Phthalates in the environment: characteristics, fate and transport, and advanced wastewater treatment technologies

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Abstract

Phthalates are well-known emerging contaminants that harm human health and the environment. Therefore, this review aims to discuss about the occurrence, fate, and phthalates concentration in the various environmental matrices (e.g., aquatic, sediment, soil, and sewage sludge). Hence, it is necessary to treat sources containing phthalates before discharging them to aqueous environment. Various advanced wastewater treatments including adsorption process (e.g., biochar, activated carbon), advanced oxidation processes (e.g., photo-fenton, ozonation, photocatalysis), and biological treatment (membrane bioreactor) have been successfully to address this issue with high removal efficiencies (70 - 95%). Also, the degradation mechanism was discussed to provide a comprehensive understanding of the phthalate removal for the reader. Additionally, key factors that influenced the phthalates removal efficiency of these technologies were identified and summarized with a view towards pilot-scale and industrial applications.

Keywords: Aquatic environment; Biodegradation; Plasticizer; Toxicity; Wastewater treatment.

1. Introduction

Phthalate esters (PAEs) are synthesized by phthalic anhydride and alcohols, also known as phthalic acid esters (Kashyap & Agarwal, 2018). They are colorless, odorless, flavorless, exist as liquid types at a large temperature range (25 °C - 50 °C), and are chemically stable (Tran et al., 2021). In the 1930s, di(2-ethylhexyl)phthalate (DEHP) was added to plastic polyvinyl chloride (PVC) to improve flexibility and elasticity. According to Organization for Economic Cooperation and Development OECD (2018), PAEs were widely used in the global amounts up to approximately 5.5 million metric tons per year, through various sources, including household stuffs (furnishings, clothing, cosmetics, children's toys, nutritional supplements/food packaging, etc.), building and traffic materials, industrial fields (paints and varnishes, adhesives, lubricants, waxes, cleaning materials, electronics, inks), agricultural

activities (insecticides, pesticides, fertilizers, mulch plastic) or others (e.g., pharmaceuticals, medical devices, etc.). As a result, PAEs are found in various environmental matrices, including the atmosphere, lithosphere (soil, sediment), and hydrosphere (surface water, and wastewater, etc.).

Human exposure to PAEs can happen through various pathways such as ingestion, inhalation, skin absorption/contact, and intravenous injection. For example, the human body can be easily exposed PAEs by oral exposure (i.e., the ingestion of food, or children's toys); inhalation from air ambient mixed with PAEs; by skin contact with plastic products (i.e., personal care products, paints, clothes or cosmetics, etc.); and intravenous exposure related to medical equipment (Zhou et al., 2019a). Meanwhile, PAEs are a type of endocrine disruptive chemical (EDCs) that can cause substantial harm to the respiratory, reproductive, and endocrine systems of humans. So far, PAE exposure was linked to a variety of health problems, including abnormal reproductive system impacts, asthma, and allergies. For example, many studies showed that PAEs toxicity leads to reproductive failure related to the testicular cell functions (Wang et al., 2018). Besides, previous researches indicated that PAEs cause adverse health risks: increasing the hypertension risk, changing the thyroid hormone concentration, and even metabolic disorders (Zhang et al., 2021; Zhou et al., 2019a).

It could be seen that the PAEs presence at high concentrations in the environment is one of the global concerns. Phthalates can migrate from landfills to the groundwater and leach into the environment. In this situation, examining the fate and transport of PAEs not only can evaluate the exposure risks but also understand their trend in the environment. Furthermore, PAEs discharged from industrial and domestic wastewater treatment plants directly enter into the water or accumulated in sewage sludge that cause serious effects on the ecosystem and human health via the food chain. Fromme et al. (2002) reported that phthalates detected in surface water was 22.7 mg L^{-1}, whereas, the highest concentration of 288 mg L^{-1} was found in the wastewater (Salaudeen et al., 2018). Thus, it is obligatory to remove PAEs from

wastewater sources by applying various potential wastewater treatment technologies.

Particularly, various advanced treatment technologies have been successfully to remove PAEs from wastewater such as adsorption processes (e.g., biochar and activated carbon) (Yao et al., 2019), advanced oxidation process (e.g., photo-Fenton, photocatalysis, and ozonation) (Medellin-Castillo et al., 2013), and biological treatment (membrane bioreactor and activated sludge) (Boonnorat et al., 2014; Kanyatrakul et al., 2020; Ye et al., 2020). The performance, advantage, and limitation of each technology for PAEs treatment were reviewed and discussed in previous studies (Gani et al., 2017; Zolfaghari et al., 2014). Gani et al. (2017) conducted a critical review on the fate and transportation of phthalate in aquatic environments (surface water, groundwater, and wastewater). Also, advanced bioremediation technologies for phthalate treatment and degradation mechanisms were summarized. In addition, Zolfaghari et al. (2016) evaluate the combination of membrane bioreactor and electro-oxidation processes to degrade phthalates in the landfill leachate. The optimum operating condition with the highest removal efficiency and cost-feasibility for phthalates treatment were identified and discussed. However, key points and the optimal conditions of advanced wastewater treatment technologies significantly affect the removal has not been addressed yet. Therefore, this review aims (1) to examine the characteristics, fate, and transport of PAEs in the environmental matrices, (2) to assess cutting-edge wastewater treatment technology, and (3) to identify the key factors of each technology. In addition, the knowledge gap and recommendations for future studies were also emphasized.

2. Overview of phthalates

2.1. Physico-chemical properties

Several PAEs compounds were detected in the environment, such as Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Di(2-ethylhexyl)phthalate (DEHP), Dibutyl phthalate (DBP), Diisobutyl phthalate (DIBP), Butyl benzyl phthalate (BBP), Diisononyl phthalate (DINP), and Dinoctyl phthalate (DnOP). PAEs are grouped into: high-molecular-weight

(HMW) PAEs with 7 to 13 carbon chains and low-molecular-weight (LMW) PAEs with 3 to 6 carbon chains. For example, DEHP ($C_{24}H_{38}O_4$) belongs to the HMW whereas; DMP ($C_{10}H_{10}O_4$), DEP ($C_{12}H_{14}O_4$), and DBP ($C_{16}H_{22}O_4$) belong to the LMW.

PAEs have different physicochemical properties depending on their chemical structure and alkyl chain length. For example, PAEs are colorless, odorless at ambient temperature (25 °C), low melting point from -25 °C to -55 °C and high boiling point (>250 °C) due to depending on their alkyl chain length. Also, the air-water (K_{AW}), octanol-air (K_{OA}), and octanol-water (K_{OW}) partition coefficients increase with increasing carbon number. For instance, the Log, K_{ow} K_{oa}, and K_{AW} of DEHP ($C_{24}H_{38}O_4$) and DBP ($C_{16}H_{22}O_4$) were 7.73, 10.13, and -3.47, and, 4.27, 8.45, and -4.27, respectively. These properties are of considerable importance in the behavior, fate/transport, and as well as the degradation of PAEs in the environment matrices such as biosphere, hydrosphere, atmosphere, and lithosphere (Staples et al., 1997). For example, K_{OW} can predict the PAEs contaminated tendency in aquatic organisms, and determined PAEs dispersion in environmental matrices.

2.2. Human exposure to phthalates

The use of PAEs-containing materials/stuffs in industrial fields or polymers/plasticizers for various purposes such as personal care products, clothing, cosmetics, toys, modeling clay, cleaning products, etc. can be led to human exposure via dermal/skin pathway. Also, PAEs have relatively abundant levels in ambient air, leading to exposure to humans via inhalation pathway, whereas PAEs caused the health risks via ingestion pathway from drinking water contains PAEs such as DBP, DMP, and Di-isodecyl Phthalate (DiDP). Furthermore, PAEs-contaminated soils also caused lead to their adsorption on sediment and impacts human health. Many previous studies had performed to determine the presence of PAEs in various foodstuffs/products and personal care items (Pereira et al., 2019). Diet and food packaging films were one of the most common sources of PAEs exposure, especially the high carbon number compounds (e.g., DEHP). Food was determined as the major contribution to human

127 exposure, up to 67% (Das et al., 2014). Tran and Kannan (2015) illustrated that the plastic
128 materials from foods packages contribute to vulnerability to DEHP level in humans.
129 Furthermore, food packaging plastic films can be contained high PAEs concentrations (e.g.,
130 DBP and DEP) by weight (Wang et al., 2019b).
131 Table 1 shows the potential human exposure to PAEs from the different intake paths. For
132 instance, in Germany, the levels of DEHP intake in adults were varied from 1,000–4,200 ng
133 kg^{-1} body weight day^{-1}, which related to food daily consumption (Fromme et al.,
134 2007). Similarly, DEHP (2,700–4,300 ng kg^{-1} body weight day^{-1}), DnBP (1,900–4,100 ng kg^{-1} body weight day^{-1}), and BBP (290–430 ng kg^{-1} body weight day^{-1}) were also reported in
136 Denmark (Petersen & Breindahl, 2000). Especially, children's potential exposure to PAEs was
137 greater than adults, leading to a higher risk to children, alarming cause mental decline. For
138 instance, in the early 1990s, the daily DEHP intake in Canada was estimated with 9, 19, 14,
139 and 6 μg kg^{-1} body weight day^{-1} for infants, toddlers, children, and adults (Meek & Chan,
140 1994). PAEs-contaminated polymer toys have been identified as a major source of hazardous
141 exposure to infants and toddlers through mouthing behaviors. DEHP exposure through
142 children's toys (by sucking or chewing) or other sources was estimated to be up to 85 g kg^{-1} body weight day^{-1} (Health & Services, 2002). Meanwhile, DINP exposures were varied from
144 5 to 44 μg kg^{-1} body weight day^{-1} and can be reached up to 183 μg kg^{-1} body weight day^{-1}
145 (Kavlock et al., 2002). Thus, the presence and exposure of PAEs can lead to potential adverse
146 impacts on human health issues.
147 *2.3. Toxic of phthalates and the effects on environment*
148 Before the 1980s, several PAE compounds (e.g., DMP, DEHP, BBP, DBP, DEP, and
149 Dinoctyl phthalate (DnOP) were listed as priority hazardous pollutants. Phthalates are
150 discharged into the environment, causing exposure risks for humans and organisms (Figure 1).
151 Health concern regarding the toxicity of PAEs is rising not only in animal experiments but
152 also in the recent human studies. In general, with lethal dosage 50 (LD50) values of 1–30 g

153 kg^{-1} bodyweight, PAEs could be demonstrated acute toxicity. PAEs are examined as one of the
154 important endocrine-disrupting chemicals (EDCs). Their exposure leads to serious health
155 problems. They can cause human health risks, including abnormal reproductive system
156 impacts, asthma and allergies, precocious puberty, obesity, developmental delay. Moreover,
157 PAEs were suggested not only to be toxic to kidneys, thyroid but also impacts on another one
158 such as testis and liver. The adverse health impacts of PAEs include neural and immune
159 disorders, infertility, and cancers. The other reports illustrated that exposure to different PAEs
160 could lead to high risks of human breast cancer cells. The U.S.EPA's studies also have
161 illustrated that a trace amount of DEHP (low levels) has a great carcinogenic risk. In addition,
162 several toxicological studies have demonstrated fetal exposures to PAEs such as DEHP or
163 DBP in the lab-scale experiments and even some PAEs (e.g., DEHP) have been found to
164 cause liver carcinogenicity in animal as well as illustrated as possibly carcinogenic to humans
165 (Category 2B).

166 PAEs can be bio-accumulated over the long-term, leading to exposure risks for the
167 ecosystems. Previous research has been done to assess the harmful effects of PAEs on the
168 environment. Based on environmental chemistry and its ecotoxicology, DBP and DEHP
169 concentrations in water have ecological danger limits of 0.19 and 10 g L^{-1}, respectively (van
170 Wezel et al., 2000). Weizhen et al. (2020) examined the risks of PAEs levels on aquatic
171 animals in sediments as well as water. In other researches, the biological impacts of PAEs
172 were found relating to estrogenic effects on wildlife. Similarly, PAEs contaminated soil also
173 seriously produced negative impacts the fauna and flora. Thus, PAEs contamination is a cause
174 for concern because of the negative consequences on human health and the ecosystem.

175 *2.4. Regulations*

176 Due to popular occurrence and its toxicity, PAEs had restricted in several countries such
177 as China, Korea, the United States and European Union (Lee et al., 2020). According to the
178 U.S.EPA, several PAEs have been confirmed as priority hazardous pollutants, involving

DEHP, BBP, DMP, DEP, DnBP, and DnOP. The Korean government has strictly regulated PAEs (e.g., DnBP, Benzyl butyl phthalate (BBzP), and DEHP) in children's stuff and expanded to DiDP, DiNP, and DnOP for medical devices or cosmetics (Lee et al., 2020). Currently, the European Union (EU) has banned child-care stuff, children's toys containing DBP, BBP, DEHP, DiNP, DnOP and Di-isodecyl Phthalate (DiDP). Similar guidelines are used in other countries such as Greece, Mexico, Norway, Sweden, Argentina, Austria, Denmark, Finland, etc. (Huang et al., 2018). Regarding DEHP, medical devices are a significant exposure source for community health. Therefore, they have banned DEHP tubes in hospitals (e.g., maternity, pediatrics, and neonatology wards). Also, the phthalates are limited to a maximum content of 0.1 percent by weight of the plasticized material and a Tolerable Daily Intake (TDI) of 50 g kg^{-1} of body weight per day for the phthalates (i.e., DBP, BBP, DEHP, and DINP). Furthermore, the regulation's particular migration limitations for phthalates, which include DEHP of 1.5 mg/kg, DBP of 0.3 mg kg^{-1}, BBP of 30 mg kg^{-1}, and Di-isodecyl Phthalate (DIDP) + Diisononyl phthalate (DINP) of 9 mg kg^{-1} (Table 2).

Moreover, the European Food Safety Authority demonstrated that a PAEs' dose of 50 μg kg^{-1} day^{-1} could be lead to testicular toxicity, and also the U.S.EPA's reference dose of 20 μg kg^{-1} day^{-1} can pose a serious health risk (Serrano Se Fau - Braun et al., 2014). Regarding PAEs levels in the water, many organizations such as World Health Organization (WHO) or European Union (EU) have regulated and recommended the PAEs values in drinking water. DEHP is a priority toxic substance in surface water, and its concentration is also regulated by European Union. For instance, DEHP maximum value in drinking water have regulated WHO (8 μg L^{-1}), the United States (6 μg L^{-1}), New Zealand (10 μg L^{-1}), Australia (9 μg L^{-1}), and Japan (100 μg L^{-1}) (WHO, 2011; Yousefi et al., 2019). Also, based on the yearly average concentrations, environmental quality standards (EQSs) have been estimated with the varied from 20 μg L^{-1} (for DEHP) to 800 μg L^{-1} (for DMP) in aquatic environments. Similarly, as sediment quality guidelines have been proposed, a threshold effect level (TEL) and probable

effect level (PEL) was 182 ng g^{-1} dry wt. and 2647 ng g^{-1} dry wt. for DEHP, respectively (Ashworth et al., 2018). Thus, the necessary solutions need to conduct to enhance public awareness and reduce PAE risk to humans and the environment. Also, reducing PAEs consumption should be a solution, and need to be encouraged to find non-toxic alternative substances.

3. Fate and transport of phthalates in the environment

Phthalates leached out from plastic products during their lifetime (Prasad, 2021). The fate and transport of PAEs in the environment are illustrated in Figure 2. PAEs are able to water, air, soil, sediment contamination through various processes such as leaching, evaporation or deposition, etc. The distribution and behavior of PAEs in the atmosphere is an important route in the environment. The main sources are anthropogenic activities including manufacturing, distribution, consumption, and discharge, which resulted in long-term transport in the atmosphere. Also, the fate of PAEs in the water, sediment, soil is based on metabolic breakdown by microorganisms (e.g., fungal, bacteria species), which is examined as one of the key pathways in the environment. The migration of PAEs depends on their physicochemical characteristics and environmental conditions (e.g., pH, temperature, and pressure). Therefore, the PAEs contamination in the environment needs to be investigated and their occurrences must be specifically evaluated.

3.1. Fate and transport in the atmosphere

PAEs are ubiquitous worldwide due to atmospheric transportation and dispersion processes. Anthropogenic activities influence PAE's behavior and distribution in the atmosphere (e.g., industrial activities, transportation, and commercial), leading to PAEs levels are reached at high concentrations in urban and the center areas (Table 3). Both DnBP and DEHP were the most common PAEs and are predominantly found in the urban atmosphere. PAEs are identified in the gas and dust phases in the atmosphere. For example, DEHP is abundant in the dust phase, whereas DIBP and DBP are predominant in the gas phase.

231 Normally, PAEs with long carbon chains are adsorbed on the particles; in contrast, PAEs with
232 shorter chains (less than 6) are found in the gas phase. Figure 3a illustrates the phthalates
233 concentration in the residential indoor environment. The characteristics of indoor PAEs
234 depended on their sources and activities in households or buildings (e.g., materials,
235 lifestyles/habits, working conditions, etc.). Bi et al. (2015) reported that BBP and DEHP
236 accounted for 46% of total PAEs in residential indoor environments. In addition, the lifetime
237 of PAEs is increased due to adsorption to particles or dust in indoor environments. Due to
238 their sorption on the surfaces of particles, dust, household stuffs, skin, etc., may lead to effects
239 on the behavior and fate of PAEs in an indoor environment. In addition, high temperature
240 (>25 °C) accelerated their fate in indoor environments (Bi et al., 2015). In contrast, because
241 the outdoor environment is more open, the fate and transport of these compounds in the
242 atmosphere are not only affected by photochemical reactions but also gas-solid partitioning.
243 Photo-degradation and direct photolysis are the important reactions related to PAE
244 degradation pathways outdoor. The half-life of photo-oxidation of PAEs showed an increase
245 consistent with the increasing OH• concentration and alkyl chain length. Furthermore, PAEs
246 detected in the atmosphere can enter the soil, water, or ecosystems through atmospheric
247 precipitation.

248 *3.2. Fate and transport of phthalates in water*

249 *3.2.1. Surface water*

250 PAEs are discharged into the marine environment related to the flows from the mainland
251 such as rivers, streams, runoff, etc. The urban road dust is also determined as a transport
252 pathway PAEs into the surface water (e.g., lakes and ponds). Figure 3b presents the PAEs
253 concentration in water, which the highest concentration occurred in the surface water. The
254 distribution of PAEs in surface water was mainly affected by natural degradation (e.g.,
255 hydrolysis, photolysis, sediment-water absorption/desorption, and microbial metabolism) and
256 its physical-chemical properties. The photolysis half-lives of DEP and DBP in surface water

were approximately 2.4 and 12 years, and 0.12 to 1.5 years for DEHP (Staples et al., 1997). However, the aqueous hydrolysis of PAEs is not significant, and their half-lives have been estimated with a large variation: DMP has a half-life of 3.2 years, whereas DEHP's half-life is 2000 years (Prasad, 2021). Therefore, high PAEs levels in surface water sources are mainly caused, leading to their serious accumulation in aquatic species and negatively impacting human health and the environment.

3.2.2. Wastewater

The fate of PAEs in domestic and industrial wastewater treatment plants (WWTPs) has been examined broadly (Table 4). Gani et al. (2017) reported that average PAEs levels of domestic wastewater varied from 1 μg L^{-1} to 100 μg L^{-1}, and DEHP has been recorded as the highest concentration. The high content of phthalate was found equal to 288.95 μg L^{-1} in wastewater (Salaudeen et al., 2018). In general, PAEs are not easily mineralized in WWTPs due to high hydrophobicity which results in low water solubility. As a result, PAE adsorption on suspended organic matter and PAEs transfer to settled sludge are improved. However, PAEs could be accumulated and degraded rapidly depending on the role of microorganisms under different conditions such as aerobic and anaerobic environments. Furthermore, Marttinen et al. (2003) examined the DEHP degradation in a WWTP by mass balance and observed that the removal was over 90%, in which around 30% was contributed by biodegradation. Similarly, the biodegradation efficiency of DEHP in a trickle filter WWTP was found to be varied from 1% to 44% (Oliver et al., 2005). Thus, it could be said that this biodegradation is considered among the main processes for the PAEs removal from wastewater sources. However, PAE biodegradation in WWTPs is dependent on important factors, e.g., reactor design, sludge characteristics, etc.

3.2.3. Landfill leachate

PAEs contamination from landfill leachate has been studied in the European Union many countries (Figure 3b). High concentration of PAEs is easily found in landfill leachate because

283 there are released from various waste sources. PAEs from landfill leachates can enter the
284 groundwater, causing potential risk for the environment. The release of PAEs is influenced by
285 several factors, including the type of landfill, its characteristics, or environmental conditions.
286 Wowkonowicz and Kijeńska (2017) detected some typical PAEs leachates from old landfills
287 such as DEHP (1.3 - 73.9 μg L^{-1}) and DMP (0.6 - 4.72 μg L^{-1}). Furthermore, the literature
288 review results also showed the highly landfill leachates were obtained 1275 μg L^{-1} (Boonnorat
289 et al., 2014). Their presence and abundance could explain high concentrations of PAEs from
290 sources related to industrial activities, household products, etc. Meanwhile, the disposal and
291 treatment of municipal solid waste by landfilling techniques, leading to plastic pollution, and
292 PAEs can be a significant danger to human health and the environment. The accumulation can
293 transfer pollutants into water bodies through surface runoff, and depth leaching flows, then
294 surface water sources (e.g., rivers, lakes, streams, and runoff) and enhance migration to
295 groundwater sources.

296 *3.3. Fate and transport in soil, sediment and sewage sludge*

297 *3.3.1. Contaminated soil*

298 In soils, the PAEs are discharged from agricultural activities (e.g., plastic film mulching
299 and plastic waste) and chemicals products (e.g., fertilizers and additives) (Kashyap &
300 Agarwal, 2018). Most PAEs were found in the topsoil, and their concentration had decreased
301 in deep soil layers (Table 5). For instance, the DEHP concentration varied from 560 mg kg^{-1}
302 in the surface to 90 mg kg^{-1} deep soil layer (40 - 60 cm) (Müller & Kördel, 1993). The highly
303 average concentration of phthalates in contaminated soil was observed about 3349 mg kg^{-1}
304 (Ferreira & Morita, 2012). Their transport and distribution are related to the pollution sources,
305 microbiological factors, physical-chemical properties (e.g., water solubility, molecular weight,
306 etc.). Also, the distribution of PAEs in the soil depends on soil type, seasonal, weather
307 conditions, and their mobility.

308 As shown in Figure 3c, DEHP, DEP, and DMP are the dominant compounds in

309 contaminated soil. For instance, DEHP accounted for 87% of total PAEs concentration in
310 contaminated soil with plasticizers, whereas the proportion of DEP and DMP were 48% and
311 52% in industrialized soil, respectively (Wang et al., 2013). The PAE half-lives varied greatly
312 from few years (DMP) to a thousand years (DEHP) (Staples et al., 1997), leading to a long-
313 time presence in the environment. Therefore, there are negative impacts on the organisms and
314 humans through the food chains. In recent periods, PAEs in soil related to public health have
315 been considered, especially human exposure uptake PAEs via ingestion crop plants such as
316 vegetables and fruits in agricultural areas.

317 *3.3.2. Sediment*

318 Sediment plays an intermediate function in an aquatic environment, relating to phthalate
319 uptake on particulates. PAEs have low solubility, and they can be adsorbed on suspended
320 particulates containing carbon-rich matter in sediments. The PAEs (e.g., DEHP and DiNP) in
321 sediments are related to their adsorption properties. Normally, PAEs with high molecular
322 weights and K_{OW} such as DiNP, DEHP, and DiDP are easily adsorbed on sediment particles
323 due to their hydrophobicity in water (Lee et al., 2019b). The kinetics of PAEs degradation in
324 sediment is affected by a variety of parameters such as temperature, pH, microbial inhibitors,
325 surfactants and contaminants/pollutants, etc. High accumulation of PAEs was observed in
326 sediments from rivers, coastal areas (Figure 3c). For example, a study investigated the
327 contamination of DEHP and DiNP in coastal sediments in a harbor in Taiwan (Chen et al.,
328 2017). These results indicated that total PAEs concentration was 8713 ng g^{-1} with DEHP
329 (3630 ng g^{-1}) and DiNP (3497 ng g^{-1}) are the dominant compounds. On the other hand, PAEs
330 in the river sediment could be biodegraded under aerobic and anaerobic environments with
331 average half-lives ranging from some days to a month. Meanwhile, primary biodegradation
332 rates of some PAEs in sediments were estimated from three to four weeks (DnBP) and three
333 months (DEHP), respectively. Therefore, sedimentary PAEs levels may be caused adverse
334 health impacts for benthic organisms (Kim et al., 2021).

335 *3.3.3. Sewage sludge*

336 Wastewater treatment plants (WWTPs) are major sources of PAEs discharged into the
337 environment. In the sewage sludge, the high PAEs concentrations are normally related to their
338 accumulation from the domestic, industrial wastewaters, and other sources such as urban
339 runoff or drainage. For instance, Staples et al. (1997) measured PAE concentrations in the
340 range 12 to 1250 mg kg^{-1} in sewage sludge. Therefore, the distribution of PAEs in sludge has
341 been examined, and DEHP was confirmed as the dominant compound, which concentrations
342 varied from dozens to hundreds of mg kg^{-1} dry weight in sewage sludge (Bauer & Herrmann,
343 1997). Furthermore, the biodegradation half-lives of PAEs in the sludge are varied from less
344 than one day to a few weeks. The environmental conditions (e.g., oxygen content,
345 temperature, moisture) influenced the PAEs biodegradation. For example, Alatriste-
346 Mondragon et al. (2003) also showed that DBP has a half-life of around five days in anaerobic
347 sludge. Similarly, the DEHP half-lives varied about 10 - 60 days (at 20 °C) and could be up to
348 300 days (at 5–10 °C) in sludge-amended soil (Madsen et al., 1999).

349 **4. Advanced wastewater treatment technologies**

350 *4.1. Physico-chemical treatment*

351 *4.1.1. Adsorption process*

352 To remove organic substances in wastewater, adsorption process is commonly applied in
353 which biochar and activated carbon were used as adsorbents. The first candidate is activated
354 carbon which is an effective adsorbent because of its large surface area and chemical
355 structure. To achieve higher removal PAEs efficiency, several types of adsorbent employed
356 innovative materials for removing phthalates, such as modified activated carbon, chitosan,
357 activated sludge, seaweed, and microbial cultures. For instance, low-grade coal modified by
358 chitosan producing coal-chitosan adsorbent was reported as an innovative utilization for
359 removing diethyl phthalate (DEP) majorly via adsorption (Shaida et al., 2018). PAEs
360 adsorption efficiency by chitosan was conducted, and Dihexyl phthalate (DHP) achieved the

highest adsorption capacity (1.52 mg g^{-1}) and about 74.9% chitosan bead could be recovered by using a mixture of methanol and water (Chen & Chung, 2006). Graphene and its derivatives have been a promising material used in various fields and adsorbents and, especially, in removing PAEs (Yang et al., 2016; Ye et al., 2020; Yin et al., 2014) and pharmaceuticals (Carmalin Sophia et al., 2016; Morales-Torres et al., 2013; Song et al., 2019). The reason is that its adsorption abilities depend on the special structure of a honeycomb resulting in a large specific surface area, extraordinary electronic and mechanical properties (Yang & Tang, 2016). In particular, more than 80% of DnBP and DEHP were obtained with 0.1 g L^{-1} graphene and 12 h as adsorption time. Using mesoporous carbon material prepared by the soft-templating method in the presence of citric acid, six types of phthalates such as DMP, DBP, DEP, BBP, DOP and DEHP were completely adsorbed by using mesoporous carbon (Jedynak et al., 2017). Another adsorbent material called zeolitic imidazolate frameworks (ZIFs) has higher adsorption capacity than activated carbon or other metal-organic frameworks due to an interaction between positive charges of ZIFs surface and negative charges of phthalates anions.

A reused vegetable waste as pepper straw was pyrolyzed at 500 °C into pepper straw biochars (PBs) and became potential high-efficiency PAEs sorbents (Yao et al., 2019). The biomass produced from activated sludge or extracellular polysaccharides can be considered a potential material for PAE absorbents since it produces stable performance and is cheap and readily available. The application of microbial immobilization technology by modifying walnut shell biochar with Fe_3O_4 (MWSB@Fe_3O_4) loaded with *Zoogloea sp* achieved the better effect of DEP removal (67.87%) (Xu et al., 2021).

4.1.2. Key factors influencing phthalates removal

In general, activated carbon is expensive, but, biochar is considered a low-cost and environmentally friendly adsorbent because the raw materials of biochar are wastes collected from agriculture and forestry. Biochar adsorbent has unique physical properties with a porous

structure, carbon-residue derived from the thermal conversion of waste biomass under limited oxygen or anaerobic conditions (Inyang and Dickenson, 2015). However, mature preparation and unstable performance have limited the practical application of biochar. Despite the obvious advantages of biochar, their application in the water/wastewater treatment field is limited. Activated carbon itself would not be a potential and effective adsorbent for phthalates removal from wastewater due to the low solubility and highly hydrophobic nature of phthalates (Julinová and Slavík, 2012). Moreover, to boost the hazardous substances removal capacity, the adsorptive capacity of activated can be impregnated into suitable chemicals (Adhoum and Monser, 2004; Monser and Adhoum, 2002).

Chen and Chung (2006) reported that PAE adsorption reduced corresponding with the increase of temperature. In the same study, the optimal pH for adsorption using chitosan bead as adsorbent was pointed at 8.0. Moreover, if the molecular weight of phthalates increased, the removal efficiency of phthalates would be improved. Activated carbon is considered as a popular process applied as means of adsorption to remove the toxic organic compounds. In addition, the activated carbon is considered as an effective adsorbent to remove phthalates from wastewater since the major essences of phthalates are low solubility and highly hydrophobic. On the other hand, ionic strength in which the isoelectric point (IEP) varies from 3.9 to 4.7 and the surface charge of plain carbon is strongly affected by pH. For instance, if pH is higher than the IEP point, the elimination of phthalates uptake could be a result of the repulsion caused by surface charges of adsorbent and anions. At neutral pH conditions, a strong interaction between the surface of carbon and aromatic ring significantly influenced the adsorption process. Furthermore, the adsorption capacity of plain carbon increased with decreasing pH according to the Langmuir model. In a previous study, the removal capacity of activated carbon at moderate pH 4 was improved by applying Cu-impregnated carbon with the highest adsorption capacity. As a result, phthalates was effectively removed which is almost 2.1 times higher than that of plain carbon (Adhoum & Monser, 2004). Likewise, the

phthalates removal capacity of activated carbon combined with tetrabutylammonium (TBA) was boosted to 1.7 times higher than the ones without TBA (Adhoum & Monser, 2004). Another material also strongly depends on pH adjustment is barium hexaferrite ($BaFe_{12}O_{19}$) containing magnetic poly(EGDMA-VP) beads since the highest adsorption capacity of 98.9 mg g^{-1} was obtained at pH 3 (Özer et al., 2012).

4.2. Advanced oxidation processes

4.2.1. Photo-Fenton

The Fenton process has gained a lot of attention which can be seen through a significant number of investigations in wastewater treatments. Furthermore, the degradation rate of organic pollution (e.g. organic azo-dye), anthraquinone sulfonate could be improved in photo-assisted Fenton processes by taking advantage of UV-Vis light. Hydrogen peroxide and Fe^{2+} (Fenton reagent) were involved in the photochemical degradation of DMP and achieved 80% removal efficiency under optimum conditions as oxidants (Zhao et al., 2004). In the Fenton process, 98% DMP was removed by an activated iron-doped carbon aerogel (AFeC) in 150 min (Zhao et al., 2017). Several mechanisms could be used to explain according to hydrophobic, π-π electron-donor-acceptor, and electrostatic interactions, and molecular imprinting affinity between template molecules and imprinted sites. The toxicity of DEHP in wastewater was firstly reduced by the photo-Fenton, and the effluent was biodegraded in a fluidized bed Fenton (FBR) containing activated sludge (Chen et al., 2009). As a result, the half-life of DEHP of this study was 48.8 ± 3.6 min, which was faster than microbial degradation (25.7 days) (Chang et al., 2005).

4.2.2. Ozonation

It is commonly implemented in drinking water treatment and sterilization worldwide. In a previous study, the membrane bioreactor coupling with the ozonation process demonstrated excellent removal of contaminants in hospital wastewater in which 45-93% of the antibiotics were effectively removed (Bui et al., 2019). In terms of removing phthalates, the degradation

kinetics of four PAEs oxidized by ozone and hydroxyl radical were also examined. Among, DEP was mainly degraded by hydroxyl radicals, but, O_3/Al_2O_3 was indicated as the cheapest and most efficient process for DEP removal in water (Mansouri et al., 2019). Although the activated carbon showed high adsorption capacity in an aqueous solution, the disadvantage of this treatment is that it needs a longer time to reach maximum removal. Therefore, the AOP-based technologies such as O_3/AC were applied, significantly improved the degradation, and showed a high DEP removal compared to conventional technologies (Medellin-Castillo et al., 2013).

4.2.3. Semiconductor photocatalysis

The semiconductor photocatalysis is a promising technology for PAE degradation in aqueous media (Pang et al., 2021). The fundamentals of various photocatalytic applications are the same based on a light-driven chemical process. The width of an energy gap which is the distance between a valence band gap and vacant conduction band decides the performance of a photocatalytic material. Among popular materials, TiO_2 film has hare pores, looser structure, smaller crystal sizes, and longer excitation wavelength by coupling with carbon black resulting in high CB of the photocatalytic activity in degrading dibutyl phthalate (DBP) (Li et al., 2005). The function of TiO_2 in degrading DBP was confirmed with two different polychromatic light sources (350 and 365 nm) and at even very low photocatalyst concentration (0.001 g $dm^{3\ -1}$) (Bajt et al., 2008). Although DEP is a commonly used PAE, difficult to be biodegraded and the treatment cost is expensive, 95.5% DEP in aqueous solution was effectively removed by using TiO_2 in photocatalytic degradation at pH 4 and TiO_2 amount of 200 mg L^{-1} (Huang & Chen, 2010). To degrade PAEs, TiO_2 can be combined with UV and ozone (TiO_2/UV/O_3) produced the photocatalytic activity many times higher than the sol-gel method.

Single metal oxides such as TiO_2, Fe_2O_3, and ZnO are commonly mentioned in previous reports on photocatalytic applications due to their commercial availability and efficiencies in

semiconductors. For example, the DBP removal efficiency of 87.9% was achieved by a graphene-loaded TiO_2 nanotube array and increased to 98% with a bias potential of +1.0V (Wang et al., 2019a). A study about CuO-gC_3N_4 used as the photocatalytic treatment of post-MFC effluent revealed that irradiation time and photocatalytic dose played a main role in the successful treatment (Sarmin et al., 2021). For instance, the highest COD and TOC removal efficiencies were 88% and 86%, respectively, using a photocatalytic dose of 0.5 g L^{-1}, then slightly dropped with further dosing.

4.2.4. Key factors influencing phthalates removal

In the study about H_2O_2/Fe^{2+}, the pH influence on photochemical degradation of DMP was systematically investigated at pH 2 to 6 (Zhao et al., 2004). Particularly, while H_2O_2 and Fe^{2+}concentrations remained, the degradation percentage gradually increased from 21 to 64% with increasing pH. However, at pH 3, the highest efficiency of 81% was observed since the photo-Fenton reactions are strongly dependent on the acidity of the solutions. Iron precipitated as hydroxide occurred at higher pH resulting in a reduction in radiation transmission and degradation percentage. Chen reported that the highest DEHP removal efficiency was obtained at 4 mM L^{-1} H_2O_2 and 3 mM L^{-1} Fe^{3+} while the degradation of DEPH rose with H_2O_2 concentration increasing between 0 and 4 mM L^{-1} (Chen et al., 2009). Contrastingly, higher H_2O_2 concentration did not contribute to higher removal efficiency since excess H_2O_2 will lead to competitive reactions i.e., recombination and formation of hydroxyl radicals. Additionally, a large amount Fe^{2+} may be released at higher Fe^{3+} concentration which will involve in a competition with the PAEs in solution for hydroxyl radical. In photocatalysis, the pH determines the surface charge of photocatalysts and the fate of reactive species. In the case of graphene-loaded TiO_2 (GR/TNA), the point of zero charges of GR/TNA is 4.2, and if the adjusted pH value is higher, the negatively charged surface of photocatalytic electrode will be created (Gong et al., 2011). Therefore, the adsorption of DBP based on electrostatic interactions was facilitated and produced the highest DBP removal efficiency of 95.6% (Wang

et al., 2019a).

The degradation mechanism of phthalate (e.g., DEP) along with its intermediate products were also determined for the AOP treatment (Mohan et al., 2019). For instance, two intermediate products such as phthalic acid and 4-hydroxy phthalic acid were detected while degrading DEP by O_3 alone and peroxone with varying concentrations of H_2O_2 (Mohan et al., 2019). Similarly, intermediates of DEP were detected such as phthalic acid, phthalic anhydride and 4-hydroxy phthalate (Jung et al., 2010). The only intermediate product to the Fenton-degradation of both DBP and DEHP was phthalatic acid (Chen et al., 2009). The main intermediates of DMP are dimethyl 3-hydroxyphthalate (3-DMHP) and dimethy 2-hydroxyphthalate (2-DMHP) which are more hydrophilic structure than DMP via photocatalytic degradation TiO_2-UV-O_2 (Yuan et al., 2008). During the photocatalytic degradation process, a range of intermediates may be produced due to the redox reactions. In the case of water treatment, it is ensured that these intermediates are not harmful and can be further treated/ oxidized if necessary (Pang et al., 2021).

4.3. Biological treatment

Different wastewater treatment technologies performed well in the removing PAEs in either combination or individual treatment steps. Among, biodegradation is one of the most widely interesting topics of PAEs removal, but the biodegradation efficiencies in nature are lower than in laboratory studies. The reason might relate to the PAE adsorption on matrices such as soils, sediments, and organic matrices. The biotransformation is the main removal mechanism contributing 74%, 65% and 37% of PAEs removed in SBR, conventional ASP, and UASB (Gani & Kazmi, 2016). Furthermore, when UASB combined with pond, removal of phthalates was 83% phthalates followed by 80% of SBR and 74% of conventional ASP. Similarly, a study conducted on UASB + polishing pond was able to remove 80% of DEP, DEHP, DBP and BBP in which the polishing pond contributed to larger removal efficiency than UASB (Gani & Kazmi, 2020). High phthalate concentrations may increasingly

accumulate in anaerobic sludge in long time of operation due to high SRT in those systems. Also, different redox conditions in the reactors supposedly provided metabolic pathways of degradation resulting in the improvement of degradation efficiency of phthalates. An anaerobic fixed film fixed bed reactor (AnFFFBR) removed 92.5% of dimethyl phthalate (DMP) (Ahmadi et al., 2017). This study also reported that only mono-methyl phthalate and phthalic acid were DMP's primary by-products since removing side chains of DMP is the only biodegradation pathway. In another study, performances of up-flow anaerobic fixed film fixed bed reactor (UAnFFFBR) and anaerobic fixed film baffled reactor (AnFFBR) for removing DEP were evaluated and compared with each other. As a result, removal efficiencies of 91.11 and 88.72% DEP as well as 90.31 and 86.91% COD, were treated by AnFFBR and UAnFFFBR, respectively (Yousefzadeh et al., 2017). However, it was reported that DEHP degradation under anaerobic conditions was 4 to 5 times slower than aerobic degradation (Madsen et al., 1999) and anoxic mineralization.

A vertical flow constructed wetlands using aquatic plants such as *Phragmites australis-based, mesocosm-scale* were examined to evaluate DBP removal efficiency and degradation mechanisms in the reclaimed water. As a result, the average removal efficiencies for DBP corresponding with the reduction of hydraulic loading rates (HLRs) were 93.77 ± 3.27% (HLR = 0.33 m d^{-1}), 94.9 ± 2.60% (HLR = 0.22 m d^{-1})and 97.0 ± 3.00% (HLR = 0.11 m d^{-1}) (Li et al., 2020). Another aquatic plant, *Wolffia arrhiza*, was studied for its capacity of decontamination of water containing phthalates and other organic compounds. After seven days, 78.9 – 99.7% of phthalates were reduced, and 75-78% of nutrient concentration was significantly removed as well (Kotowska et al., 2018). The petrochemical wastewater containing DMP was treated by MFC and produced a power density of 50 mW m^{-2} with COD removal efficiency of 47% (Sarmin et al., 2021). On the other hand, 84% DMP was removed by using an applied-voltage bioelectrochemical system comparing with a conventional anaerobic system (68%) (Zhou et al., 2019b).

Another major routes for PAE degradation is the metabolic breakdown by microorganisms under aerobic, anoxic, and anaerobic conditions (Staples et al., 1997). Several studies reported degradation efficiency under an aerobic condition with acclimated activated sludge such as 90% of DMP and DBP (Wang et al., 1996), 100% of DBP (Jianlong, 2004). To improve the aerobic degradation of four phthalic acid esters, including DEP, BBP, DBP, and DEHP, ultrasonic pretreatment was applied, resulting in the orders of degradation rate were DBP > BBP> DEP > DEHP and was further enhanced by the addition of yeast extract (Chang et al., 2007).

4.3.1. Membrane bioreactor

Among potential advanced wastewater treatment systems, membrane bioreactor (MBR) is considered an effective approach to remove organic compounds which are toxic and hardly biodegradable. In a biological system, the environmental conditions (aerobic, anaerobic, or anoxic conditions) supposedly play key roles since they will assign the microbial activities in the system. Comprehensive studies about membrane bioreactors applied to remove phthalates were summarized in Table 6. The combination of biological and membrane filtration processes in an MBR enhanced the removal efficiency of micro-pollutants compared to other conventional biological treatment processes such as integrated fixed-film activated sludge membrane bioreactor (IFAS-MBR) (De la Torre et al., 2015). However, the compounds of some phthalate esters were not completely removed by MBR, which might require further treatments such as the ozone and ultraviolet radiation. Similarly, a study employed UV/O_3 together with biological activated carbon to treat WWTP secondary effluent and indicated that the presence of UV effectively supported ozone utilization and biodegradability of the effluent (Li et al., 2007). Although they achieved the phthalate removal of 79% to 100%, the high cost would be the reason limiting their practical applications. Reverse osmosis, nanofiltration, and ultrafiltration utilizing high effort of pressure-driven techniques have been applied to remove phthalates in water, with 97.6 – 99.9% removal efficiencies.

A two-stage MBR was employed to treat landfill leachate containing DEHP for 300 days under long sludge age conditions (Boonyaroj et al., 2012). The removal efficiency through a fouled membrane was investigated. In detail, DEHP was effectively removed by fouled membrane comprising both cake and gel fouling layers (93.41%) and only gel layer (88.97%). However, only 22.21% DEHP was removed with only membrane retention as the presence of fouling raised the retention of the compounds on the membrane. Similarly, after 500 days under the same operating condition, about 97.9% DEP, 96.8% DBP and 95.7% DEHP were removed (Boonnorat et al., 2014). In this study, the long-term operation and removal kinetics of the same system was performed. As a result, the mechanism relating to adsorption and biodegradation contributed differently depending on the chemical properties of the targeted compounds. For instance, biodegradation was a primary mechanism in the case of DEP and DBP under aerobic conditions, whereas the means of DEHP removal was adsorption. It was explained that the molecular structure of DEHP was the largest but the biodegradation rate was very low. Meanwhile, DEP is hydrophilic and highly soluble in water, so its biodegradation rate was reported higher. Phthalates (e.g. BMNP, DEHP, DIDP, and DnDP) were found to accumulate at a high concentration of 5.79 g L^{-1} in an AnMBR treating landfill leachate since they were not degraded due to long alkyl-chains (Zayen et al., 2015). In SMBR, the removal efficiency of DEHP (97.75%) distinctly depended on the sludge concentration and initial concentration of micro-pollutants but DEHP in the effluent (1.5 μg g^{-1}VS dry wt.) still exceeded the discharge limit in Canada (Zolfaghari et al., 2015). It was found that DEHP was adsorbed onto sludge due to its high hydrophobicity according to its octanol-water partition coefficient (log K_{OW} > 7.0). Only 50% of DEHP was removed by either activated sludge or activated sludge (AS) combined with flocculation (F), but, flocculation improved the adsorption of DEHP onto sludge by increasing removal efficiency from 25% to 76% (Medellin-Castillo et al., 2013). However, when an MBR using ultrafiltration membrane (UF) is involved in the process, higher membrane retention capability resulted higher DEHP

595 removal efficiency with ultrafiltration membrane than the three-step process (AS-F-UF).
596 Under an aerobic conditions, 94.96% of DEP and 93.85% diallyl phthalate (DAP) were
597 removed in a moving bed biofilm reactor (MBBR) and DEP had a higher biodegradation rate
598 compared to DAP with initial concentrations ranging from 100 to 300 mg L^{-1} (Ahmadi et al.,
599 2015). The high OLR and HRT also enhanced DEP and DAP removal efficiency due to higher
600 contact time for enzymes secreted by the biofilm and increasing the bio-availability of biofilm
601 to substrates. In terms of aeration rate, the increases of aeration and consequently dissolved
602 oxygen resulted in the highest DEP, and DAP removal due to the increasing catabolic activity
603 of biofilm. However, higher aeration rate (e.g., 220 L h^{-1}) caused extreme biofilm washout;
604 hence, the removal efficiency of both phthalates was slightly reduced. The biomass
605 acclimated in MBR/UF system could effectively treat landfill leachates and demonstrated
606 high potential for PAEs biodegradation/biotransformation by using a metagenomic approach
607 (Fudala-Ksiazek et al., 2018). As PAEs are hydrophobic compounds, the foremost
608 mechanisms for the removal are their adsorption on activated sludge flocs and biodegradation.
609 Moreover, a complex bacterial community could help to obtain complete degradation of PAEs
610 including *Clostridium*, *Mycobacterium*, *Rhodococcus* from *Actinobacteria* and
611 *Alphaproteobacteria*-affiliated *Sphingomonas* sp and other bacteria from
612 *Sphingomonodaceae*.
613 *4.3.2. Key factors influencing phthalates removal*
614 The influent of ambient temperature such as seasonal variations is positive on removing
615 phthalates in wastewater and better removal is supposed during summer (Gani & Kazmi,
616 2016). For instance, in the summer, DEP, DBP, and DEHP concentrations in untreated
617 wastewater increased only from 2-7 µg L^{-1}. However, in the winter, large molecular weight
618 phthalates BBP and DEHP increased in sludge by 3 mg kg^{-1} and 12 mg kg^{-1}, respectively
619 (Gani & Kazmi, 2016). Boonnorat et al. (2014) reported that the removal mechanism of
620 DEHP was mainly caused by adsorption under the aerobic conditions, not biodegradation due

621 to its large molecular structure resulting in low biodegradation rate. Moreover, heterotrophic
622 bacteria were also found to play a major role in biodegradation, and ammonia-oxidizing
623 bacteria (AOB) assisted in elevating the removal efficiencies through co-metabolism by
624 releasing soluble microbial products as the carbon sources for heterotrophic growth and
625 attributed to higher enzyme activities. In the same study, the removal efficiencies of targeted
626 micro-pollutants were 90-99% at the C/N ratio of 10 and 6. When SRT was adjusted to 15
627 days, only 50-60% DEHP was removed, whereas more than 90% DEHP was removed under
628 long SRT of 90 days despite the same C/N ratio of 6. However, although the biodegradation
629 rate of DEHP was improved due to long SRT of 140 days, the concentration of DEHP in
630 sludge increased 15 times more than the concentration regulated in Canada (100 μg g^{-1} dry
631 weight) (Zolfaghari et al., 2015). On the other hand, HRT was evaluated as another
632 influencing factor favorable to bacterial growth, then, improved the enzyme activity in the
633 MBR system (Boonnorat et al., 2016b). These enzymes are important for degradation of the
634 micro-pollutant and pharmaceutical pollutants, which is similarly reported in biodegradation-
635 recalcitrant pharmaceuticals. Similarly, it was found that DEHP could be removed more
636 effectively at higher HRT and when MLSS increased. At the same time, MLVSS decreases,
637 indicating that the adsorption mechanism played an important role in PAEs removal in MBR.
638 Some PAEs including phthalic acid butyl 4-octyl ester became more recalcitrant under
639 cryophilic conditions at a mean solid residence time of 300 days (Trzcinski & Stuckey, 2010).
640 The phthalates with shorted ester chains (e.g., DMP, DEP, DBP, DPP, DPrP and BBP) can
641 be biodegraded and mineralized. But, the ones with longer ester chains (e.g. DHP, DOP and
642 DEHP) cannot be effectively treated by biodegradation (Fang and Zheng, 2004). The primary
643 degradation pathway of phthalates under anaerobic conditions is de-esterification with common
644 intermediates such as monoester phthalate and phthalic acid (Liang et al., 2007). Anaerobic
645 reactors were successful in the degradation of phthalates in wastewater. Over 99% of DMP was
646 successfully degraded in UASB reactors (Liang et al., 2007). Firstly, DMP was de-esterified

647 during anaerobic degradation, first to mono-methyl phthalate (MMP) and then to phthalate,
648 before being de-aromatized and subsequently converted to CH_4 and CO_2. On the other hand,
649 under anoxic conditions, the degradation of PAEs is limited (Gao and Wen, 2016). Under the
650 aerobic condition, the initial step associated with a division of ester linkages between alkyl
651 chains and the aromatic ring is then hydrolyzed to phthalic acid via monoesters. Moreover, the
652 major step of the biodegradation process of phthalate ester through the dioxygenase-catalyzed
653 pathway is the mineralization pathway (Gao and Wen, 2016). Comparing with abiotic (or non-
654 biological) degradation, microbial degradation is faster and more environmentally friendly to
655 remove phthalates from various environments since microorganisms such as a wide range of
656 bacteria and actinomycetes have been detected playing a major role in the phthalates
657 degradation under various conditions (Liang et al., 2008; Chatterjee and Karlovsky, 2010;
658 Camacho-Munoz et al., 2012).

659 Using pure culture or mixed culture to degrade phthalates has been reported in previous
660 studies. The pure cultures capable of degrading phthalates consist of four divisions in bacteria
661 (*Proteobacteria*, *Actinobacteria*, *Firmicutes* and *Bacteroids/Chlorobi*). The common genera
662 are *Sphingomonas* (α-Proteobacteria), *Comamonas* (β-Proteobacteria), *Pseudomonas* (γ-
663 Proteobacteria) as well as *Arthrobacter* and *Rhodococcus* (Liang et al., 2008). Additionally,
664 besides bacteria, few fungi species can also degrade phthalates such as *Aspergillus niger* AG-
665 1 (Ganji et al., 1995), *Sclerotium rolfsii* (Sivamurthy et al., 1991), *Penicillium lilacinum*
666 (Engelhardt et al., 1977), *Fusarium oxysporum* (Kim and Lee, 2005), *Phanerochaete*
667 *chryososporium*, *Trametes versicolor*, *Daldinia concentrica* (Lee et al., 2004), *Polyporus*
668 *brumalis* (Lee et al., 2007), as well as microalga *Closterium lunula* (Yan and Pan, 2004) and
669 *Chlorella pyrenoidosa* (Yan et al., 2002). Different phthalates isomers perform different
670 biodegradation rates. Phthalate-hydrolyzing enzymes are structurally specific such as a
671 dimethyl isophthalate (DMI)-hydrolyzing enzyme purified from *Rhodococcus erythopolis* (Gu
672 et al., 2005). The non-classified *Pseudomonas* strain P136 was reported to mainly deriving the

673 phthalate degradation in an anaerobic environment (Nozawa and Maruyama, 1988). In
674 another study, the half-life of DEHP was 2-5 days in a sequencing batch reactor inoculating
675 with mixed culture composed of *Brevibacterium iodinum*, *Rhodococcus luteus* and *Bacillus*
676 *brevis* which can utilize DEHP as a sole source (Juneson et al., 2001). Furthermore, other
677 pathways have been proposed such as converting phthalic acid via β-oxidation applied for
678 removing DOP (Wu et al., 2010). DMP and DBP with shorted side chains could be directly
679 converted to phthalic acid without monoesters (Jackson et al., 1996).

680 **5. Future recommendations**
681
682 Aforementioned above, advanced technologies have exhibited very promising for
683 phthalates treatment with removal efficiencies (70 - 95%) for each process. However, these
684 technologies commonly required high-level operation and maintenance costs; therefore, these
685 recommendations were provided for future research to maintain the optimal conditions and
686 apply for practical conditions.

687 • The sorption efficiency of absorbents (e.g., activated carbon, biochar) is limited,
688 significantly depending on their characteristics such as surface area and porosity. Therefore,
689 to enhance the capacity of this process, solid separation should be conducted during the
690 phthalates treatment.

691 • Moreover, the research on PAEs removal by adsorption is still at the lab scale.
692 Therefore, it is necessary to conduct a real scale such as a pilot- or industrial scale to
693 determine whether these kinds of absorbents could be practically applied based on results
694 achieved from the laboratory or required to couple with other treatment technologies in
695 wastewater treatment plants.

696 • Advanced oxidation processes (AOPs) generally consume a huge amount of chemicals
697 or additives, leading to increased cost-efficiency. Moreover, it has generated by-products with
698 high toxicity. Therefore, AOPs should be applied as pre-treatment or combining different

processes (e.g., adsorption, photocatalysis) to enhance the phthalates treatment and reduce operating costs.

- A great challenge remaining in AOP technologies is the presence of degradation intermediates which are more harmful than the original compounds. However, in terms of removing phthalates, only a few papers on the intermediates or by-products of phthalate treated by AOP have been discussed. Therefore, further investigations about this issue need to be communicated.
- Aerobic biodegradation is commonly higher efficiency than anaerobic conditions and fully understood the overall mechanisms and biodegradation pathway through many previous studies. However, the phthalates biodegradation under anaerobic conditions is still ambiguous. Therefore, further studies should address this issue to fill-up the knowledge gap in this area.
- A membrane bioreactor is considered more effective than the treatment process as activated sludge due to the combination of the biological process with membrane separation resulting in more efficient solid-liquid separation. Their removal efficiency also depends on the configuration of reactors and sources of sludge which have been broadly studied and investigated in either wastewater treatment plants or laboratories. Moreover, the development of effective microorganisms should be enabled to adapt to treat wastewater containing phthalates. And, biodegradation process is time-consuming and long-chain PAEs are not easily biodegradable.

6. Conclusions

This review discussed about the occurrence, fate, behavior and contamination of phthalates in the environment worldwide. Wastewater treatment technologies currently applied in PAEs removal had high efficiencies of 70 – 95% achieved by ozonation and/or photocatalysis, and membrane bioreactor. Membrane bioreactor is robust for phthalates treatment due to its high efficiency (>90%), environmentally friendly, and cost-feasible for

726 different scales. In details, several key points contributing to successful removal, in which, pH
727 plays major roles in controlling the effects of physico-chemical treatment and advanced
728 oxidation processes. While temperature, retention time and microbial communities
729 significantly involve in polishing up in biological treatment.
730
731 **CRediT authorship contribution statement**
732 **Huu Tuan Tran**: Conceptualization, Formal analysis, Writing – original draft. **Chitsan**
733 **Lin**: Data curation, Supervision, Review & editing. **Xuan-Thanh Bui**: Data curation
734 Methodology, Review & editing. **Minh Ky Nguyen**: Methodology, Formal analysis, Writing
735 – original draft. **Ngoc Dan Thanh Cao**: Methodology, Review & editing. **Hussnain**
736 **Mukhtar**: Review & editing. **Hong Giang Hoang**: Review & editing. **Sunita Varjani**:
737 Review & editing. **Huu Hao Ngo**: Review & editing. **Long D. Nghiem**: Review & editing.
738
739 **Declaration of Competing Interest**
740 The authors declare that they have no known competing financial interests or personal
741 relationships that could have appeared to influence the work reported in this pa

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Table 1. Potential human exposure to phthalates

PAEs	Sources	Intake paths	Objects	Exposures (μg kg^{-1} bodyweight day^{-1})	References
DEHP, DINP	Soft plastic toys, food, dust	Mouthing	Infants and toddlers	> 100	(Wormuth et al., 2006)
DEHP	Medical devices	Leaching	Infants	2500	(FDA, 2001)
DEHP	Daily exposure	Daily exposure	Children women	12.4 41.7	(Koo & Lee, 2005)
DEHP DnBP BBP DEP DMP	Indoor	Respiratory tract	Household	1458 191.8 164.3 107.7 79.1	(Martine et al., 2013)
DEHP	Food daily consumption	Food/diet	Adults	1.0–4.2	(Fromme et al., 2007)
DnBP BBP DEHP	Foodstuffs/baby food/diet	Food/daily intake	Baby food and infant	1.90–4.10 0.29–0.43 2.70–4.30	(Petersen & Breindahl, 2000)
ΣPAEs (DBP, BBP, DEHP, DINP)	Food	Dietary exposure	All age groups	0.9–7.2	(European Food Safety et al., 2019)
ΣPAEs	Indoor air Personal care products Dust	Inhalation Dermal Ingestion	Children Toddlers Infants	0.2030 0.0059 1.1200	(Tran & Kannan, 2015)
ΣPAEs	Indoor dust	Ingestion, dermal, inhalation	Children Adults	0.4380 0.0723	(Li et al., 2021)
ΣPAEs (DEHP, DnBP, DiBP)	Indoor dust	Daily intake/oral, dermal	Male and female	0.0973 – 0.3360	(Qu et al., 2021)

***Remarks**: Phthalate Acid Esters (PAEs), Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DIBP), Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP), Diethylhexyl phthalate (DEHP), Dinoctyl phthalate (DnOP), Diisononyl phthalate (DINP), Benzylbutyl phthalate (BzBP), Di-n-butyl phthalate (DnBP).*

Table 2. Restriction of phthalates regulations for plastic food contact materials and drinking water

Phthalate (PAEs)	Regulation of European Union (EU) for phthalate in plastic food contact materials		
	Maximum content by weight (%)	Specific migration limit (mg kg^{-1})	Tolerable daily intake (μg kg^{-1} bodyweight day^{-1})
BBP	≤ 0.1	≤ 30	50
DBP	≤ 0.05	≤ 0.3	50
DEHP	≤ 0.1	≤ 1.5	50
DIDP	≤ 0.1	≤ 9	-
DINP	≤ 0.1	≤ 9	50

	Regulation of organizations for DEHP levels in drinking water (μg L^{-1})			
	WHO	EU	U.S.EPA	Japan
DEHP	8 μg L^{-1}	8 μg L^{-1}	6 μg L^{-1}	100 μg L^{-1}

Remarks: Phthalate Acid Esters (PAEs), Butyl benzyl phthalate (BBP), Dibutyl phthalate (DBP), Diethylhexyl phthalate (DEHP), Diisobutyl phthalate (DIBP), Diisononyl phthalate (DINP).

Table 3. Worldwide phthalates concentration in the atmosphere

Locations	Characteristics	Concentration (ng m^{-3})								References
		DMP	DEP	DnBP	BBP	DEHP	DnOP	DBP	DiBP	
China	Summer, indoor air	2560.3	321.3	7286.5	N/A	9028.8	10.87	N/A	1123.6	(Huang et al., 2020)
China	Outdoor	133.29	296.72	N/A	91.544	215.83	120.01	122.32	185.58	(Ouyang et al., 2019)
France	Indoor airborne	8.2	157	82.9	N/A	N/A	N/A	N/A	326	(Blanchard et al., 2014)
Germany	Indoor airborne	436	643	1083	N/A	156	N/A	N/A	N/A	(Fromme et al., 2004)
Japan	Bedrooms, indoor air	42	74	257	N/A	323	N/A	N/A	249	(Toshiaki et al., 2020)
Norway	Houses, indoor air	69	496	233	N/A	N/A	N/A	N/A	456	(Sakhi et al., 2019)
Saudi Arabia	Living room, indoor	N/A	17	N/A	N/A	520	N/A	320	N/A	(Ali et al., 2021)
US	Indoor airborne	N/A	330	140	N/A	110	N/A	N/A	130	(Rudel et al., 2010)
Vietnam	Homes, indoor air	26.5	66.5	84.3	N/A	14.2	3.79	N/A	111	(Anh et al., 2021)

Remarks: Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DiBP), Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP), Diethylhexyl phthalate (DEHP), Dinoctyl phthalate (DnOP), Di-n-butyl phthalate (DnBP), N/A – Not Available.

Table 4. Worldwide phthalates concentration in the aqueous environment

Locations	Characteristics	Concentration (ng L^{-1})								References
		DMP	DEP	DnBP	BBP	DEHP	DnOP	DBP	DiBP	
China	Surface water	224.20		N/A	N/A	328.74	118.88	144.36	76.87	(Weizhen et al., 2020)
Denmark	Wastewater	1880	N/A	N/A	37870	71890	N/A	20480	N/A	(Roslev et al., 2007)
France	Wastewater	N/A	9480	1290	1600	63000	N/A	N/A	N/A	(Bergé et al., 2014)
Germany	Surface water	N/A	N/A	N/A	N/A	22700	N/A	500	N/A	(Fromme et al., 2002)
India	Surface water	21.3	241	N/A	39	514	28.8	250	N/A	(Selvaraj et al., 2015)
Korea	Surface water	180	50	N/A	N/A	134	20	340		(Lee et al., 2019a)
Malaysia	Surface water	7.1	28.6	N/A	22.1	130.9	2.3	108.9	N/A	(Santhi & Mustafa, 2013)
Netherlands	Freshwater	N/A	N/A	N/A	N/A	330	N/A	210	N/A	(Peijnenburg & Struijs, 2006)
Poland	Landfill leachate	7320	2930	N/A	N/A	75600	N/A	1860	3430	(Kotowska et al., 2020)
South Africa	Wastewater	5740	12820	N/A	33710	28830	12710	195140	N/A	(Salaudeen et al., 2018)
Saudi Arabia	Wastewater	228	182	N/A	388	468	195	748	N/A	(Al-Saleh et al., 2017)
Thailand	Landfill leachate	N/A	394000	N/A	N/A	284000	N/A	597000	N/A	(Boonnorat et al., 2014)

Remarks: Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DiBP), Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP), Diethylhexyl phthalate (DEHP), Dinoctyl phthalate (DnOP), Di-n-butyl phthalate (DnBP), N/A – Not Available.

Table 5. Worldwide phthalates concentration in the soil and sediment

Locations	Characteristics	Concentration (μg g^{-1})								References
		DMP	DEP	DnBP	BBP	DEHP	DnOP	DBP	DiBP	
China	Agricultural soils	ND	ND	0.00612	0.000861	0.183	0.00697	N/A	N/A	(Wei et al., 2020)
France	Urban soil	0.0010	0.0047	0.0040	0.00039	0.121	0.0035	N/A	0.0026	(Tran et al., 2015)
	Rural soil	0.00125	0.093	0.0925	0.0026	0.310	0.0034		0.0215	
Korea	Sediment, Masan and Haengam Bays	292	0.00082	0.0106	N/A	0.460	N/A	N/A	0.00292	(Kim et al., 2020)
Korea	Sediment, Asan Lake	0.0003	0.0003	N/A	N/A	2.056	N/A	0.0736	0.003	(Lee et al., 2019a)
Korea	Sewage sludge	1.2	0.072	5.9	N/A	92	N/A	N/A	0.77	(Lee et al., 2019b)
Mediterranean sea	Sediment, Gulf of Lion	0.00283	0.00127	0.01406	N/A	0.06690	0.00536	N/A	0.00684	(Alkan et al., 2021)
Russia	Top soil	0.47 ± 0.80	0.42 ± 0.68	31.74 ± 42.40	N/A	17.20 ±34.28	N/A	N/A	12.89 ± 32.95	(Brodskiy et al., 2019)
Scotland	Surface soils	N/A	N/A	N/A	N/A	0.258	N/A	N/A	N/A	(Rhind et al., 2013)
South Africa	Sewage sludge	1.08	4.84	N/A	76.36	N/A	5	27.99	N/A	(Salaudeen et al., 2018)
Thailand	Sediment, U-Tapao canal	N/A	N/A	N/A	N/A	0.484	N/A	0.08882	N/A	(Kingsley & Witthayawirasak, 2020)
Taiwan	Agricultural soil	0.0004 ± 0.001	ND	0.01 ± 0.01	ND	0.44 ± 0.51	0.2 ± 0.25	N/A	N/A	(Kaewlaoyoong et al., 2018)

Remarks: Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DiBP), Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP), Diethylhexyl phthalate (DEHP), Dinoctyl phthalate (DnOP), Di-n-butyl phthalate (DnBP). ND (Non-Detectable), N/A – Not Available.

Table 6. Comprehensive studies about membrane bioreactor applied to remove phthalate

Type of treatment	Targeted pollutants	Substrate	Operating conditions	Removal (%)	References
MBR	DEHP	Landfill leachate (COD 6740 mg L^{-1}, BOD 3260 mg L^{-1} and NH_3-N 170 mg L^{-1}	C/N = 6 HRT = 24 h SRT = 90 days	> 90	(Boonnorat et al., 2016a)
MBR	DBP DEHP	Landfill leachate (COD 14200 mg L^{-1}, BOD 6060 mg L^{-1} and NH_3-N 360 mg L^{-1})	C/N = 6 HRT = 12 h	98.3 96.5	(Boonnorat et al., 2016b)
AnMBR	PAEs	Landfill leachate (COD 3.3 ± 0.58 g L^{-1}, BOD 1.2 ± 0.35 g L^{-1} and NH_3-N 360 mg L^{-1})	HRT = 7 days	PAEs increased inside the reactor	(Zayen et al., 2015)
Anoxic MBR/UF/NF	PAEs	Landfill leachate mixture (COD 3948 – 6509 mg L^{-1}, 631 - 1371 mgN-NH_4^+ L^{-1}, 1152-1458 mgN L^{-1})	F/M = 0.43-1.86 kgCOD kg^{-1} MLVSS·d^{-1} HRT = 8 – 10 days SRT = 25 days	100 (almost lower than limit of detection)	(Fudala-Ksiazek et al., 2018)
MBBR	DEP DAP	Synthetic wastewater (COD 200 mg L^{-1})	HRT < 7 h	94.96 93.85	(Ahmadi et al., 2015)
IFAS-MBR	DEHP	Municipal wastewater	SRT = 10 – 20 d	10 – 30	(De la Torre et al., 2015)
MBR (inoculated with *Arthrobacter sp.*)	DEP			81	(Zhang et al., 2016)
MBR integrating with electro-oxidation process	DEHP	Landfill leachate (COD 1550 mg L^{-1}, 288 ± 112 mgN L^{-1}, 4.3 ± 1.5 mgP L^{-1})	F/M = 0.203 ± 0.081 kgCOD kg^{-1} VS day^{-1} HRT = 48 h SRT = 200 days VS = 2.5 – 7.1 g L^{-1}	59 ± 24.3 (in summer) 66.4 ± 28.8 (in winter)	(Zolfaghari et al., 2016)
Two-stage MBR (Anoxic-Aerobic)	DEP DBP DEHP	Landfill leachate (COD 2400 ± 120 mg L^{-1})	HRT = 24 h MLSS = 5 g L^{-1}	100 94 93	(Kanyatrakul et al., 2020)
AnMBR	DEHP, DINP	Middle/old landfill leachate (COD 7041 ± 250 mg L^{-1}, NH_4^+ 1000 ± 200 mg L^{-1}, PO_4^{3-} 78 ± 10 mg L^{-1})	HRT = 48 h	100	(Cirik & Gocer, 2020)

***Remarks**: Membrane Bioreactor (MBR), Submerged Membrane Bioreactor (SMBR), Ultra filtration (UF), Nano filtration (NF), Moving Bed Biofilm Reactor (MBBR), The integrated fixed-film activated sludge membrane bioreactor (IFAS-MBR), Anaerobic Membrane Reactor (AnMBR), Hydraulic Retention Time (HRT), Food to Microorganism Ratio (F/M), Carbon to Nitrogen ratio (C/N), Sludge Retention Time (SRT), Total Solids (TS), Chemical Oxygen Demand (COD), Phthalate esters (PAEs); Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Butyl benzyl phthalate (BBP), Diethylhexyl phthalate (DEHP), Dinoctyl phthalate (DnOP), Diisononyl phthalate (DINP), Di-n-butyl phthalate (DnBP), Dinonyl Phthalate (DNP), Diallyl Phthalate (DAP).*

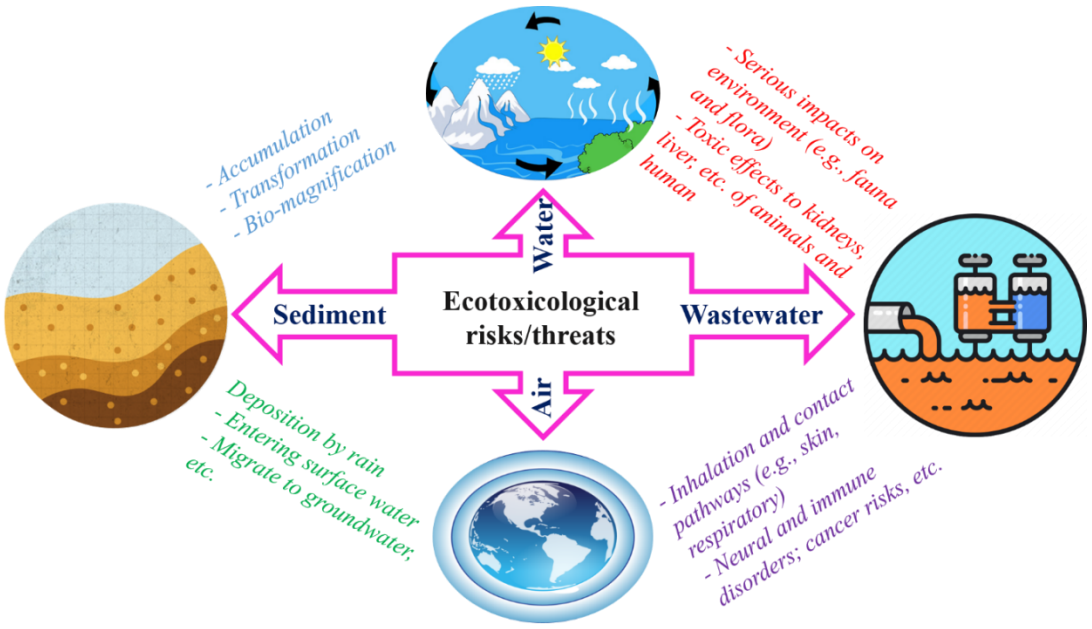

Figure 1. Effect of PAEs on the environment, associated with health and ecotoxicological risks

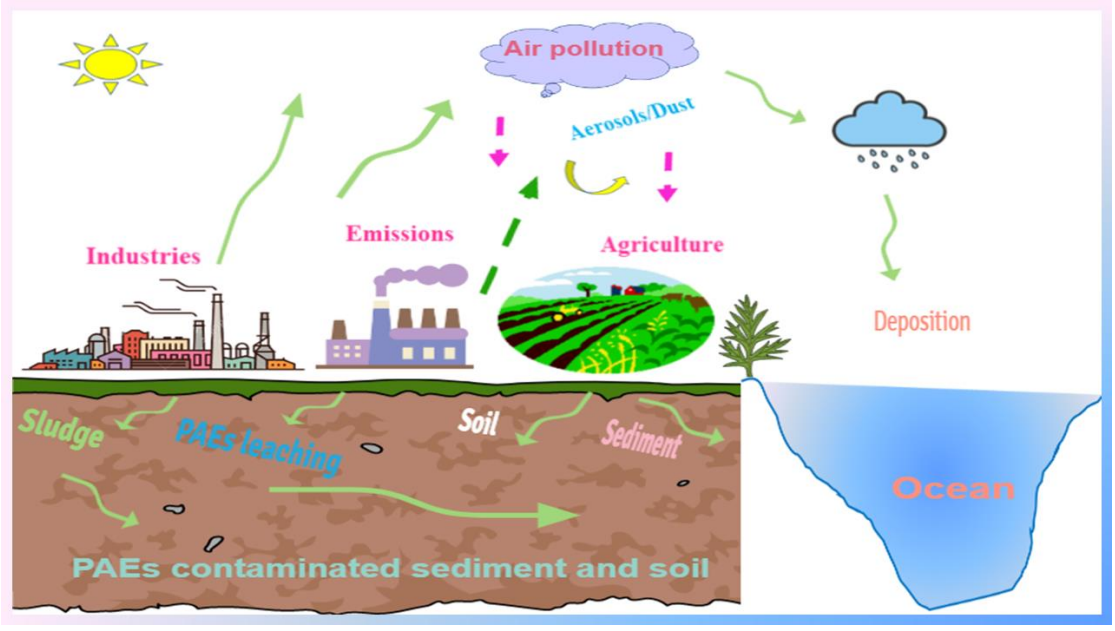

Figure 2. Fate and transport of phthalates related to their main sources in environment

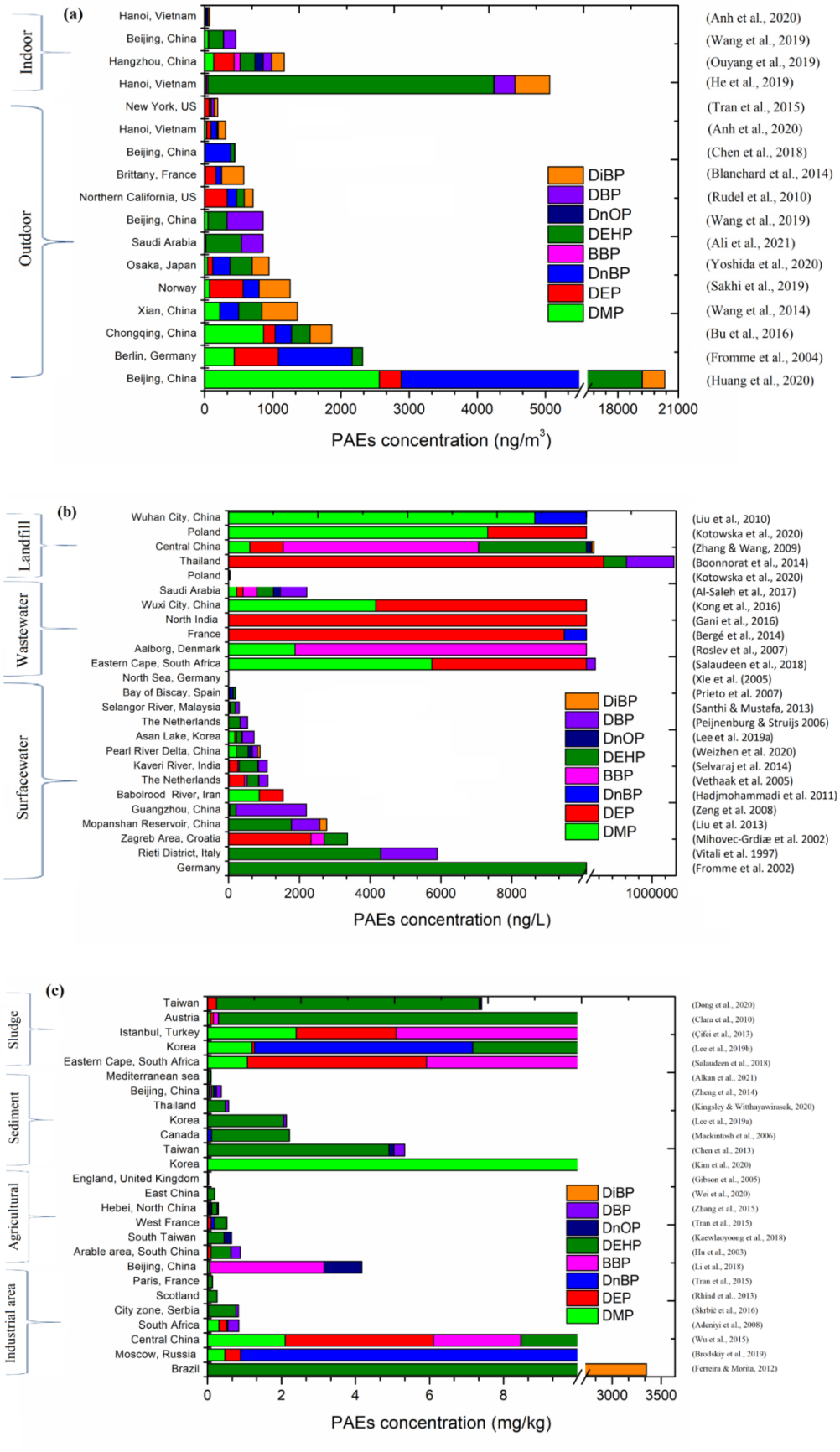

Figure 3. Worldwide phthalates level in the environmental matrices (a) atmosphere, (b) water, (c) soil and sediment