PAEs, 100% of the sampling stations were > MPC and < SRCeco, suggesting that DEHP is considered to be posing moderate ecological risk in U-Tapao Canal. This method employs the maximum permissible concentration (MPC) and Ecotoxicological Serious Risk Concentrations (SRCeco) of PAEs. The MPC, SRCeco concentrations for DnBP and DEHP have been set on a 10% organic matter (OM)-normalized basis. For DnBP, the MPC values obtained was 2100 ng/g and 36000 ng/g for SRCeco. For DEHP, the MPC value obtained was1000 ng/g and the SRCeco was 10000 ng/g. In addition, the ∑PAEs values of 1400 and 57000 for MPC and SRCeco respectively, were also obtained.

Moreover, previous studies indicated that if the pollutants level exceeds the environmental risk levels (ERLs), it may generate several adverse effects on both environmental and human health (Staples et al., 1997;Zeng et al., 2008; Sun et al., 2013; Net et al., 2015). Van Wezel et al. (2000), proposed the ERLs for DnBP and DEHP capable of causing adverse ecological effects in an ecosystem as 700 ng/g and 1000 ng/g in sediments containing 10% of organic matter. For DnBP, 20% of the sampling sites were > ERLs and <ERLs in 80% of the sites, indicating that DnBP is posing adverse ecological effects in 2 sampling sites of the canal. For DEHP, 90 % of the sampling sites were > ERLs and < ERLs in 10% of the sites, suggesting that DEHP is the main PAEs congener posing ecological risk in the canal via sediments. As ERLs values have not been proposed for DiNP, values proposed for DEHP (1000 ng/g) was employed to evaluate the ecological risk of this PAEs congener. This is because current evidences have been reported that DiNP may pose adverse effects on aquatic biota via another pathway. Application of DiNP data from this study shows that DiNP concentration in 80% of sampling sites in the canal, exceeded the ERLs. Indicating that DiNP poses several adverse effects on both aquatic biota and human. Thus, it is important to pay attention to the ecological risk of DiNP, because they accounted for the highest concentration in this present work, which is consistent with previous studies (Chen et al., 2017; Chiu et al., 2017). Although, NOECs of DiNP have been reported in benthic organisms at a very high concentration and the low water solubility of DiNP with maximum saturation of this PAEs in sediments, with no significance adverse effects in aquatic biota (Oehlmann et al., 2008). However, current studies have reported that DiNP poses adverse effects on aquatic biota via modulation of the endocannabinoid systems, a new target for assessing the activity of endocrine disrupting chemicals. In addition, DiNP poses adverse effects on terrestrial organisms and human (Shea 2003; Babich et al., 2004; Bornehag etal., 2004; Huang et al., 2014; Arbuckle et al., 2016). Moreover, DiNP may occur in different forms in aquatic ecosystems, such as free phase or matrices that contain high concentration of DiNP. These necessitates the need to carry out further studies on the occurrence and distribution of DiNP in sediments to understand the potential toxicity effects on benthic organisms (Chen et al., 2017).

Furthermore, ecological risk of PAEs was evaluated using the risk quotient (RQ) methods. RQ values of PAEs in sediments as shown in Figure 4.7, indicated that RQ values of < 1, for all the PAEs congeners including DnBP, DEHP and DiNP, suggesting that PAEs poses low ecological risk to sensitive algae, crustacean and fish. However, DEHP is considered as the main cogener with higher ecotoxicological risk of PAEs in U-Tapao sediments. Based on the overal result above, there is need for routine monitoring and control of PAEs pollution of the U-Tapao Canal to prevent further PAEs pollution and protect the aquatic biota and human.

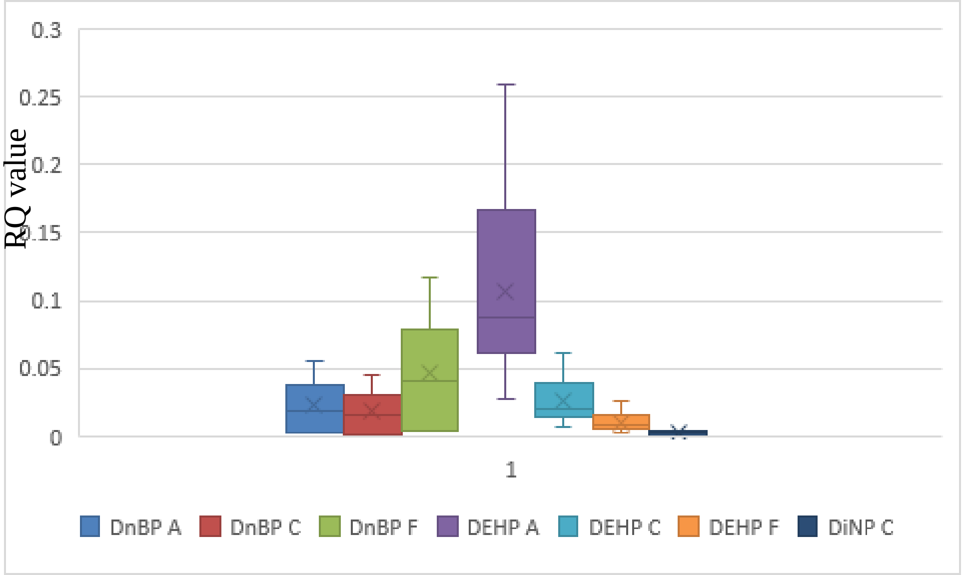

Figure 4.7 Box plot of RQ values of Ecological risk of PAEs in sediment of U-Tapao Canal

Table 4.8 Comparison of the values of PAEs with Sediments Quality Guidelines (TEL, PEL, MPC, SRCeco and ERLs)

PAEs	TEL (ng/g)	PEL (ng/g)	MPC (ng/g at 10% OM)	SRCeco (ng/g at 10%OM)	ERL (ng/g at 10% OM)	Sample stations (ng/g at 10% OM)
DnBP	-	-	2100	36000	700	ND-1110
DEHP	182	2647	1000	10000	1000	242-3298
DiNP	-	-	-	-	-	ND-4833
∑3PAEs			1400	57000	-	242-8655
% of site>SQG	100[b]	0[b]	90[b] 100[d]	0[b] 0[d]	20[a] 90[b] 80[c]	-
% of sites< SQG	0[b]	100[b]	100[a] 10[b]	100[a] 100[b]	80[a] 10[b] 20[c]	

[a] DnBP

[b] DEHP

[c] DiNP

[d] total PAEs

4.2.5 Inventory of PAEs in the suburban river sediments

Riverine runoffs are an important vector in transporting organic pollutants from terrestrial sources to oceans. Clearly determining the amounts of organic pollutants transferred by riverine runoff can shed light into the cross-boundary transfer and help estimate the regional contributions of chemical contaminants to global inventory (Guan et al., 2009). Sediments serves as sinks and transfer agents of chemicals. Studies on inventory and burden have revealed that riverine sediments do not only acts as sinks to organic pollutants but can also serves as vectors to transfer organic contaminants from riverine ecosystems to coastal environment. In this study, the inventory of sedimentary transfer of PAEs from U-Tapao Canal to Songkla Lake was evaluated using equations 13 (Zhao et al., 2011):

$$Inventory = C \times p \times A \times D \times a \qquad 13$$

where C (ng/g) is the mean concentration of PAEs in the sediment
ρ (g/cm^3) is regarded as the dry density of the sediments obtained from the canal
A (cm^2) simply represents the area of the watershed
D (cm/y) the sedimentation rate
a (y) is the number of years considered in the inventory

In this work, the sedimentation rate and the dry bulk density of the U-Tapao canal as 0.78 cm/y and 1.0 g/cm^3, respectively (Santi Rakswong, 2017). Based on the total mean value of PAEs of in this work, the sedimentation rate and the dry bulk density of the U-Tapao canal as 0.78 cm/y and 1.0 g/cm^3, respectively (Santi Rakswong, 2017). Based on the total mean value of PAEs of 772.06 ng/g, total area of U-Tapao subbasin of 2393 km and 5 years accumulation, it was estimated that the inventories of the total PAEs was 7.3 tons, which was transferred from U-Tapao canal to Songkla lake. Calculation details in Appendix s7. The uncertainties in the estimation of the inventories were propagated from the analytical error from the chemical analysis of C and the uncertainty in ρ, and D values. Error from the analytical procedure was estimated to be 10% for C. The assumption of ρ of 1.0 g/cm^3 and D value of 0.78 cm/y may contain an error of 10% and 30% for the mud areas of the U-Tapao subbasin. Therefore, a propagated uncertainty was approximately 50% for the estimated inventories, indicating estimated total PAEs inventory to be 3.6-7.2 tons in period of 5 years (Mi et al., 2019). Figure 4.8 shows the inventroty of PAEs in sediments of U-Tapao canal. Based on the estimated inventory from this study, the value was approximately more than 8 and 3-fold lower than those previously reported for yellow sea and Bohai Sea in China, respectively (Mi et al., 2019). The inventory of total PAEs congeners reported for Bohai and Yellow seas were 20.73 tons and 65.87 tons, respectively. No study has reported on the inventory of DiNP in sediment, making it difficult to compare the inventory of DiNP. The inventories reflected in this present work would represent deposits in the last five years. Presumably, sediments of U-Tapao canal may have served as a significant reservoir and a potential source of PAEs transfer to Songkla Lake, the largest natural lagoon in Thailand.

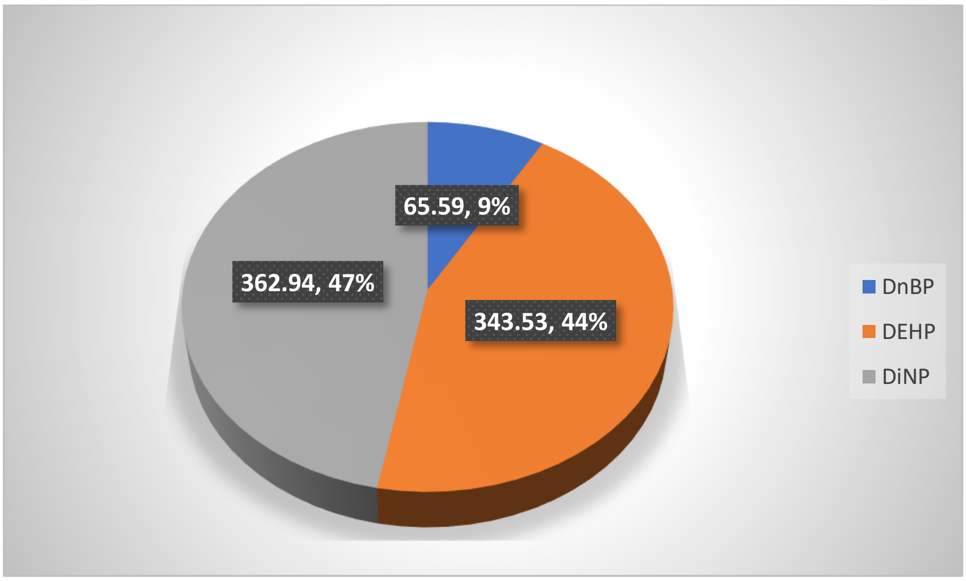

Figure 4.8 Inventory of PAEs in sediments of U-Tapao Canal

4.3 Occurrence and health risk of phthalate esters in a Tap water source and filtration plants in Songkhla Province, Southern Thailand

4.3.1 PAEs in source water

The concentrations of PAEs in raw water collected from the influent of four waterworks that obtain their raw water from U-Tapao canal, were examined and the results are presented in Table 4.7. The four waterworks include Sadao, Phang La, Priks and Hat Yai provincial waterworks. Of the six targeted PAEs analyzed in water samples, only three PAEs congeners (DnBP, DEHP and DiNP) were detected at levels above detection limits (LOD). The results revealed that PAEs were detected in all samples analyzed, suggesting that PAEs are ubiquitous pollutants in all the source water investigated. The highest mean concentration of PAEs including DnBP = 2.77±0.83 µg/L, DEHP = 4.07±1.05 µg/L and DiNP = 3.16±0.39 µg/L, were detected in Hat Yai waterworks. This was not unexpected as this waterwork is in Hat Yai city, the most urbanized city located along the investigated canal. The lowest mean concentration of PAEs such as DnBP (1.14±0.08 µg/L), DEHP (1.95±0.068 µg/L) and DiNP (2.3±0.43 µg/L) were measured at Phang La, which is in suburban area of the canal. These 3 PAEs congeners are significantly and extensively applied as additives in several industrial, consumers, household and personal care products, suggesting that these uses may be the major sources or contributors of these endocrine disrupting (EDCs) organic pollutants in water bodies (Peijnenburg & Struijs, 2006; Kong et al., 2017). In addition, PAEs may be present in source water due to industrial and domestic discharge as well as surface runoff from municipal solid waste sites, urban runoffs, effluent from agricultural and aqua cultural activities and atmospheric deposition (Clara et al., 2010; Gao & Wen, 2016; Sulentic et al., 2018). The 3 PAEs found in source water in this study, are classified as priority pollutants and endocrine disrupting organic chemical by USEPA (Babich et al., 2004, Park et al., 2008). Many studies have investigated the occurrence of DEHP and DnBP in raw water and tap water, but few studies have assessed DiNP in raw water and tap water including raw water and tap water in this present study as well as those in China and South Africa (Wen et al. 2018; Van Zijl et al. 2017). It is therefore recommended to include DiNP when screening source water and tap water samples for PAEs. The remaining 3 PAEs congeners were below detection limit, this may be attributed to lower amount of usage at present in Thailand.

Table 4.9 PAEs concentrations in raw water collected from U-Tapao Canal (μg/L) (n=4)

`	Sadao **(n=4)**			Phang La **(n=4)**			Prik **(n=4)**			Hat Yai **(n=4)**		
	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD
DnBP	ND	1.28	1.16±0.17	ND	1.2	1.14±0.08	1.06	2.88	1.79±0.96	ND	3.36	2.77±0.83
DEHP	1.36	3.28	2.27±0.96	1.44	2.72	1.95±0.68	1.84	3.21	2.73±0.77	3.45	5.28	4.07±1.05
DiNP	ND	2.4	2.4±0.87	ND	2.6	2.3±0.42	ND	3.62	3.15±0.66	ND	3.44	3.16±0.39
BBP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-
DIDP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-
DNOP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-

The spearman correlations matrix (SCM) in Table 4.10 showed the relationship between the levels of DEHP, DnBP, and DiNP with the concentrations of total PAEs in the water samples. As seen, there is significant correlation between ΣPAEs and DEHP as well as DiNP, suggesting the significant role played by DEHP and DiNP in total concentrations of PAEs in the investigated source water. However, the contribution of DEHP to total concentration of PAEs congeners was higher than DiNP, thus, can be used as a marker to predict the concentration of other PAEs congeners in the investigated source water. DEHP is the most commonly used PAEs and accounts for approximately 50% of the total industrial PAEs output in several countries, including Malaysia, Canada, Nigeria, South Africa and China (Tan, 1995; Fatoki & Noma, 2002; Adeniyi et al., 2011; He et al., 2013). This study observed that DEHP is the most predominate PAEs congener in raw water due to its high production, consumption volume and low degradation rate. In addition, the legislations regulating the discharge of industrial and domestic wastewater in Thailand, does not specify limits for PAEs congeners into aquatic environment (Sirivithayapakorn et al., 2014). In this study, DEHP is the most predominate PAEs in water, which is consistent with those of previous studies (He et al., 2013; Sirivithayapakorn et al., 2014; Liu et al., 2014; Selvaraji et al., 2015).

Table 4.10 Spearman correlation matrix of individual PAEs concentration and total PAEs in raw water

spearman correlation matrix				
	DnBP	DEHP	DiNP	∑PAEs
DnBP	1			
DEHP	0.246	1		
DiNP	0.014	0.656*	1	
∑PAEs	0.518	0.869**	0.804**	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Although research on the occurrence and distribution of DnBP, BBP, DEHP and DnOP have been widely reported in water samples, the data on 2 congeners (DiNP and DIDP) in water are lacking. Therefore, DnBP, DEHP and DiNP that were detected in source water in this present study were selected for comparison with few available previous studies in other locations in the world. The maximum concentration of DEHP (5.28±1.05 µg/L) found in the present study was approximately 3 to 4-fold lower than those reported for raw water samples from Jiulong river in China. In comparison the maximum concentration of DEHP detected in our study were approximately 2, 12 and 23 times higher than those reported for raw water samples from Songha River in China, False Creek Harbor, Canada and Coastal waters in Sweden respectively. Maximum concentration of DnBP (3.36±0.87 µg/L) detected in this study was lower than the level determined in Songhua River in China and well above levels reported for Jiulong river. The concentration of DiNP measured in raw water was higher than those determined for all the waterbodies in other locations in the world. In conclusion, as compared to the results of other locations, the raw water for tap water production collected from U-Tapao Canal are moderately polluted by PAEs. Thus, the need to set up a definite and well-planned strategy and systematic approach to control water pollution of PAEs in U-Tapao Canal, especially in areas near the waterworks.

4.3.2 PAE Congener Profiles in the Water.

Many researchers have suggested that the analysis of the composition or congeners profile as well as the concentration of individual PAEs can be useful in the identification of the sources and biogeochemical characteristic of PAEs in multimedia environments (Zeng et al., 2008; Sun et al., 2013a; Wang et al., 2014; Arfaeinia et al., 2019). It is clear, that DEHP was the most predominate congeners in the water samples, with relative contributions ranging from 34% to 60.1%, followed by DiNP, ranging from 6.8 % to 47.1% and DnBP, ranging from 4. 4% 45.8%. As indicated in Figure 4.9, the relative contribution of PAEs in this study is in the order of DEHP> DiNP> DnBP. These PAEs congeners profile pattern could reflect numerous factors, plus source configurations, sediment dispersion and accumulation pattern, water solubility, environmental degradation and hydrological conditions(Cousins and Mackay 2000).

The results indicated different patterns of PAEs contamination in different raw water near different waterworks. For instance, PAEs congener profile in source water near Hat Yai waterworks has the highest levels of the 3PAEs congeners measured in source water samples, DnBP (3.36±0.87 µg/L), DEHP (5.28±1.05 µg/L) and DiNP (3.44±0.74 µg/L). These may be attributed to the fact that Hat Yai city, where the waterworks is located is the most urbanized, industrialized and commercialized city in southern Thailand. The higher urbanization and industrialization in this area, may be the major factor responsible for the higher concentration of PAEs in the source water. This findings is consistent with previous studies that reported that PAEs concentration are usually higher in aquatic environment that are located in urban and industrialized areas as compared to those in suburban or rural (Bergé et al., 2013; He et al., 2013; Sun et al., 2013; Wang et al., 2014).

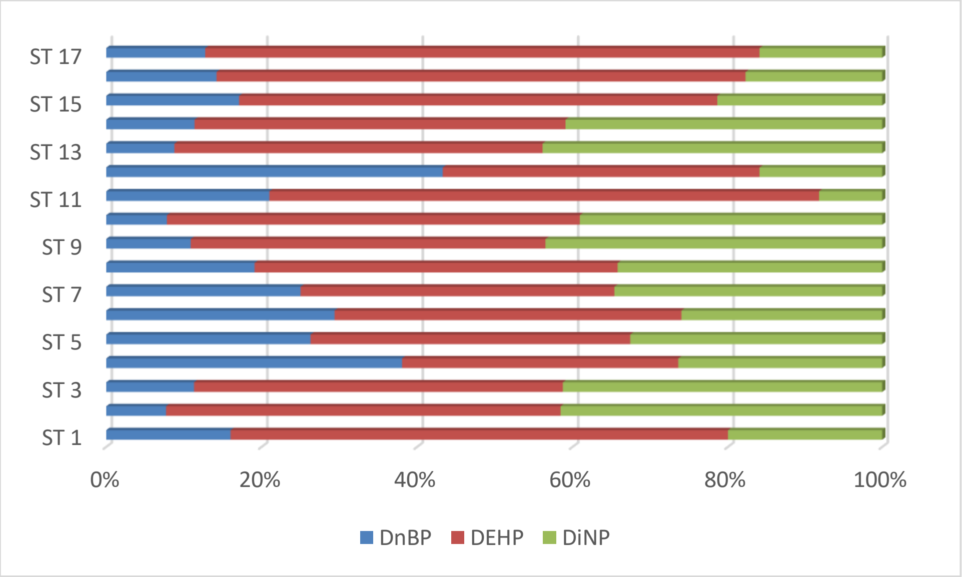

Figure 4.9: Relative concentration of PAEs in raw water samples from waterworks

4.3.3 PAEs in Waterworks

All the four water filtration plants which draw raw water from U-Tapao Canal was investigated in order to evaluate the fate or removal efficiency of the PAEs during the tap water treatment process. It is worthy of note that all the waterworks are conventional or traditional water filtration plants. Their mode of operation includes coagulation, sedimentation and filtration process, which are the typical process for tap water (Fig 2). The measured concentration of PAEs in the raw and Tap water of the four investigated waterworks are shown in Table 4.9 and 4.11. Three out of six PAEs were detected in raw water and finished tap water from the four waterworks. The three detected PAEs in raw water and finished tap water include DnBP, DEHP, and DiNP. The other 3 PAEs, including BBP, DnOP and DIDP, which were investigated were of minor significance in this study, because their concentrations were all below the limit of detection (LOD). In the raw water from the different waterworks, DnBP and DEHP levels in Hat Yai waterworks, located in urban area of the river were higher than the levels in the other three waterworks located in suburban region of the canal. As show in Table 4.10, indicated that the measured concentrations of the analyzed PAEs in tap water were below the USA tap waterstandards for DEHP (6.0 µg/L). Three of the PAEs congeners detected in tap water are used as plasticizers in plastic pipes and slats used in tap water distribution systems. The relatively elevated level of PAEs, especially DEHP in finished tap water may be largely contributed by the leaching of DEHP from Polyvinyl Chloride (PVC) pipes and slates, in public water distribution systems built with high-density polyethylene (HDPE) or PVC (Sulentic et al., 2018). Figure 4.10 shows that the removal efficiency of PAEs by these four waterworks ranged from 14.3% to 71%, which differed significantly without steady removal efficiencies. The lower removal efficiencies for DnBP, DEHP and DiNP were 42%, 14.3% and 16.4%. For all the waterworks, removal efficiencies obtained for the detected PAEs congener were not soundly efficient. These findings indicated that the traditional tap water treatment plants used in the study areas cannot show good performance to eradicate the PAEs congeners detected in the tap water, which is not influence by the level of PAEs pollution in the water source. Traditional, tap water treatment process concentrate on dealing with the particles and colloids in terms of physical processes. Many works of the environmental fate and transport characteristic of PAEs have reported that oxidation or microbial action is the major mechanism for their removal or elimination in the aquatic ecosystems (Yuan et al., 2002; Gavala et al., 2004; Yuan et al., 2008). Therefore, we recommend that the treatment processof tap water should be the combinations of the key techniques for removing PAEs from the raw water. Furthermore, since there is scanty of information on removal efficiencies of PAEs by both traditional and advance tap watertreatments in waterworks, the need for further research in this direction is imperative.

Table 4.11 PAEs concentration in tap water collected from U-Tapao Canal (µg/L), (n=4)

	Sadao (n=4)			Phang La (n=4)			Prik (n=4)			Hat Yai (n=4)		
	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD
DnBP	ND	0.98	0.93±0.07	ND	0.8	0.80±0.01	0.72	1.89	1.24±0.59	ND	2.70	2.2±0.71
DEHP	1.02	3.42	2.15±1.20	1.12	2.84	1.85±0.89	1.74	3.00	2.54±0.69	3.77	4.83	4.15±0.59
DiNP	ND	1.94	1.94±0.01	ND	1.64	1.54±0.14	ND	2.82	2.36±0.65	ND	2.80	2.36±0.62
BBP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-
DnOP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-
DIDP	ND	ND	-	ND	ND	-	ND	ND	-	ND	ND	-

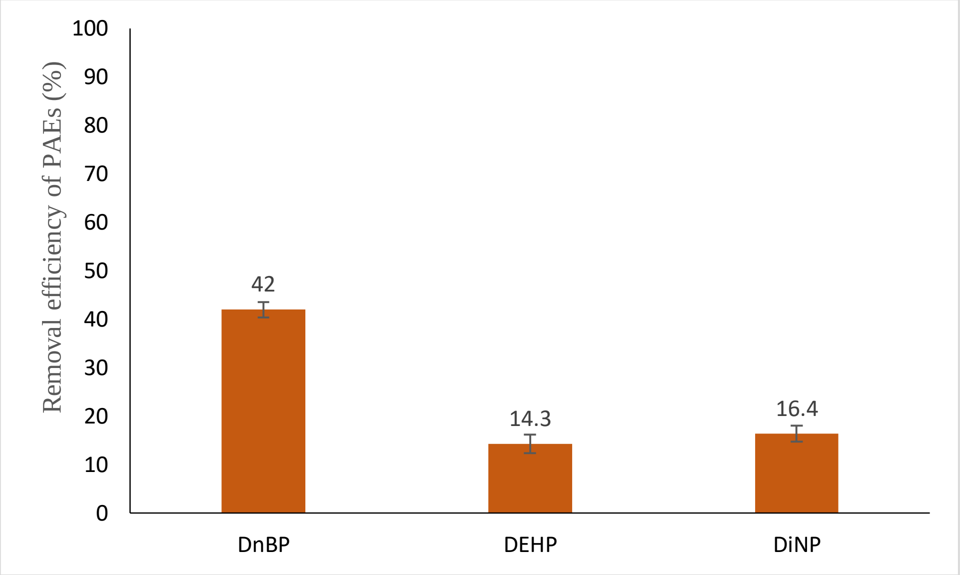

Figure 4.10 Removal efficiency of individual PAES from raw water

4.3.4. Exposure Assessment of PAEs in Water

In recent decades, the occurrence of PAEs in source water and tap water is generating serious public health concerns, majorly due to its endocrine disrupting activities (Shi et al., 2012; Tang et al., 2012; Liu et al., 2013). Tap water ingestion have been observed to be a significant source of human exposure in China (Ji et al. 2014). In order to evaluate the potential and harmful effects of PAEs in human via tap water, quality guidelines for source water and tap (drinking) water standard and tolerable daily intake (TDI) were used. The result of this present study indicated that the mean concentration of DEHP and DnBP were well below the Reference dose (RfD) of 8.0 µg/L and 3.0 µg/L respectively, for the surface water quality of China. Similarly, the mean concentration of DEHP in source water did not exceed the RfD values of 16 µg/L and 8.0 µg/L of the environmental quality standards of surface water in Canada and Korea, respectively.

On the other hand, the concentration of DEHP in public water supplies did not exceed the RfD of tap waterstandards such as DEHP 6.0 µg/L for USEPA, 8.0 µg/L of WHO, 8.0 µg/L of China. Likewise, the concentration of DnBP was lower than RfD of

3.0 µg/L of China. According to the results obtained in this study, the concentration of DnBP and DEHP in tap watersamples did not exceed any of the above RfDs.

Nevertheless, PAEs have been classified as endocrine disrupting organic chemical pollutants (EDCs). EDCs are chemicals that can adversely affects the normal functioning of endocrine systems in human as well as wildlife. These effects may not appear until the exposure becomes chronic or prolonged and may also be irreversible. According to the result of this work, PAEs were detected in tap water, which may be constantly ingested in daily life, suggesting that tap water is a significant source or pathway of human exposure to these endocrine disrupting organic contaminants. The human health risk assessment of PAEs via ingestion and bathing of tap water are presented in Table 4.12, 4.13, 4.114 and 4.115, 4.16 and 4.17, respectively. While Table 4.18, 4.19, 4.20 and 4.21, 4.22 and 4.23, respectively showed the hazard index of PAEs in children, adolescents and adults. Using the value of the mean concentration of each PAEs in tap water, the HQ for DnBP, DEHP and DiNP were below 1, indicating acceptable risk of PAEs via drinking and bathing of tap water. Which implies that none of these PAEs congeners will cause any bad health effects on adults, adolscents and children through ingestions or dermal contact. Similarly, the cancer risk evaluated for DEHP, the only PAEs congener classified as carcinogenic agent was lower than $1x10^{-6}$ indicating acceptable risk as stipulated by WHO (Fatoki et al., 2010). This suggest that the level of DEHP in the investigated tap water collected from the public tap water supply and distribution systems (waterworks) cannot trigger cancer risk in both children, adolescent and adults via drinking and bathing. Moreover, HI index of PAEs was evaluated to assess the cumulative effects of PAEs from both ingestion and bathing of tap water on children, adolescents and adults. The result indicated that the HI in all the waterworks were less than one, suggesting that the concentration of PAEs in tap water can not constitute cumulative health risk on children, adolscents and adults. However, DEHP poses higher health risk effects on human when compared to DnBP and DiNP.

Table 4.12 Health risk assessment of PAEs in adults via ingestion of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	LADD	RfD mg/kg/d	HQ	Slope factor	Cancer Risk
Sadao	DnBP	0.93	1.05×10^{-5}	1.10×10^{-5}	0.1	0.000151		
	DEHP	2.15	2.95×10^{-5}	2.15×10^{-5}	0.02	0.00147	0.014	3.161 x 10^{-7}
	DiNP	1.94	2.12×10^{-5}	2.28×10^{-5}	0.115	0.000271		
Phang La	DnBP	0.80	1.01×10^{-5}	1.08×10^{-5}	0.1	0.000148		
	DEHP	1.85	2.54×10^{-5}	1.85×10^{-5}	0.02	0.00127	0.014	2.590 x10^{-7}
	DiNP	1.54	1.99×10^{-5}	1.60×10^{-5}	0.115	0.000260		
Prik	DnBP	1.24	2.33×10^{-5}	1.70×10^{-5}	0.1	0.000233		
	DEHP	2.54	3.25×10^{-5}	2.59×10^{-5}	0.02	0.00178	0.014	3.626 x10^{-7}
	DiNP	2.36	3.10×10^{-5}	2.99×10^{-5}	0.115	0.000356		
Hat Yai	DnBP	2.20	3.43×10^{-5}	2.63×10^{-5}	0.1	0.000360		
	DEHP	4.15	5.29×10^{-5}	3.86×10^{-5}	0.02	0.00265	0.014	5.404 x10^{-7}
	DiNP	2.36	3.11×10^{-5}	3.00×10^{-5}	0.115	0.000357		

Table 4.13 Health risk assessment of PAEs in children via ingestion of tap water

Waterworks	PAEs	Mean (μg/L)	ADD	LADD	RfD mg/kg/d	HQ	Slope factor	Cancer Risk
Sadao	DnBP	0.93	1.08×10^{-5}	1.16×10^{-6}	0.1	0.000281		
	DEHP	2.15	3.18×10^{-5}	2.27×10^{-5}	0.02	0.00182	0.014	3.178 x10^{-7}
	DiNP	1.94	2.36×10^{-5}	2.40×10^{-5}	0.115	0.000235		
PhangLa	DnBP	0.80	1.02×10^{-5}	1.14×10^{-5}	0.1	0,000160		
	DEHP	1.85	2.63×10^{-5}	1.95×10^{-6}	0.02	0.00119	0.014	2.730 x10^{-7}
	DiNP	1.54	2.12×10^{-5}	2.30×10^{-5}	0.115	0.000199		
Prik	DnBP	1.24	2.11×10^{-5}	1.79×10^{-6}	0.1	0.000251		
	DEHP	2.54	3.72×10^{-5}	2.73×10^{-6}	0.02	0.00187	0.014	3.822 x10^{-8}
	DiNP	2.36	3.21×10^{-5}	3.15×10^{-5}	0.115	0.000362		
Hat Yai	DnBP	2.22	3.11×10^{-5}	2.77×10^{-5}	0.1	0.000166		
	DEHP	4.15	5.47×10^{-5}	4.07×10^{-6}	0.02	0.00281	0.014	5.698 x10^{-8}
	DiNP	2.36	3.42×10^{-5}	3.16×10^{-5}	0.115	0.000384		

Table 4.14 Health risk assessment of PAEs in adolescent via ingestion of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	LADD	RfD mg/kg/d	HQ	Slope *factor*	Cancer Risk
Sadao	DnBP	0.93	1.62×10^{-5}	9.78×10^{-7}	0.1	0.000162		
	DEHP	2.15	2.17×10^{-5}	1.59×10^{-6}	0.02	0.00114	0.014	$2.226 \text{ x } 10^{-8}$
	DiNP	1.94	2.72×10^{-5}	2.28×10^{-5}	0.115	0.000271		
Phangla	DnBP	0.80	1.01×10^{-5}	1.08×10^{-5}	0.1	0.000148		
	DEHP	1.85	2.44×10^{-5}	1.85×10^{-5}	0.02	0.00127	0.014	$2.590 \text{ x}10^{-7}$
	DiNP	1.54	1.99×10^{-5}	1.60×10^{-5}	0.115	0.000260		
Prik	DnBP	1.24	2.14×10^{-5}	1.70×10^{-5}	0.1	0.000233		
	DEHP	2.54	3.45×10^{-5}	2.59×10^{-5}	0.02	0.00187	0.014	$3.626 \text{ x}10^{-7}$
	DiNP	2.36	3.17×10^{-5}	2.99×10^{-5}	0.115	0.000362		
Hat Yai	DnBP	2.20	3.34×10^{-5}	2.63×10^{-5}	0.1	0.000360		
	DEHP	4.15	5.49×10^{-5}	3.86×10^{-5}	0.02	0.00265	0.014	$5.404 \text{ x}10^{-7}$
	DiNP	2.36	3.11×10^{-5}	2.80×10^{-5}	0.115	0.00357		

Table 4.15 Health risk assessment of PAEs in adults via bathing of tap water

Waterworks	PAEs	Mean (μg/L)	ADD	LADD	RfD mg/kg/d	HQ	Slope *factor*	Cancer Risk
Sadao	DnBP	0.93	8.66×10^{-4}	1.00×10^{-2}	0.1	0.00988		
	DEHP	2.15	2.17×10^{-5}	2.59×10^{-6}	0.02	0.00114	0.014	3626x 10^{-8}
	DiNP	1.94	2.86×10^{-5}	2.28×10^{-5}	0.115	0.000275		
Phangla	DnBP	0.80	1.03×10^{-5}	1.08×10^{-5}	0.1	0.000146		
	DEHP	1.85	2.74×10^{-5}	1.75×10^{-5}	0.02	0.00137	0.014	2.450 x10^{-7}
	DiNP	1.54	1.89×10^{-5}	1.60×10^{-5}	0.115	0.000251		
Prik	DnBP	1.24	2.01×10^{-5}	1.70×10^{-5}	0.1	0.000233		
	DEHP	2.54	3.25×10^{-5}	2.89×10^{-5}	0.02	0.00178	0.014	4.046 x10^{-7}
	DiNP	2.36	3.16×10^{-5}	2.99×10^{-5}	0.115	0.000357		
Hat Yai	DnBP	2.20	3.67×10^{-5}	2.63×10^{-5}	0.1	0.000367		
	DEHP	4.15	5.69×10^{-5}	3.74×10^{-5}	0.02	0.00265	0.014	5.236 x10^{-7}
	DiNP	2.80	3.88×10^{-5}	3.00×10^{-5}	0.115	0.000363		

Table 4.16 Health risk assessment of PAEs in children via bathing of tap water

Waterworks	PAEs	Mean *(µg/L)*	ADD	LADD	RfD mg/kg/d	HQ	Slope *factor*	Cancer Risk
Sadao	DnBP	0.93	1.04×10^{-5}	9.78×10^{-7}	0.1	0.000164		
	DEHP	2.15	2.17×10^{-5}	1.69×10^{-6}	0.02	0.00114	0.014	2.366 x 10^{-8}
	DiNP	1.94	2.86×10^{-5}	2.28×10^{-5}	0.115	0.000301		
Phangla	DnBP	0.80	1.08×10^{-5}	1.08×10^{-5}	0.1	0.000148		
	DEHP	1.85	2.47×10^{-5}	1.65×10^{-5}	0.02	0.00127	0.014	2.310 x10^{-7}
	DiNP	1.94	2.16×10^{-5}	1.60×10^{-5}	0.115	0.000257		
Prik	DnBP	1.24	2.16×10^{-5}	1.70×10^{-5}	0.1	0.000233		
	DEHP	2.54	3.25×10^{-5}	2.89×10^{-5}	0.02	0.00176	0.014	3.626 x10^{-7}
	DiNP	2.36	3.18×10^{-5}	2.99×10^{-5}	0.115	0.000362		
Hat Yai	DnBP	2.20	3.30×10^{-5}	2.63×10^{-5}	0.1	0.000166		
	DEHP	4.17	5.49×10^{-5}	3.86×10^{-5}	0.02	0.00281	0.014	7.868 x10^{-7}
	DiNP	2.36	3.31×10^{-5}	3.00×10^{-5}	0.115	0.000357		

Table 4.17 Health risk assessment of PAEs in adolescent via bathing of tap water

Waterworks	PAEs	Mean (μg/L)	ADD	LADD	RfD mg/kg/d	HQ	Slope factor	Cancer Risk
Sadao	DnBP	0.93	1.01×10^{-5}	9.78×10^{-7}	0.1	0.000281		
	DEHP	2.15	2.21×10^{-5}	1.59×10^{-6}	0.02	0.00182	0.014	$3.57\ \mathrm{x}\ 10^{-7}$
	DiNP	1.94	2.82×10^{-5}	2.28×10^{-5}	0.115	0.000235		
Phangla	DnBP	0.80	1.05×10^{-5}	1.08×10^{-5}	0.1	0.000148		
	DEHP	1.85	2.48×10^{-5}	1.85×10^{-5}	0.02	0.001195	0.014	$3.346\ \mathrm{x}10^{-7}$
	DiNP	1.54	1.79×10^{-5}	1.60×10^{-5}	0.115	0.000199		
Prik	DnBP	1.24	2.01×10^{-5}	1.70×10^{-5}	0.1	0.000233		
	DEHP	2.54	3.15×10^{-5}	2.59×10^{-5}	0.02	0.00187	0.014	$5.236\ \mathrm{x}10^{-7}$
	DiNP	2.36	3.45×10^{-5}	2.99×10^{-5}	0.115	0.000362		
Hat Yai	DnBP	2.20	3.60×10^{-5}	2.63×10^{-5}	0.1	0.000166		
	DEHP	4.15	5.59×10^{-5}	3.86×10^{-5}	0.02	0.00281	0.014	$7.868\ \mathrm{x}10^{-7}$
	DiNP	2.36	3.21×10^{-5}	3.00×10^{-5}	0.115	0.00366		

Hazard Index (HI) of PAEs via ingestion and bathing of tap water

Using the formular HI = ∑HQ, the HI of PAEs health risk of combine effects or mixture effects of PAEs via ingestion and bathing with tap water. Results are indicated below

Table 4.18 Hazard Index of PAEs in adults via ingestion of tap water

Waterworks	PAEs	Mean (μg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	1.05×10^{-5}	0.1	0.000151
	DEHP	2.15	2.95×10^{-5}	0.02	0.00147
	DiNP	1.94	2.12×10^{-5}	0.115	0.000271
Hazard Index of PAEs					0.001892
Phang La	DnBP	0.80	1.01×10^{-5}	0.1	0.000148
	DEHP	1.85	2.54×10^{-5}	0.02	0.00127
	DiNP	1.54	1.99×10^{-5}	0.115	0.000260
Hazard Index of PAEs					0.001678
Prik	DnBP	1.24	2.33×10^{-5}	0.1	0.000233
	DEHP	2.54	3.25×10^{-5}	0.02	0.00178
	DiNP	2.36	3.10×10^{-5}	0.115	0.000356
Hazard Index of PAEs					0.002369
Hat Yai	DnBP	2.20	3.43×10^{-5}	0.1	0.000360
	DEHP	4.15	5.29×10^{-5}	0.02	0.00265
	DiNP	2.36	3.11×10^{-5}	0.115	0.000357
Hazard Index of PAEs					0.003367

Table 4.19 Hazard Index of PAEs in adults via bathing of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	8.66×10^{-4}	0.1	0.00688
	DEHP	2.15	2.17×10^{-5}	0.02	0.00114
	DiNP	1.94	2.86×10^{-5}	0.115	0.000275
Hazard Index of PAEs					0.008295
Phangla	DnBP	0.80	1.03×10^{-5}	0.1	0.000146
	DEHP	1.85	2.74×10^{-5}	0.02	0.00137
	DiNP	1.54	1.89×10^{-5}	0.115	0.000251
Hazard Index of PAEs					0.001767
Prik	DnBP	1.24	2.01×10^{-5}	0.1	0.000233
	DEHP	2.54	3.25×10^{-5}	0.02	0.00178
	DiNP	2.36	3.16×10^{-5}	0.115	0.000357
Hazard Index of PAEs					0.00237
Hat Yai	DnBP	2.20	3.67×10^{-5}	0.1	0.000367
	DEHP	4.15	5.69×10^{-5}	0.02	0.00265
	DiNP	2.80	3.88×10^{-5}	0.115	0.000363
Hazard Index of PAEs					0.00338

Table 4.20 Hazard Index of PAEs in children via ingestion of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	$1.08×10^{-5}$	0.1	0.000281
	DEHP	2.15	$3.18×10^{-5}$	0.02	0.00182
	DiNP	1.94	$2.36 ×10^{-5}$	0.115	0.000235
Hazard Index of PAEs					0.002336
PhangLa	DnBP	0.80	$1.02×10^{-5}$	0.1	0,000160
	DEHP	1.85	$2.63×10^{-5}$	0.02	0.00119
	DiNP	1.54	$2.12 ×10^{-5}$	0.115	0.000199
Hazard Index of PAEs					0.001549
Prik	DnBP	1.24	$2.11×10^{-5}$	0.1	0.000251
	DEHP	2.54	$3.72 ×10^{-5}$	0.02	0.00187
	DiNP	2.36	$3.21×10^{-5}$	0.115	0.000362
Hazard Index of PAEs					0.002441
Hat Yai	DnBP	2.22	$3.11×10^{-5}$	0.1	0.000166
	DEHP	4.15	$5.47×10^{-5}$	0.02	0.00281
	DiNP	2.36	$3.42×10^{-5}$	0.115	0.000384
Hazard Index of PAEs					0.00336

Table 4.21 Hazard Index of PAEs in children via bathing of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	1.04×10^{-5}	0.1	0.000164
	DEHP	2.15	2.17×10^{-5}	0.02	0.00114
	DiNP	1.94	2.86×10^{-5}	0.115	0.000301
Hazard Index of PAEs					0.001605
Phangla	DnBP	0.80	1.08×10^{-5}	0.1	0.000148
	DEHP	1.85	2.47×10^{-5}	0.02	0.00127
	DiNP	1.94	2.16×10^{-5}	0.115	0.000257
Hazard Index of PAEs					0.001675
Prik	DnBP	1.24	2.16×10^{-5}	0.1	0.000233
	DEHP	2.54	3.25×10^{-5}	0.02	0.00176
	DiNP	2.36	3.18×10^{-5}	0.115	0.000362
Hazard Index of PAEs					0.002355
Hat Yai	DnBP	2.20	3.30×10^{-5}	0.1	0.000166
	DEHP	4.17	5.49×10^{-5}	0.02	0.00281
	DiNP	2.36	3.31×10^{-5}	0.115	0.000357
Hazard Index of PAEs					0.003333

Table 4.22 Hazard Index of PAEs in adolescent via ingestion of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	1.62×10^{-5}	0.1	0.000162
	DEHP	2.15	2.17×10^{-5}	0.02	0.00114
	DiNP	1.94	2.72×10^{-5}	0.115	0.000271
Hazard Index of PAEs					0.001573
Phangla	DnBP	0.80	1.01×10^{-5}	0.1	0.000148
	DEHP	1.85	2.44×10^{-5}	0.02	0.00127
	DiNP	1.54	1.99×10^{-5}	0.115	0.000260
Hazard of PAEs					0.001678
Prik	DnBP	1.24	2.14×10^{-5}	0.1	0.000233
	DEHP	2.54	3.45×10^{-5}	0.02	0.00187
	DiNP	2.36	3.17×10^{-5}	0.115	0.000362
Hazard Index of PAEs					0.002435
Hat Yai	DnBP	2.20	3.34×10^{-5}	0.1	0.000360
	DEHP	4.15	5.49×10^{-5}	0.02	0.00265
	DiNP	2.36	3.11×10^{-5}	0.115	0.00357
Hazard Index of PAEs					0.00658

Table 4.23 Hazard Index of PAEs in adolescent via bathing of tap water

Waterworks	PAEs	Mean (µg/L)	ADD	RfD mg/kg/d	HQ
Sadao	DnBP	0.93	1.01×10^{-5}	0.1	0.000281
	DEHP	2.15	2.21×10^{-5}	0.02	0.00182
	DiNP	1.94	2.82×10^{-5}	0.115	0.000235
Hazard Index of PAEs					0.002336
Phangla	DnBP	0.80	1.05×10^{-5}	0.1	0.000148
	DEHP	1.85	2.48×10^{-5}	0.02	0.001195
	DiNP	1.54	1.79×10^{-5}	0.115	0.000199
Hazard Index of PAE					0.001542
Prik	DnBP	1.24	2.01×10^{-5}	0.1	0.000233
	DEHP	2.54	3.15×10^{-5}	0.02	0.00187
	DiNP	2.36	3.45×10^{-5}	0.115	0.000362
Hazard Index of PAEs					0.002465
Hat Yai	DnBP	2.20	3.60×10^{-5}	0.1	0.000166
	DEHP	4.15	5.59×10^{-5}	0.02	0.00281
	DiNP	2.36	3.21×10^{-5}	0.115	0.00366
Hazard Index of PAEs					0.006636

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

The objectives of this study were to investigate the concentrations and distribution of PAEs in surface water and sediments of U-Tapao Canal in Songkhla Province, southern Thailand. In addition, human health risk and ecological risk of PAEs would also be assessed. A cross-sectional study was designed and was carried out during August 2018 to March 2019. Seventeen sampling sites were located from the beginning of the canal to the end of the canal which opens to Songkhla lake, the largest natural lagoon in Thailand. Samples of surface water and sediments were collected at each sampling sites (n=4) and were analyzed for quantities and specific congeners of PAEs by using GC-MS. In addition, samples of raw water and tap water were also collected from 4 waterworks which get their source water from U-Tapao Canal, including Sadao Waterworks, Phang La Waterworks, Prik Waterworks and Hat Yai Waterworks. Both raw water and tap water samples were also analyzed qualitatively and quantitatively for PAEs by using GC-MS. The health risk of PAEs in children, adolescents and adults via ingestions and bathing of tap water was evaluated by using EXPOFIRST, an exposure and health risk assessment model of USEPA. The potential ecological risk of PAEs in water was assessed using aquatic life criteria (ALC) and risk quotient methods. Whereas in sediments, the ecological risk of PAEs was evaluated by using five sediment quality guidelines (SQGs), including TEL, PEL, MPC, SRC_{eco} and ERLs. In addition, risk quotient method was also used in the ecological risk assessment of PAEs in sediments.

Three out of 6 PAE congeners measured in surface water, including DEHP, DiNP and DnBP were found. The remaining PAEs, including BBP, DnOP and DIDP, were not detected. The mean concentration of DEHP, DiNP and DnBP were 2.54±0.02µg/L (1.28-5.28 µg/L), 1.46±0.01 µg/L (ND-3.44 µg/L) and 0.985±0.04

µg/L (ND-3.36 µg/L), respectively. The highest concentrations of each PAE congener were all found at a sampling site located in Hat Yai City, the most urbanized city on the U-Tapao canal. The congener profile analysis showed that DEHP was the richest congener in surface water with frequency of detection= 100%, followed by DiNP (65%) and DnBP (41.2%). Using hierarchal cluster analysis, the sampling sites could be classified into two groups, group1 with relatively low concentrations of PAEs was located in rural areas, and group 2 with moderate to high concentrations of PAEs was located in urban areas.

Similarly, the highest mean concentrations of PAE congeners in raw water samples were detected at Hat Yai Waterworks which is located in Hat Yai city. They included DEHP = 4.07±1.05 µg/L, DiNP = 3.16±0.39 µg/L and DnBP = 2.77±0.83 µg/L. The lowest mean concentrations of PAEs in raw water samples were found at Phang La Waterwork, which is located in suburban area of the canal. Here the mean concentrations of DEHP = 1.95±0.068 µg/L, DiNP = 2.3±0.43 µg/L and DnBP = 1.14±0.08 µg/L. The highest mean concentrations of PAE congeners in tap water samples were found at Hat Yai Waterworks, including DEHP = 4.15±0.59 µg/L, DiNP = 2.36±0.62 µg/L and DnBP = 2.20±0.71 µg/L. The lowest mean concentrations of PAEs in tap water samples were found at Phang La Waterwork, including DEHP = 1.85±0.89 µg/L, DiNP = 1.54±0.14 µg/L and DnBP = 0.80±0.01 µg/L. The average removal efficiency of all 4 waterworks for DEHP, DiNP and DnBP were 14.3%, 16.4% and 43.0%, respectively. These waterworks used conventional process for tap water production including coagulation, flocculation, sedimentation, filtration and disinfection, respectively.

The ecological risk assessment of the ALC method showed that DEHP and DnBP posed a high risk (HQ>10) and moderate risk (1<HQ<10), respectively, on the investigated aquatic ecosystem. The RQ method revealed that DEHP posed a significant potential for adverse effects (10<RQ<100) on sensitive algae, a small potential for adverse effects (1<RQ<10) on crustacean and no significant risk (RQ<1) on fish. For DiNP, RQ values indicated a small potential for adverse effects (1<RQ<10) on sensitive crustaceans. The RQ values for DnBP indicated no significant risk (RQ<1) on sensitive aquatic biota.

In sediment analyses, similar to water analyses, 3 out of 6 PAE congeners were identified and quantified, including DEHP, DiNP and DnBP. The concentrations of DEHP, DiNP and DnBP in sediment samples ranged from 80±0.47 - 840±0.35 ng/g, ND - 790±0.58 ng/g and ND – 140±0.78 ng/g, respectively. The frequency of detection for individual PAE congeners followed the order of DEHP>DiNP > DnBP. Urbanization was found to influence the concentration and distribution of PAEs in sediments of U-Tapao canal. The estimated sedimentary transfer of PAEs were approximately 3.6 – 7.2 tons in five years. The ecological risk assessment using SQGs showed that DEHP posed a moderate risk on benthic organisms, while DnBP posed a low risk. Using the RQ method revealed that DEHP and DnBP posed low risk on algae, crustacean and fish, respectively, whereas DiNP posed a low risk on crustacean.

Human health risk assessment revealed that HQ of DnBP, DEHP and DiNP via ingestion or bathing of tap water were less than 1, indicating an acceptable risk of PAEs. In addition, the hazard index (HI) of total PAEs via ingestion and bathing of tap water were also less than 1 indicating an acceptable risk for children, adolescents and adults through ingestions and bathing of tap water. Similarly, evaluation of the cancer risk of DEHP, the only PAE congener classified as possible carcinogenic agent, showed acceptable risk ($< 1.0 \times 10^{-6}$) as stipulated by WHO.

In conclusion, the study revealed that the U-Tapao Canal was contaminated with DEHP, DiNP and DnBP to some extent. The level of DEHP contamination posed a moderate ecological risk, while those of DiNP and DnBP posed a low risk to the aquatic ecosystem. However, the levels of PAEs in tap water posed acceptable health risk of both carcinogenic and noncarcinogenic risks. Anyway, the moderate contamination of DEHP raised concerns over the adverse effect to the aquatic ecosystem of U-Tapao Canal since this canal is a major water resource for drinking water, balancing aquatic ecosystem, industrial and agricultural utilizations, and transfer PAEs to lower Songkhla lake which acts as a sink for the chemical to accumulate there. The endocrine disruptive effect of PAEs has a potential to cause infertility to aquatic animals, especially fishes, shrimps and crabs which are abundant there.To prevent negative impacts on local economy and food security, both point source and nonpoint source of PAEs should be strictly regulated and monitored continuously.

5.2 Recommendations

1) The baseline data of PAEs contamination in U-Tapao canal should be informed to policy makers and regulatory agencies in the formulation of policies and intervention measures as well as future sustainable strategies of the pollutant control along the U-Tapao canal network**.**
2) A survey program should be launched to identify and monitor all point sources and nonpoint sources of PAEs released to U-Tapao Canal. Pollution control measures should be planned among responsible government agencies, industries and communities along the canal. Active campaigns of keeping U-Tapao Canal clean should be launched together with strict enforcement of the relevant laws and regulations. Collaboration among the tripartite is essential to the sustainability of this mission.
3) Since PAEs was observed to leach from waste disposal sites into aquatic environment, especially during rainy season and high flooding episodes, all open dump sites should be destroyed or changed to lined landfills which must be constructed and operated in accordance to national and/or international standards

4) Suggested topics for future research projects:
    - Contamination of PAEs in aquatic biotas, surface water and sediments of Lower Songkhla Lake and ecological and human health risk assessment
    - Development of new technology for a wastewater treatment system that can eliminate PAEs more efficiently.
    - Development of new technology to reduce consumption, reuse and recycle of PAEs in consumer’s and industrial products.
    - Development of new process for tap water production with more efficient removal of PAEs in raw water.

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APPENDIX

Appendix:1

Procedure for determination of physicochemical properties of sediments

Procedure to determine EC

Method

1. 10 grams of sediment was placed in a 125 ml centrifuge tube.

2. 50 ml of deionized water was added the mixture was thoroughly homogenized by agitation for 1 hour, it was allowed to settle for 5 minutes.

3. The measurement of electrical conductivity of the sediment mixture in recorded by using EC meter.

Procedure to determine moisture Content

Sediment analysis will always be reported in an oven dried basis. Therefore, for quality result of sediment analysis, moisture content in the sediment is imperative.

Method

1. The moisture can was weighed and recorded value as W1.

2. 10 g of sediment sample was placed in the moisture can, weighed and recorded as W2

3 The sediment sample was baked in the oven at 105 ^{o}C overnight, removed from the oven and placed in a desiccator to cool to room temperature.

4. Thereafter, was weighed and value obtained recorded as W3

Moisture content was calculated by using equation 5

$$\%\ \text{Moisture Content} = (W_2-(W_3-W_1))/(W_3-W_1) \times 100 \qquad 5$$

In calculating the analysis value is in the form of an oven dried basis, therefore must be multiplied by

$$\text{Moisture correction factor (mcf)} = (100 + \%\ \text{MC}) / 100 \qquad 6$$

Procedure to determine organic Matter (OM) & organic Carbon (OC) (Walkley and Black 1998)

Chemicals

1**.** **1.0 normality (N)** is prepared of was prepared by dissolving 49**.**07g of $K_2Cr_2O_7$ **(**at the temperature in 1 litre of deionized water**.**

2. Conc**entrated** H_2SO_4 solution

3. $Fe(NH_4)_2(SO_4)_2.6H_2O$ 0.5 N of $Fe(NH_4)_2(SO_4)_2.6H_2O$ was prepared by adding 15ml of concentrated H2SO4 to 196.07g, it was allowed to cool and made up to a total volume 1liter with deionized water.

4. 10-phenanthroline ferrous sulfate indicator was prepared by dissolving 1.485 grams and 0.695 grams of FeSO4.7H2O in 100 ml of in deionized water stored in a brown bottle**.**

Method

1**.** 2 g sediments was placed in a 250 ml Erlenmayer flask**.**

2**.** 10 ml of 1.0 N $K_2Cr_2O_7$ was placed in the flask by using pipette, it was agitated for homogenous mixture**.**

3. 15 ml of concentrated H_2SO_4 was thoroughly mixed with 85ml deionized water for 30 minutes.

4. The indicator was added by dropping into the titrator with Fe^{2+} solution until the color of the suspension gradually turn into green and dark green. the, dropping was further continued until the Fe^{2+} solution until the color was changed to reddish brown.

5. Make Blank (Article 2-4).

Calculating

Determine the actual concentration of Fe^{2+} solution

$$N_1V_1 = N_2V_2 \qquad 7$$

Where**:**

N_1= the concentration of Fe^{2+} solution**.**

V_1= the volume of Fe^{2+} solution using Blank titration **(**ml**).**

N_2= the concentration of $K_2Cr_2O_7$ solution**.**

V_2= the volume of $K_2Cr_2O_7$ solution**.**

% Organic C = **((**N_2 x V_2**)-(**N_1 x V_1**))** x 0.399 x mcf/ wt**.**

% Organic Matter = **%** Organic C x 1.**7**2 8

Procedure to determine total phosphorus (Total P) using Spectrophotometric Method (Walkely and black 19908)

Chemicals

1. Concentrated $HClO_4$

2. Color reagent

2.1 0.1% antimony potassium tartrate

2.2 0.8 M of H_3BO_3 was prepared by dissolving 24**.**73 grams in 350 mls of deionized water, the mixture was heated on hot plate until it is melted and then made up to 500ml with deionized water**.**

2**.**3 Ammonium molybdate was prepared by dissolving 15g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 250ml deionized water, 140 ml of concentration of H_2SO_4 was added and allowed to cool and was made up to 500ml, stored in brown bottle.

Mixing 30ml of ammonium molybdate and 90 ml of 0**.**8M of H_3BO_3 in 330ml deionized water with 30ml of 0**.**1**%** of and antimony potassium tartate, the solutions were thoroughly mixed together and stored in brown bottles**.**

3. 0.5% Ascorbic acid

4. Standard P concentration (1000 mg / l)

5. Standard P concentration (10 mg / l)

Method

1**.** 2 grams of sediments sample was placed in the 125 ml Erlenmayer flask and mixed with 10 ml of $HClO_4$**.**

2**.** Glass cone was used to cover the flask to prevent splashes**.** It was heated on the hot plate by gradually increasing the temperature and digested until the solution becomes clear**.**

3. The temperature was allowed to cool down to room temperature and transferred to 100 ml volumetric flask and made up to 100ml of deionized water.
4. 5 ml of 0.5% Ascorbic acid and 5ml of color reagent was placed in 25 ml volumetric flask.
5. 10 mg/l of standard solution P was used to obtain serial dilutions of 0, 0.2, 0.4, 0.6, 0.8, 1.0 mg/L, respectively.
6. 2 ml of blank solution was placed in volumetric flask containing 5ml of 0.5% of ascorbic acid.
7. The absorbance was read by using a wavelength of 720 nm in Spectrophotmeter
8. Using a standard chart the absorbance value and the concentration of P in the standard solution was recorded.

Calculating

Total P (mg/kg soil) = 100x25 (X – b)/V x Wt

Where X = the concentration of P in the sample solution Compared from the standard chart (Mg / l)

b = the concentration of P in blank compared to the standard chart (Mg / l)

V =The volume of sample solution used (ml)

Procedure to evaluate sediment texture

Hydrometer Method

Chemicals

1. Calgon solution was prepared by dissolving 50 grams of sodium hexa-metaphosphate and 8.3 gram of Na_2CO_3 in 1 litre of deionized water.

2. 30% Hydrogen peroxide (H_2O_2)

3. Amyl alcohol

Method

1. 50 grams of sediments was placed in a 500 ml beaker, weighed (W1) and recorded as W1
2. Organic matter was digested by adding 5ml of of hydrogen perioxide and deionized water to the sediment sample in the beaker and heated on hot plate to achieve complete digestion of organic matter.
3. The sediment mixture was baked at 105 ° C for 2 nights (until the weight is constant), weighed and recorded as W2
4. 200 ml of deionized water and 100 ml of Calgon was added and mixed by using stirring rod and allowed to settle for 10 minutes.
5. Sediments was aggregated into smaller particles by ultrasonic disperser for 3 minutes.
6. Aggregated sediment samples was sprayed with deionized water and made up to 1 litret and drpos Amyl Alcohol was used to remove bubbles.
7. Blank solutions was prepared by adding 100 ml of Calgon solution in a 1 liter measuring cylinder and made up to 1 liter with deionized water.
8. A plunger was used to agitate the sediment samples for 10 minutes.
9. Hydrometer was gently dip into the sediments mixture and reading recorded at intervals of 50 seconds and 2 hours. Temperature of the sediment samples was also recorded at intervals of 50 seconds and 2 hours.

Calculating

$R_c = A - 0.5\,(T - B)$

Where R_c= Calgon's value after adjusting the temperature (g / L).

A= the value that can be read from the hydrometer of blank (g / L) at 50 s or 2 h.

T= the temperature of the soil solution (°C) at 50 seconds or 2 hours.

B= the temperature of the Calgon solution (blank) (°C) at 50 s or 2 h.

$R_s = R - R_c$

Where R= the value that can be read from the hydrometer at 50 s or 2s.

$R_s' = R_s + 0.36\,(T - 20)$

Where T= the temperature of the soil solution (°C) when 50 s or 2 hours

Calculating the soil particle size

% clay = Rs'(2hr) x 100/soil wt.

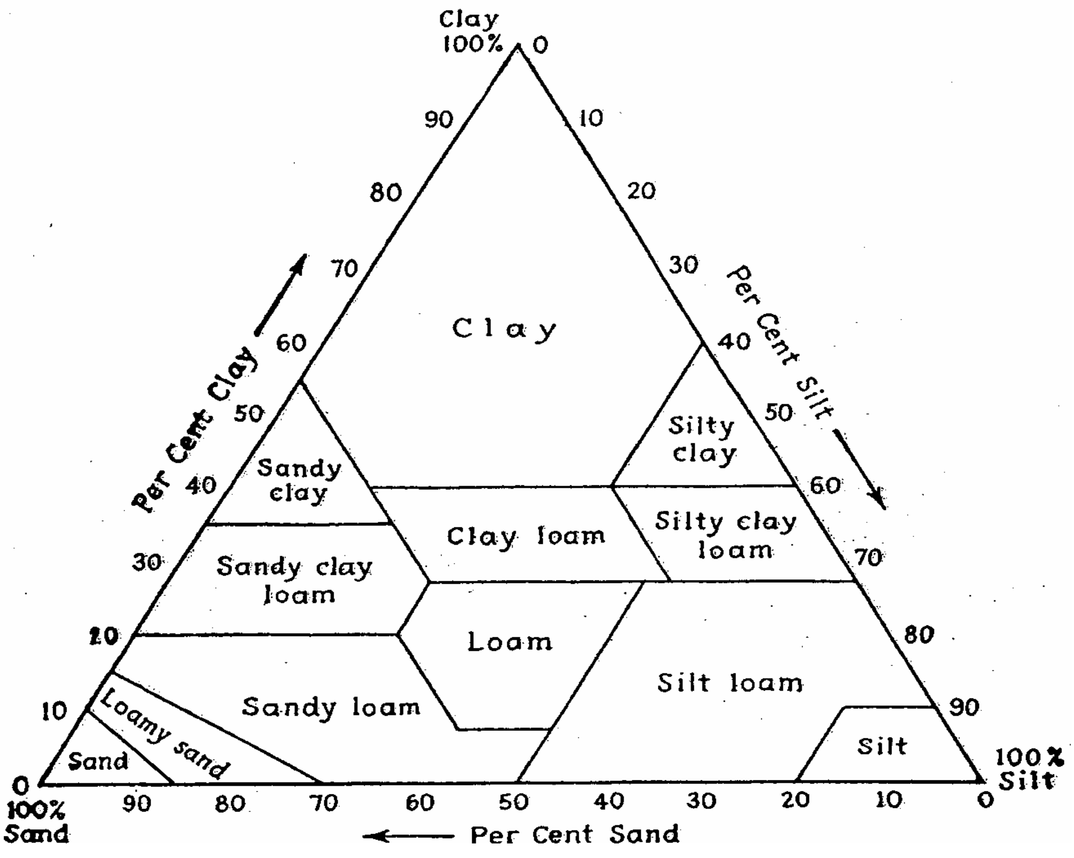
% silt = [Rs'(50 sec) - Rs'(2hr)] x 100/soil wt.

=100 - (% sand + % clay)

% sand = [ms - Rs'(50sec)] x 100/soil wt.

Where ms= soil wt. = $W_2 - W_1$ 10

Take the % clay, % silt and % sand values to compare the soil texture from the standard triangle diagram



Standard triangle diagram for sediment texture classification

Appendix 2: HQ values of PAEs in surface water

Sites	DnBP	DEHP
ST 1	0.645161	40
ST 2	0.645161	66
ST 3	0.645161	42
ST 4	4.83871	70
ST 5	2.967742	72
ST 6	3.354839	79
ST 7	1.677419	42
ST 8	2.16129	82
ST 9	0.645161	42
ST 10	0.645161	68
ST 11	2.064516	108
ST 12	2.193548	32
ST 13	0.645161	54
ST 14	0.645161	42
ST 15	0.645161	36
ST 16	0.645161	48
ST 17	0.645161	56

Appendix3: RQ values of PAEs in water

Site	DnBP A	DnBPC	DnBP F	DEHP A	DEHP C	DEHP F	DiNP C
ST 1	0.019048	0.015385	0.04	16	1.904762	0.266667	1.470588
ST 2	0.019048	0.015385	0.04	26.4	3.142857	0.44	6.352941
ST 3	0.019048	0.015385	0.04	16.8	2	0.28	4.294118
ST 4	0.142857	0.115385	0.3	28	3.333333	0.466667	6.117647
ST 5	0.087619	0.070769	0.184	28.8	3.428571	0.48	6.705882
ST 6	0.099048	0.08	0.208	31.6	3.761905	0.526667	5.411765
ST 7	0.049524	0.04	0.104	16.8	2	0.28	4.235294
ST 8	0.06381	0.051538	0.134	32.8	3.904762	0.546667	7.058824
ST 9	0.019048	0.015385	0.04	16.8	2	0.28	4.705882
ST 10	0.019048	0.015385	0.04	27.2	3.238095	0.453333	5.882353
ST 11	0.060952	0.049231	0.128	43.2	5.142857	0.72	1.470588
ST 12	0.064762	0.052308	0.136	12.8	1.52381	0.213333	1.470588
ST 13	0.019048	0.015385	0.04	21.6	2.571429	0.36	5.882353
ST 14	0.019048	0.015385	0.04	16.8	2	0.28	4.235294
ST 15	0.019048	0.015385	0.04	14.4	1.714286	0.24	1.470588
ST 16	0.019048	0.015385	0.04	19.2	2.285714	0.32	1.470588
ST 17	0.019048	0.015385	0.04	22.4	2.666667	0.373333	1.470588

Appendix 4: RQ values of PAEs in sediments

DnBP A	DnBP C	DnBP F	DEHP A	DEHP C	DEHP F	DiNP C
0.002146	0.001736	0.004505	0.058462	0.013971	0.005846	2.76E-05
0.025751	0.020833	0.054054	0.061538	0.014706	0.006154	2.76E-05
0.034335	0.027778	0.072072	0.104615	0.025	0.010462	0.002536
0.055794	0.045139	0.117117	0.172308	0.041176	0.017231	0.004355
0.04721	0.038194	0.099099	0.083077	0.019853	0.008308	0.002646
0.017167	0.013889	0.036036	0.061538	0.014706	0.006154	0.002536
0.021459	0.017361	0.045045	0.08	0.019118	0.008	0.003197
0.051502	0.041667	0.108108	0.166154	0.039706	0.016615	0.003969
0.034335	0.027778	0.072072	0.166154	0.039706	0.016615	0.003749
0.017167	0.013889	0.036036	0.132308	0.031618	0.013231	0.003693
0.002146	0.001736	0.004505	0.258462	0.061765	0.025846	0.00419
0.002146	0.001736	0.004505	0.092308	0.022059	0.009231	0.001599
0.002146	0.001736	0.004505	0.027692	0.006618	0.002769	0.0000276
0.002146	0.001736	0.004505	0.04	0.009559	0.004	0.0000276
0.002175	0.036667	0.003406	0.062188	0.012723	0.004676	0.0000542
0.037854	0.024432	0.002611	0.016782	0.015609	0.005987	0.0000672
0.002126	0.001675	0.005732	0.007654	0.021165	0.007541	0.000872

Appendix 5 Details of selected sites

Sites	DnBP	DEHP	DiNP	∑PAEs
ST1	508	2344	3085	5937
ST2	999	5045	5765	11809
ST3	354	1843	5788	7985
ST4	760	3275	4620	8655
ST5	1110	2700	4800	8610
ST6	222	1111	2556	3889
ST7	ND	2167	4833	7000
ST8	ND	3293	4390	7683
ST9	ND	1888	2378	4266
ST10	158	1700	2648	4506
ST11	100	275	Nd	375
SST12	540	1981	ND	2521
ST13	376	2258	2043	4677
ST14	316	1422	632	2370
ST15	280	1888	4390	8415
ST16	ND	431	ND	431
ST17	199	591	299	1089

Appendix 6 Values of PAEs using 10% OM Normalization

SITES	latitude	longitude	Urban	Rural	Population	subdisricts
ST 1	6.979739	100.4634	/		46,184	Kor Hong
ST 2	6.97974	100.4634	/		46184	Kor Ho
ST 3	7.002145	100.456	/		14,499	Sam Nak Teaw
ST 4	6.673192	100.4334	/		21,753	Sadao
ST 5	6.639564	100.4361		/	14,500	Sam Nak Teaw
ST 6	6.931202	100.4399	/		25,128	Ban Pru
ST 7	6.59652	100.487	/		14,178	Sam Nak Kham
ST 8	7.108381	100.465	/	/	2,261	Mae Thorn
ST 9	6.705086	100.4332	/		11,831	Prik
ST10	7.075167	100.4758	/		38,156	Khlonghae
ST11	6.823206	100.438	/	/	6,934	Tha Pho
ST12	6.779266	100.4439	/		11,831	Prik
ST13	6.602124	100.4069	/		158,910	Hat Yai
ST14	6.856377	100.4645		/	7,790	Pa Tong
ST15	7.033356	100.4524		/	2,994	Khlong U-Tapao
ST16	6.823206	100.438		/	4,406	Pang La
ST17	7.126859	100.4555		/	3,766	Bangklam

Appendix 7 Calculation of Inentory of PAEs in sediments

$Inventory = C \times p \times A \times D \times a$ 13

C (ng/g) mean concentrations of total PAEs in the sediment = 772.06 ng/g

ρ (g/cm^3) dry density of the sediment = 1 g/cm^3

A (cm^2) area of U-Tapao subbasin = 2393 km

D (cm/y) sedimentation rate = 0.78 cm/y

a (y) number of years considered in the inventory = 5 yrs

772.06 × 1 × 2393 × 0.78 × 5 = 7205404.362

Convert to tons = 7205404.362/1000000 = 7.2 tons

Uncertanity of 50% 7.2 ton = 3.6 tons

Appendix 8 Health risk assessment of PAEs results by EXPOFIRST MODEL

SADAO WATERWORKDnBP via ingestion of tap water

DnBP VIA TAP WATER INGESTION SADAO WW

Exposure Group	Data Type	Result	Units
Birth to < 70 years	ADD	2.92E-05	mg/kg-day
Birth to < 1 month	ADD	1.12E-04	mg/kg-day
1 month to < 3 months	ADD	1.04E-04	mg/kg-day
3 months to < 6 months	ADD	1.12E-04	mg/kg-day
6 months to < 1 year	ADD	8.86E-05	mg/kg-day
1 year to < 2 years	ADD	4.97E-05	mg/kg-day
2 years to < 3 years	ADD	4.97E-05	mg/kg-day
3 years to < 6 years	ADD	3.89E-05	mg/kg-day
6 years to < 11 years	ADD	3.02E-05	mg/kg-day
11 years to < 16 years	ADD	2.16E-05	mg/kg-day
16 years to < 21 years	ADD	1.94E-05	mg/kg-day
21 years to < 70 years	ADD	2.81E-05	mg/kg-day

DEHP VIA TAP WATER INGES IN SADAOWW

Exposure Group	Data Type	Result	Units
Birth to < 70 years	ADD	4.70E-05	mg/kg-day
Birth to < 1 month	ADD	3.84E-04	mg/kg-day
1 month to < 3 months	ADD	3.33E-04	mg/kg-day
3 months to < 6 months	ADD	2.24E-04	mg/kg-day
6 months to < 1 year	ADD	1.48E-04	mg/kg-day
1 year to < 2 years	ADD	7.56E-05	mg/kg-day
2 years to < 3 years	ADD	7.28E-05	mg/kg-day
3 years to < 6 years	ADD	5.88E-05	mg/kg-day
6 years to < 11 years	ADD	4.76E-05	mg/kg-day
11 years to < 16 years	ADD	3.36E-05	mg/kg-day
16 years to < 21 years	ADD	2.97E-05	mg/kg-day
21 years to < 70 years	ADD	4.48E-05	mg/kg-day

DEHP VIA TAP WATER INGES SADAOWW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	LADD	3.79E-05	mg/kg-day

DiNP via tap water SADAO WW

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.82E-05	mg/kg-day
Birth to < 1 month	ADD	1.08E-04	mg/kg-day
1 month to < 3 months	ADD	9.98E-05	mg/kg-day
3 months to < 6 months	ADD	1.08E-04	mg/kg-day
6 months to < 1 year	ADD	8.53E-05	mg/kg-day
1 year to < 2 years	ADD	4.78E-05	mg/kg-day
2 years to < 3 years	ADD	4.78E-05	mg/kg-day
3 years to < 6 years	ADD	3.74E-05	mg/kg-day
6 years to < 11 years	ADD	2.91E-05	mg/kg-day
11 years to < 16 years	ADD	2.08E-05	mg/kg-day
16 years to < 21 years	ADD	1.87E-05	mg/kg-day
21 years to < 70 years	ADD	2.70E-05	mg/kg-day

DnBP via Tap water HAT YAI WW

qry_results

Data Type	**Exposure Group**	**Result**	**Units**
ADD	Birth to < 70 years	1.73E-05	mg/kg-day
ADD	Birth to < 1 month	6.66E-05	mg/kg-day
ADD	1 month to < 3 months	6.14E-05	mg/kg-day
ADD	3 months to < 6 months	6.66E-05	mg/kg-day
ADD	6 months to < 1 year	5.25E-05	mg/kg-day
ADD	1 year to < 2 years	2.94E-05	mg/kg-day
ADD	2 years to < 3 years	2.94E-05	mg/kg-day
ADD	3 years to < 6 years	2.30E-05	mg/kg-day
ADD	6 years to < 11 years	1.79E-05	mg/kg-day
ADD	11 years to < 16 years	1.28E-05	mg/kg-day
ADD	16 years to < 21 years	1.15E-05	mg/kg-day
ADD	21 years to < 70 years	1.66E-05	mg/kg-day

DEHP via tap water in Hat Yai WW

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	5.85E-05	mg/kg-day
Birth to < 1 month	ADD	2.25E-04	mg/kg-day
1 month to < 3 months	ADD	2.07E-04	mg/kg-day
3 months to < 6 months	ADD	2.25E-04	mg/kg-day
6 months to < 1 year	ADD	1.77E-04	mg/kg-day
1 year to < 2 years	ADD	9.94E-05	mg/kg-day
2 years to < 3 years	ADD	9.94E-05	mg/kg-day
3 years to < 6 years	ADD	7.78E-05	mg/kg-day
6 years to < 11 years	ADD	6.05E-05	mg/kg-day
11 years to < 16 years	ADD	4.32E-05	mg/kg-day
16 years to < 21 years	ADD	3.89E-05	mg/kg-day
21 years to < 70 years	ADD	5.62E-05	mg/kg-day

DEHP via tap water in Hat Yai (LADD)

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	LADD	5.85E-05	mg/kg-day

DEHP via Tap water

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	3.90E-05	mg/kg-day
Birth to < 1 month	ADD	1.50E-04	mg/kg-day
1 month to < 3 months	ADD	1.38E-04	mg/kg-day
3 months to < 6 months	ADD	1.50E-04	mg/kg-day
6 months to < 1 year	ADD	1.18E-04	mg/kg-day
1 year to < 2 years	ADD	6.62E-05	mg/kg-day
2 years to < 3 years	ADD	6.62E-05	mg/kg-day
3 years to < 6 years	ADD	5.18E-05	mg/kg-day
6 years to < 11 years	ADD	4.03E-05	mg/kg-day
11 years to < 16 years	ADD	2.88E-05	mg/kg-day
16 years to < 21 years	ADD	2.59E-05	mg/kg-day
21 years to < 70 years	ADD	3.74E-05	mg/kg-day

DEHP via tap water PRIKWW

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	LADD	3.90E-05	mg/kg-day

DiNP via Tap water PRIK

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	4.33E-05	mg/kg-day
Birth to < 1 month	ADD	1.66E-04	mg/kg-day
1 month to < 3 months	ADD	1.54E-04	mg/kg-day
3 months to < 6 months	ADD	1.66E-04	mg/kg-day
6 months to < 1 year	ADD	1.31E-04	mg/kg-day
1 year to < 2 years	ADD	7.36E-05	mg/kg-day
2 years to < 3 years	ADD	7.36E-05	mg/kg-day
3 years to < 6 years	ADD	5.76E-05	mg/kg-day
6 years to < 11 years	ADD	4.48E-05	mg/kg-day
11 years to < 16 years	ADD	3.20E-05	mg/kg-day
16 years to < 21 years	ADD	2.88E-05	mg/kg-day
21 years to < 70 years	ADD	4.16E-05	mg/kg-day

DEHP via Tap water Phang LA

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.49E-05	mg/kg-day

qry_results			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 1 month	ADD	9.57E-05	mg/kg-day
1 month to < 3 months	ADD	8.83E-05	mg/kg-day
3 months to < 6 months	ADD	9.57E-05	mg/kg-day
6 months to < 1 year	ADD	7.54E-05	mg/kg-day
1 year to < 2 years	ADD	4.23E-05	mg/kg-day
2 years to < 3 years	ADD	4.23E-05	mg/kg-day
3 years to < 6 years	ADD	3.31E-05	mg/kg-day
6 years to < 11 years	ADD	2.58E-05	mg/kg-day
11 years to < 16 years	ADD	1.84E-05	mg/kg-day
16 years to < 21 years	ADD	1.66E-05	mg/kg-day
21 years to < 70 years	ADD	2.39E-05	mg/kg-day

DEHP via Tap water in PRIK WW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	LADD	2.49E-05	mg/kg-day

DiNP via Tap water in PRIK WW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.38E-05	mg/kg-day
Birth to < 1 month	ADD	9.15E-05	mg/kg-day
1 month to < 3 months	ADD	8.45E-05	mg/kg-day
3 months to < 6 months	ADD	9.15E-05	mg/kg-day
6 months to < 1 year	ADD	7.22E-05	mg/kg-day
1 year to < 2 years	ADD	4.05E-05	mg/kg-day

DiNP via Tap water in PRIK WW			
Exposure Group	**Data Type**	**Result**	**Units**
2 years to < 3 years	ADD	4.05E-05	mg/kg-day
3 years to < 6 years	ADD	3.17E-05	mg/kg-day
6 years to < 11years	ADD	2.46E-05	mg/kg-day
11 years to < 16 years	ADD	1.76E-05	mg/kg-day
16 years to < 21 years	ADD	1.58E-05	mg/kg-day
21 years to < 70 years	ADD	2.29E-05	mg/kg-day

SADAO DnBP TAP WATER VIA INGESTION

DnBP TAP WATER 2C			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.92E-05	mg/kg-day
Birth to < 1 month	ADD	1.12E-04	mg/kg-day
1 month to < 3 months	ADD	1.04E-04	mg/kg-day
3 months to < 6 months	ADD	1.12E-04	mg/kg-day
6 months to < 1 year	ADD	8.86E-05	mg/kg-day
1 year to < 2 years	ADD	4.97E-05	mg/kg-day
2 years to < 3 years	ADD	4.97E-05	mg/kg-day
3 years to < 6 years	ADD	3.89E-05	mg/kg-day
6 years to < 11 years	ADD	3.02E-05	mg/kg-day
11 years to < 16 years	ADD	2.16E-05	mg/kg-day
16 years to < 21 years	ADD	1.94E-05	mg/kg-day
21 years to < 70 years	ADD	2.81E-05	mg/kg-day

DnBP TAP W SADAO 2C			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	1.97E-05	mg/kg-day

DEHP TAP WATER SADAO 2c			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	3.79E-05	mg/kg-day
Birth to < 1 month	ADD	1.46E-04	mg/kg-day
1 month to < 3 months	ADD	1.34E-04	mg/kg-day
3 months to < 6 months	ADD	1.46E-04	mg/kg-day
6 months to < 1 year	ADD	1.15E-04	mg/kg-day
1 year to < 2 years	ADD	6.44E-05	mg/kg-day
2 years to < 3 years	ADD	6.44E-05	mg/kg-day
3 years to < 6 years	ADD	5.04E-05	mg/kg-day
6 years to < 11 years	ADD	3.92E-05	mg/kg-day
11 years to < 16 years	ADD	2.80E-05	mg/kg-day
16 years to < 21 years	ADD	2.52E-05	mg/kg-day
21 years to < 70 years	ADD	3.64E-05	mg/kg-day

DEHP INGESTION VIA TAP WATER SADAO			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	2.55E-05	mg/kg-day

DiNP INGESTION VIA TAP WATER SADAO WW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.82E-05	mg/kg-day
Birth to < 1 month	ADD	1.08E-04	mg/kg-day
1 month to < 3 months	ADD	9.98E-05	mg/kg-day
3 months to < 6 months	ADD	1.08E-04	mg/kg-day
6 months to < 1 year	ADD	8.53E-05	mg/kg-day
1 year to < 2 years	ADD	4.78E-05	mg/kg-day
2 years to < 3 years	ADD	4.78E-05	mg/kg-day
3 years to < 6 years	ADD	3.74E-05	mg/kg-day
6 years to < 11 years	ADD	2.91E-05	mg/kg-day
11 years to < 16 years	ADD	2.08E-05	mg/kg-day
16 years to < 21 years	ADD	1.87E-05	mg/kg-day
21 years to < 70 years	ADD	2.70E-05	mg/kg-day

DiNP INGESTION VIA TAP WATER SADAO WW			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	1.89E-05	mg/kg-day

PHLANG LA WATERWORKS

DEHP INGESTION VIA TAP WATER PLWW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	2.49E-05	mg/kg-day
Birth to < 1 month	ADD	9.57E-05	mg/kg-day
1 month to < 3 months	ADD	8.83E-05	mg/kg-day
3 months to < 6 months	ADD	9.57E-05	mg/kg-day
6 months to < 1 year	ADD	7.54E-05	mg/kg-day
1 year to < 2 years	ADD	4.23E-05	mg/kg-day
2 years to < 3 years	ADD	4.23E-05	mg/kg-day
3 years to < 6 years	ADD	3.31E-05	mg/kg-day
6 years to < 11 years	ADD	2.58E-05	mg/kg-day
11 years to < 16 years	ADD	1.84E-05	/mg/kg-day
16 years to < 21 years	ADD	1.66E-05	mg/kg-day
21 years to < 70 years	ADD	2.39E-05	mg/kg-day

DEHP VIA ING TAP WATER PLWW			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	1.67E-05	mg/kg-day

DiNP ING VIA TAP WATER PLWW			
Exposure Group	**DataType**	**Result**	**Units**
Birth to < 70 years	ADD	2.38E-05	mg/kg-day
Birth to < 1 month	ADD	9.15E-05	mg/kgday
1 month to < 3 months	ADD	8.45E-05	mg/kg-day
3 months to < 6 months	ADD	9.15E-05	mg/kg-day
6 months to < 1 year	ADD	7.22E-05	mg/kg-day
1 year to < 2 years	ADD	4.05E-05	mg/kg-day
2 years to < 3 years	ADD	4.05E-05	mg/kg-day
3 years to < 6 yars	ADD	3.17E-05	mg/kg-day
6 years to < 11 ears	ADD	2.46E-05	mg/kg-day
11 years to < 16 years	ADD	1.76E-05	mg/kg-day
16 years to < 21 years	ADD	1.58E-05	mg/kg-day
21 years to < 70 years	ADD	2.29E-05	mg/kg-day

PRIK WATERWORKS

DEHP VIA INGESTION OF TAP WATER PRWW			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	3.90E-05	mg/kg-day
Birth to < 1 month	ADD	1.50E-04	mg/kg-day
1 month to < 3 months	ADD	1.38E-04	mg/kg-day
3 months to < 6 months	ADD	1.50E-04	mg/kg-day
6 months to < 1 year	ADD	1.18E-04	mg/kg-day
1 year to < 2 years	ADD	6.62E-05	mg/kg-day
2 years to < 3 years	ADD	6.62E-05	mg/kg-day
3 years to < 6 years	ADD	5.18E-05	mg/kg-day
6 years to < 11 ears	AD	4.03E-05	mg/kg-day
11 years to < 16 years	ADD	2.88E-0	mg/kg-day
16 years to < 21 years	ADD	2.59E-05	mg/kg-day
21 years to < 70 years	ADD	3.74E-05	mg/kg-day

DEHP INGESTION VIA TAP WATER IN PRIK			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	2.62E-05	mg/kg-day

HAT YAI WATERWORK

DnBP INGESTION VIA TAP WATER HATYAI			
Exposure Group	**Data Type**	**Result**	**Units**
Birth to < 70 years	ADD	1.73E-05	mg/kg-day
Birth to < 1 month	ADD	6.66E-05	mg/kg-day
1 month to < 3 months	ADD	6.14E-05	mg/kg-day
3months to < 6 months	ADD	6.66E-05	mg/kg-day
6 months to < 1 year	ADD	5.25E-05	mg/kg-day
1 year to < 2 years	ADD	2.94E-0	mg/kg-day
2 years to < 3 yars	ADD	2.94E-05	mg/kg-day
3 years to < 6 years	ADD	2.30E-05	mg/kg-day
6 years to < 11 ears	ADD	1.79E-05	mg/kg-day
11 years to < 16 years	ADD	1.28E-05	mg/kg-day
16 years to < 21 years	ADD	1.15E-05	mg/kg-day
21 years to < 70 years	ADD	1.66E-05	mg/kg-day

DnBP INGESTION VIA TAPWATER HATYAI			
Exposure Group	**Data Type**	**Result**	**Units**
21 years to < 70 years	LADD	1.16E-05	mg/kg-day

Appendix 8: Pictures of field work

VITAE

Name Okpara Kingsley Ezechukwu

Student ID 5910930019

Educational Attainment

Degree	Name of Institution	Year of Graduation
Master's degree	Imo State University, Nigeria	2008
Bachelor's degree	University of Port Harcourt Nigeria	2006
Higher National Diploma	University of Port Harcourt Nigeria	1998

Scholarship Awards during Enrolment

1. Grant by Higher Education Research Promotion, Thailand's Education Hub for Southern Region of ASEAN Countries Project Office of Higher Education Commission (THE-AC) (THE-AC/053/2016).
2. Thesis support grant by Graduate school, Prince of Songkla University, Hat Yai Thailand.

Work – Position and Address (If Possible)

Chief Lecturer: Rivers State College of Health Science and Management Technology, Port Harcourt, Nigeria.

List of Publication and Proceeding (If Possible)

1. Okpara K.E, Banchong W, Agbozu I. W, (2019). Occurrence and distribution of Phthalate Esters in Surface water in U-Tapao canal, Songkla Province, southern Thailand
2. Okpara K.E, Banchong W, Agbozu I. W, (2019). Occurrence and distribution of Phthalate Esters in Surface sediment in U-Tapao canal, Songkla Province, southern Thailand
3. Okpara K.E, Banchong W, Agbozu I. W, (2019). Ecological risk assessment of Phthalate Esters in Surface water in U-Tapao canal, Songkla Province, southern Thailand

4. Okpara K.E, Banchong W, Agbozu I. W, (2019). Ecological risk and Health risk assessment of Phthalate Esters in Surface sediment in U-Tapao canal, Songkla Province, southern Thailand