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A review of polycyclic aromatic hydrocarbons and their substitutions in full-scale wastewater treatment plants

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Abstract

Wastewater treatment plants (WWTPs) become a main contributor of polycyclic aromatic hydrocarbons (PAHs) and their substitutions present in freshwater systems. This paper reviews PAHs and their substitutions in full-scale WWTPs including their fate and behaviors, analytical techniques, biological treatments, feasibility examination, and modeling. In addition, challenges and future outlook are also highlighted. This study found that PAHs and their substitutions have been detected in WWTPs. GC-MS and HPLC analytical methods have been found to be acceptable for the detection and analysis of PAHs and their substitutions. Although some biological treatments such as activated sludge and membrane bioreactors are capable for the treatment process, their technical, social, economic, and environmental aspects must be considered. The fate and treatability estimator (FATE) model has been used for the modeling of removal of PAHs in full-scale WWTPs, but in some cases their shortcoming has been reported, which calls for an evaluation and modification of the model based on physicochemical processes.

KEYWORDS
biological treatments of wastewater, FATE model, polycyclic aromatic hydrocarbons, treatment plants

1 | INTRODUCTION

There has been increasing concern about the importance of investigation of the fate and behaviors of polycyclic aromatic hydrocarbons (PAHs) in water systems (Al Farraj et al., 2019; Hadibarata, Syafiuddin, & Ghfar, 2019; He, Yang, He, & Xu, 2020; Nizzetto et al., 2008). The presence of PAHs in these systems is mainly due to the incomplete combustion of organic matter. PAHs can be categorized as low molecular weight (LMW) by having two to three rings structure, while high molecular weight (HMW) is PAHs, which include four or more rings structure. It has been well known that the aqueous solubility of PAHs can be decreased with the rise of their molecular mass (Balati, Shahbazi, Amini, & Hashemi, 2014). In addition, an increase in molecular weight of PAHs, their melting, and boiling point can be increased while vapor pressure can be decreased. Moreover, PAHs are carcinogenic in nature and their carcinogenicity increases with the rise of molecular weight. The physicochemical properties of PAHs are listed in **Exhibit 1**.

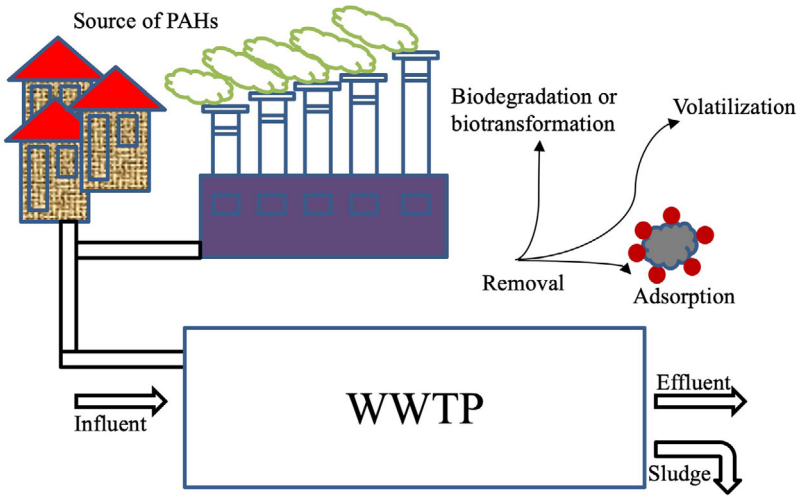
The presence of PAHs in water systems can come from natural and anthropogenic processes. Natural processes include eruption of volcanic and wild fires, while anthropogenic processes can be burning of fossil fuel, cooking, and oil spill. However, PAHs produced by natural processes are lower than those produced from anthropogenic processes. Significant amounts of PAHs are released due to anthropogenic activities into the environment (Balati et al., 2014).

Currently, the fate of PAHs in wastewater treatment plants (WWTPs) has become a central issue for water treatment management. It has been reported that PAHs have been detected in some WWTPs, which receive effluent from domestic and industrial activities as illustrated in **Exhibit 2**. These organic pollutants have been found in the concentration varying from ng/L to μg/L and ng/g to μg/g in the aqueous and sludge samples, respectively, depending on the

EXHIBIT 1 List of PAHs and their substitutions found in WWTPs. The data are modified from (Qiao et al., 2014b)

Name	Abbreviation	Molecular formula	Molecular weight	Boiling point (°C)	log K_{ow}	Solubility (μg/L)	Vapor pressure (mm Hg)	Henry's law constant (atm-m^3/mole)
Naphthalene	Nap	$C_{10}H_8$	128.17	218	-	31,700	8.50E−02	4.40E−04
Acenaphthylene	Acy	$C_{12}H_8$	152.19	280	4.03	1,930	6.68E−03	1.14E−04
Acenaphthene	Ace	$C_{12}H_{10}$	154.21	279	3.96	3,930	2.15E−03	1.84E−04
Fluorene	Fluo	$C_{13}H_{10}$	166.22	298	4.17	1,680–1,980	6.00E−04	9.26E−05
Phenanthrene	Phe	$C_{14}H_{10}$	178.23	340	4.55	1,200	1.12E−04	4.23E−05
Anthracene	Ant	$C_{14}H_{10}$	178.23	342	4.47	76	-	5.56E-05
Fluoranthene	Flua	$C_{16}H_{10}$	202.25	384	5.08	200–260	9.22E−06	8.86E−05
Pyrene	Pyr	$C_{16}H_{10}$	202.25	393	5.00	1.271	4.50E−06	1.19E−05
Benzo[*a*]anthracene	BaA	$C_{18}H_{12}$	228.29	437	5.68	10	2.10E−07	1.20E−05
Chrysene	Chry	$C_{18}H_{12}$	228.29	448	5.74	2.8	6.23E−09	5.23E−06
Benzo[*b*]fluoranthene	BbF	$C_{20}H_{12}$	252.31	-	6.20	1.2	5.00E−07	6.57E−07
Benzo[*k*]fluoranthene	BkF	$C_{20}H_{12}$	252.31	480	6.19	0.76	-	5.84E−07
Benzo[*a*]pyrene	BaP	$C_{20}H_{12}$	252.31	495	6.13	2.3	-	4.57E−07
Indeno[*1,2,3-cd*]pyrene	IncdP	$C_{22}H_{12}$	276.33	530	6.91	62	1.25E−10	3.48E−07
Dibenzo[*a,h*]anthracene	DBA	$C_{22}H_{14}$	278.35	524	6.55	0.5	1.00E−10	1.23E−07
Benzo[*g,h,i*]perylene	BghiP	$C_{22}H_{12}$	276.33	550	6.51	0.00026		-
2-Methylnaphthalene	2-MN	$C_{11}H_{10}$	142.08	240	3.38	24,600	5.50E−02	5.18E−04
2,6-Dimethylnaphthalene	2,6-DMN	$C_{12}H_{12}$	156.09	264	3.49	2,000	-	6.41E−04
3,6-Dimethylphenanthrene	3,6-DMP	$C_{16}H_{14}$	206.11	363	3.98	71	1.82E−05	6.25E−05
1-Methylfluoranthene	1-MF	$C_{17}H_{12}$	216.09	387	4.29	-	-	-
9-Fluorenone	9-FL	$C_{13}H_8O$	180.06	341	3.82	25,300	5.72E−05	6.77E−07
2-Methylanthraquinone	2-MAQ	$C_{15}H_{10}O_2$	222.07	408	4.24	-	-	-
Benz[*a*]anthracene-7,12-dione	BA-7,12-D	$C_{18}H_{10}O_2$	258.07	473	5.47	289	3.50E−08	3.10E−07
2-Nitrofluorene	2-NF	$C_{13}H_9NO_2$	211.06	375	4.75	216	9.54E−06	6.60E−07
9-Nitroanthrancene	9-NA	$C_{14}H_9NO_2$	223.06	403	4.45	114	1.35E−06	2.03E−07
3-Nitrofluoranthene	3-NF	$C_{16}H_9NO_2$	247.06	445	5.55	19.5		-
1-Nitropyrene	1-NP	$C_{16}H_9NO_2$	247.06	445	4.75	11.8	5.52E−08	3.27E−08
7-Nitrobenz[*a*]anthracene	7-NBA	$C_{18}H_{11}NO_2$	273.08	495	5.63	-	-	-

EXHIBIT 2 Illustration of the presence of PAHs in WWTP [Color figure can be viewed at wileyonlinelibrary.com]



environmental condition and treatment system. There is a possibility of some fraction of PAHs to be released into freshwater systems if they cannot be completely removed by existing treatment system. WWTPs have been well established as a major contributor of PAHs present in freshwater systems (Ozaki, Takamura, Kojima, & Kindaichi, 2015). Although some treatment processes used in WWTPs have focused on the reduction of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), current trends exhibit that effluent standards have also considered the removal of organic pollutants such as PAHs. Therefore, the fate and behaviors of PAHs present in WWTPs is a subject of present concern.

Several published review articles have discussed on the behaviors and removal of PAHs in the environment. Review articles have focusing on treatments of PAHs in aqueous environment by biodegradation (Haritash & Kaushik, 2009), wetlands (García et al., 2020), extractive membrane bioreactor (Wenten, Friatnasary, Khoiruddin, Setiadi, & Boopathy, 2020), chemical (Rubio-Clemente, Torres-Palma, & Peñuela, 2014), sorption (Lamichhane, Bal Krishna, & Sarukkalige, 2016), and nanotechnology (Borji, Ayoub, Al-Hindi, Malaeb, & Hamdan, 2020) have been reported. Methods for detection of PAHs in sediment (Wu, Sun, Li, & Sun, 2019) and aqueous as well as soil matrices (Pulleyblank, Cipullo, Campo, Kelleher, & Coulon, 2019) have been reviewed. Currently, methods for the removal of PAHs in road surfaces (Gbeddy, Goonetilleke, Ayoko, & Egodawatta, 2020) and their toxicity for aquatic animals (Honda & Suzuki, 2020) have also been reported. For a comprehensive overview, a list of current review articles discussing the topic of PAHs is presented in **Exhibit 3** (Abdullah et al., 2020; Gbeddy et al., 2020; Honda & Suzuki, 2020; Jalili, Barkhordari, & Ghiasvand, 2020; Jinadasa, Monteau, & Fowler, 2020; Li et al., 2020; Mojiri, Zhou, Ohashi, Ozaki, & Kindaichi, 2019; Mukhopadhyay, Dutta, & Das, 2020; Sayara & Sánchez, 2020; Sun et al., 2020; Zhang et al., 2019). A review of PAHs in wastewater has been carried out by Zhang et al. (2019) and found that the LMW and HMW PAHs were dominant in wastewater and sludge. However, the article reviews PAHs in wastewater not only in the field observation but also in the laboratory experiments. Another review paper carried out by Mojiri et al. (2019) showed that PAHs in aquatic environment ranged from 0.03 to 8,310,000 ng/L and have impact on microorganisms, plants, animals, and humans. Abdullah et al. (2020) reviewed the application of plants for remediation of PAHs in water and soil and identified their limitation in the field application. Alternatively, a review article by Li et al. (2020) indicated that the activated carbon and biochar are the most commonly used carbonaceous adsorbents to remove PAHs in sediments. Current review articles related to PAHs can be seen in Exhibit 3.

It is noted that review article specifically focused on the description of PAHs in full-scale WWTPs (untreated water at influent, treated water at effluent, and sludge) is hard to find in the literature. Therefore, the aim of this paper was to review the state of knowledge concerning PAHs in full-scale WWTPs including their fate and behaviors, analytical techniques, biological treatments, feasibility examination, and modeling. Also, new in this review is the discussion on substituted PAHs (SPAHs) such as methyl PAHs (MPAHs), chlorinated PAHs (ClPAHs), oxygenated PAHs (OPAHs), and monohydroxylated PAHs (OHPAHs) present in WWTPs, which is absent in published reviews elsewhere.

2 | FATE AND BEHAVIORS OF PAHS IN WWTPS

Recently, a number of WWTPs has been increasingly associated with the industrial development and the rise of population. PAHs can be created by combustion of organic materials and then transfer into a surface runoff via atmospheric deposition. As a result, PAHs can enter WWTPs through the drainage networks (Liu et al., 2017b). It has been well established that the current design of WWTPs has not considered for the removal of PAHs by the biodegradation process. Consequently, the common mechanism for the PAHs removal is achieved via adsorption on sludge (Bernal-Martinez, Patureau, Delgenès, & Carrère, 2009). In addition, the European Commission has established an allowable limit by 6 mg/kg for the sum of 11 PAHs from acenaphthene to indeno(1,2,3-*cd*)pyrene before sludge spreading. Thus, it is important to identify their fate and behaviors in WWTPs

EXHIBIT 3 List of current review articles discussing the topic of PAHs

Concern of paper	Findings	Reference
Fate and removal of PAHs in wastewater and sludge	It was exhibited that the low-molecular-weight (LMW) and high-molecular-weight PAHs were dominant in wastewater and sludge.	Zhang et al. (2019)
Fate, effects, and remediation of PAHs in water	PAHs have been detected in aquatic environment in the range of 0.03—8,310,000 ng/L and have impact on microorganisms, plants, animals, and humans. Adsorption and combined treatment techniques are recommended as the most effective to remove PAHs.	Mojiri et al. (2019)
Properties and behaviors of PAHs in urban road surfaces	It was found that the photolysis became the most significant transformation and degradation process because of the light absorption capacity of most PAHs	Gbeddy et al. (2020)
Toxicities of PAHs for aquatic animals	The study found that the toxicity of PAHs included the endocrine disruption and tissue-specific toxicity.	Honda and Suzuki (2020)
Plant-assisted remediation of PAHs in water and soil	Plant-assisted remediation can be considered one of the best technologies for the removal of PAHs in water and soil since it is environmentally friendly and relatively cheap. Field application of this method is still a challenge because of variations in weather and nutrients, moisture content, harmful insects, and plant pathogens, which can affect the remediation performance.	Abdullah et al. (2020)
Solid-phase microextraction technique for sampling and preconcentration of PAHs	Solid-phase microextraction provides several advantages such as good performance, being a single-step process, easy coupling with chromatographic systems, noninvasiveness for biological monitoring, and being ecofriendly. This method has limitations such as memory effects, fiber damage at extreme pH levels, and low performance in biological matrices.	Jalili et al. (2020)
Biomonitoring of PAHs	Biomonitoring of PAHs can be carried out using plants, lichens, and mosses. There is a need for studies on the effects of environmental and meteorological parameters, and seasonal flux on uptake efficiency of the pollutant by bioaccumulators.	Mukhopadhyay et al. (2020)
Separation and detection methods for nitro-PAHs	Rapid and sensitive methods for the simultaneous determination of multi-nitro-PAHs in various samples are still needed.	Sun et al. (2020)
Bioremediation of PAHs in soils	The implementation of compost and composting is promising for the bioremediation of PAHs in soils.	Sayara and Sánchez (2020)
Carbonaceous adsorbents to remove PAHs in sediments	Field application of this method has not been demonstrated. Activated carbon and biochar are the most commonly used carbonaceous adsorbents to remove PAHs in sediments.	Li et al. (2020)
Fate and behaviors of PAHs fish and fisheries products	The smoked fish from Sri Lanka were found to be not safe for human consumption based on the allowable limits permitted by the European Union.	Jinadasa et al. (2020)

including in influent, effluent, and sludge, which are important for environmental management practices.

Exhibit 4 lists the concentration of PAHs in WWTPs collected from previous works. It is noted from the table that this paper has identified the occurrence of WWTPs in several regions, which include in Asia, Europe, America, and Middle East. Based on the current analysis from the listed countries, the detected concentration of PAHs ranged from 190 to 547 $\times$ 10^4 ng/L in the influent and 14 to 4700 ng/L in the effluent. In Asia, the sum of PAHs ($\sum$PAHs) at effluent recorded in China becomes the highest concentration, which is up to 4.700 ng/L. In Europe, Poland recorded the highest concentration in the effluent. Moreover, Jordan recorded a higher concentration of $\sum$PAHs compared to that reported in Canada.

Moreover, the presence of PAHs in sludge is presented in **Exhibit 5**. It is noted from the figure that $\sum$PAHs reported in Zheijiang, China, recorded the highest concentration among the region (Asia), which is up to about 13 times higher (at the maximum level) than recorded in Guangdong, Qindao, and Kuwait. In the region of Europe, the reported concentration varied between 300 and 80,000 ng/g with Germany recorded the highest values compared to others. At the maximum level, the presence of PAHs recorded in Germany was about 133 times higher than reported in Italy and about 10 times higher than reported in Spain and Finland. Moreover, Canada reported the presence of PAHs in the sludge by up to 209,000 ng/g, which is about 27 times higher than recorded in Tunisia.

The occurrence of PAHs in influent and effluent (treated and sludge) can also be varied by temporal. For instance, the presence of PAHs in these factions was evaluated at two different seasons, which are in summer and winter (Qiao et al., 2014a). The analysis was conducted using the LMW and HMW PAHs. The study observed that the total effluents of LMW PAHs can be decreased compared to the influent both in the summer and winter. In the summer, the loss percentages of these compounds were higher compared to in the winter (**Exhibit 6**),

EXHIBIT 4 The occurrence of PAHs in WWTPs at different regions

Region	Country	Influent (ng/L)	Effluent (ng/L)	Reference
Asia	Korea	550–311410	120–630	Lee et al. (2011)
	China	$(5{,}470 \pm 907) \times 10^3$	$(4.7 \pm 0.4) \times 10^3$	Zhang et al. (2012a)
	China	5759 ± 2239	2240 ± 187	Wang et al. (2013)
	China	372–749	182–241	Qiao et al. (2014a)
	Japan	219 ± 210	43.5 ± 42.5	Ozaki et al. (2015)
	China	333 ± 41 to 474 ± 51	98 ± 21 to 161 ± 25	Qiao et al. (2017)
	China	301 ± 217	63.3 ± 54.1	Man et al. (2017)
	China	301 ± 255	14.9 ± 12.1	Man et al. (2017)
	China	4,080	864	Sun et al. (2018)
	China	190–250	92–150	Qiao et al. (2019)
Europe	Greece	4,574	745	Manoli and Samara (1999)
	France	1,277–3,241	-	Blanchard et al. (2001)
	France	1,300–8,000		Blanchard et al. (2004)
	Norway	620 ± 340	286 ± 290	Vogelsang et al. (2006)
	Italy	620 ± 340	286 ± 290	Busetti et al. (2006)
	Greece	11,534	5,636	Manoli and Samara (2008)
	Spain	14,300	3,910	Sánchez-Avila, Bonet, Velasco, and Lacorte (2009)
	Italy	760 ± 570	50.0–195	Fatone et al. (2011)
	Ireland	-	376	Jones, Kinsella, Furey, and Regan (2012)
	Poland	255,050–311,907	940–4465	Burmistrz and Burmistrz (2013)
	Italy	2,400–5,300	150–260	Mezzanotte, Anzano, Collina, Marazzi, and Lasagni (2016)
	Italy	5,600–6,600	30–60	Berardi et al. (2019)
America	Canada	2,070	400	Pham and Proulx (1997)
Middle East	Jordan	1,168–1,224	303–496	Jiries et al. (2000)
	Jordan	1,163–2,866	518–1,635	Alawi, Tarawneh, and Ghanem (2018)

which can be associated with the biodegradation/transformation and volatilization that are responsible in the removal process. For HMW PAHs, their concentrations in the effluent were relatively similar with the influent in winter and higher compared to the influent in summer. It is speculated that increase in HMW PAHs in the effluent in summer possibly came from the residues of the HMW PAHs in the activated sludge.

3 | FATE AND BEHAVIORS OF SUBSTITUTED PAHS IN WWTPS

It has been well known that SPAHs could be transformed from the PAHs origin, or they can be discharged directly (Lee, Peart, Hong-You, & Gere, 1993; Lundstedt et al., 2007). Previous study exhibited that the toxicity of the SPAHs can be similar or greater compared to their parent PAHs (Durant, Busby, Lafleur, Penman, & Crespi, 1996). Due to the presence of nitro (NO_2) groups, some studies clearly exhibited that SPAHs such as nitrated PAHs (NPAHs) were more mutagenic and carcinogenic compared to their parent PAHs (Alves et al., 2016; Lin et al., 2015).

In the 1990s, identification of SPAHs in sewage sludges of WWTPs in Poland were carried out and quantified using GC-MS or HPLC (Bodzek, Janoszka, & Warzecra, 1996; Tyrpień, Janoszka, & Bodzek, 1997). Bodzek et al. (1996) reported the presence of SPAHs such as nitroarenes and azaarenes in the sewage sludges of Siliria, Poland. A year after the study, Tyrpień et al. (1997) also confirmed the presence of several carbonyl, nitro polycyclic aromatic compounds, azaarenes, and polar PAHs, which are very dangerous to human health, detected in the sewage sludge samples of Siemianowice, Poland. However, their studies did not clearly present the concentration for each SPAHs in the samples. The study only focused on the applicability of GC-MS and HPLC for the investigation of mass spectrum characteristics and their retardation factor (R_F) values.

Identification of monohydroxylated PAHs (OHPAHs) in WWTPs of Venice, Italy, was carried out by Pojana and Marcomini (2007) as presented in **Exhibit 7**. OH-PAHs such as 1-OH-phenanthrene (1-OH-PHE), 1-OH-phyrene (1-OH-PYR), and 6-OH-chrysene (6-OH-CHR)

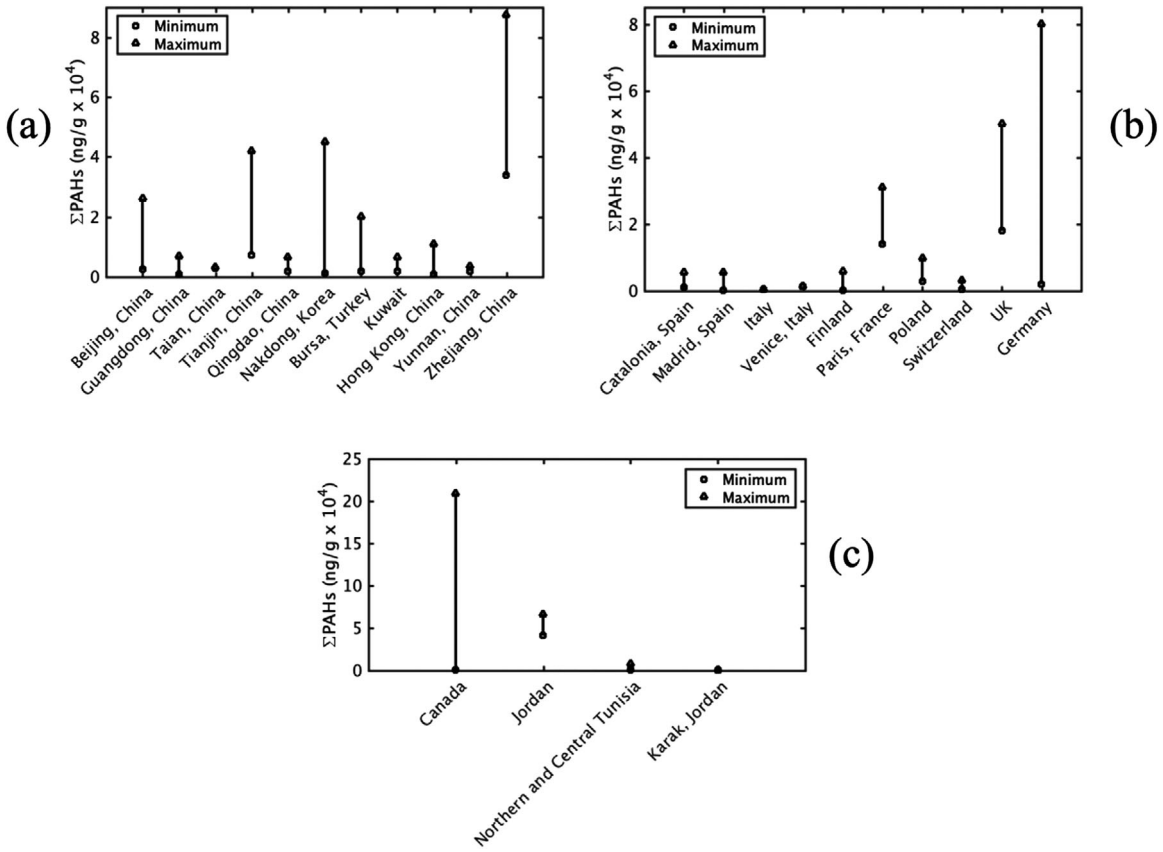


EXHIBIT 5 PAHs concentration in WWTPs in sludge at different regions of (a) Asia, (b) Europe, and (c) America and Middle East. The data were collected from: Asia: Beijing, China (Dai, Xu, Chen, Yang, & Ke, 2007), Guangdong, China (Zeng et al., 2010), Taian, China (Tian et al., 2012), Tianjin, China (Qi et al., 2011), Qingdao, China (Zhai, Tian, & Liu, 2011), Nakdong, Korea (Ju, Lee, Sim, Eun, & Oh, 2009), Bursa, Turkey (Salihoglu et al., 2010), Kuwait (Helaleh, Al-Omair, Nisar, & Gevao, 2005), Hong Kong, China (Cai, Mo, Wu, Zeng, & Katsoyiannis, 2007), Yunnan, China (Xiaoming et al., 2013), and Zhejiang, China (Hua, Wu, Liu, Tientchen, & Chen, 2008). Europe: Catalonia, Spain (Pérez et al., 2001), Madrid, Spain (Sánchez-Brunete, Miguel, & Tadeo, 2007), Italy (Suciu, Lamastra, & Trevisan, 2015), Venice, Italy (Busetti et al., 2006), Finland (Kapanen, Vikman, Rajasärkkä, Virta, & Itävaara, 2013), Paris, France (Blanchard, Teil, Ollivon, Legenti, & Chevreuil, 2004), Poland (Oleszczuk, 2009), Switzerland (Brändli et al., 2007), UK (Stevens, Northcott, Stern, Tomy, & Jones, 2003), and Germany (Schnaak et al., 1997). America, Africa, and Middle East: Canada (Kohli, Lee, & Peart, 2006), Jordan (Batarseh, 2011), Northern and Central Tunisia (Khadhar, Higashi, Hamdi, Matsuyama, & Charef, 2010), and Karak, Jordan (Jiries et al., 2000)

were successfully identified. The recorded ∑OH-PAHs was observed in the range of 44 and 342 ng/L and 293 and 477 ng/L for the municipal influent and the industrial influent, respectively. In the effluent, these SPAHs were detected mostly in the particulate phase compared to adsorbed phase. The study also confirmed log K_{ow} values of 1-OH-PHE, 1-OH-PYR, and 6-OH-CHR by 3.9, 4.5, and 5.30, which are only 0.49–0.22 units lower compared to their origin of Phe, Phy, and Chry, respectively. Moreover, the absorption mechanism on the sludge was proposed as the main removal process of the SPAHs.

Alternatively, the occurrence and behavior of MPAHs in WWTPs in Beijing, China, were investigated (Qiao et al., 2014a). The study found that the ΣMPAHs concentrations varied from 149 to 221 ng/L, 29.6 to 56.3 ng/L, and 202 to 375 ng/g, in the influent, effluent, and sludge samples, respectively. In addition, the ΣOPAHs concentrations in the corresponding samples were 139–155 ng/L, 69.9-109 ng/L, and 695–1533 ng/g, respectively. In another investigation, the concentration of ΣMPAHs, ΣOPAHs, and ΣClPAHs was monitored in WWTPs in Beijing, China (Qiao et al., 2017). The detected ΣMPAHs, ΣOPAHs, and ΣClPAHs in the influent were 65 ± 33 to 147 ± 56, 199 ± 67 to 264 ± 35, and 33 ± 4 to 44 ± 3 ng/L, respectively. In addition, the corresponding values in the effluent can be reduced to 12 ± 4 to 22 ± 13, 36 ± 5 to 132 ± 11, and 17 ± 0 to 23 ± 3 ng/L.

SPAHs were also monitored in WWTPs in Beijing, China (Cao, Qiao, Liu, & Zhao, 2018). The inspected MPAHs and OPAHs in the influent were 684.9 and 844.9 ng/L, respectively. In the effluent, the corresponding values were decreased to be 271.8 and 312.3 ng/L, respectively. It was observed that the ΣOPAHs were found to be higher compared to MPAHs. This is possibly due to their polarity of OPAHs, which is higher compared to MPAHs, enhancing better solubility in water.

In another WWTPs, the presence of SPAHs including OPAHs, ClPAHs, and MPAHs were investigated in a WWTP in Guangdong, China (Qiao et al., 2019). The ΣMPAHs, ΣOPAHs, and ΣCIPAHs in the influent were 30–64, 216–312, and 2–3 ng/L, respectively. In the effluent, the corresponding ΣMPAHs, ΣOPAHs, and ΣCIPAHs values were

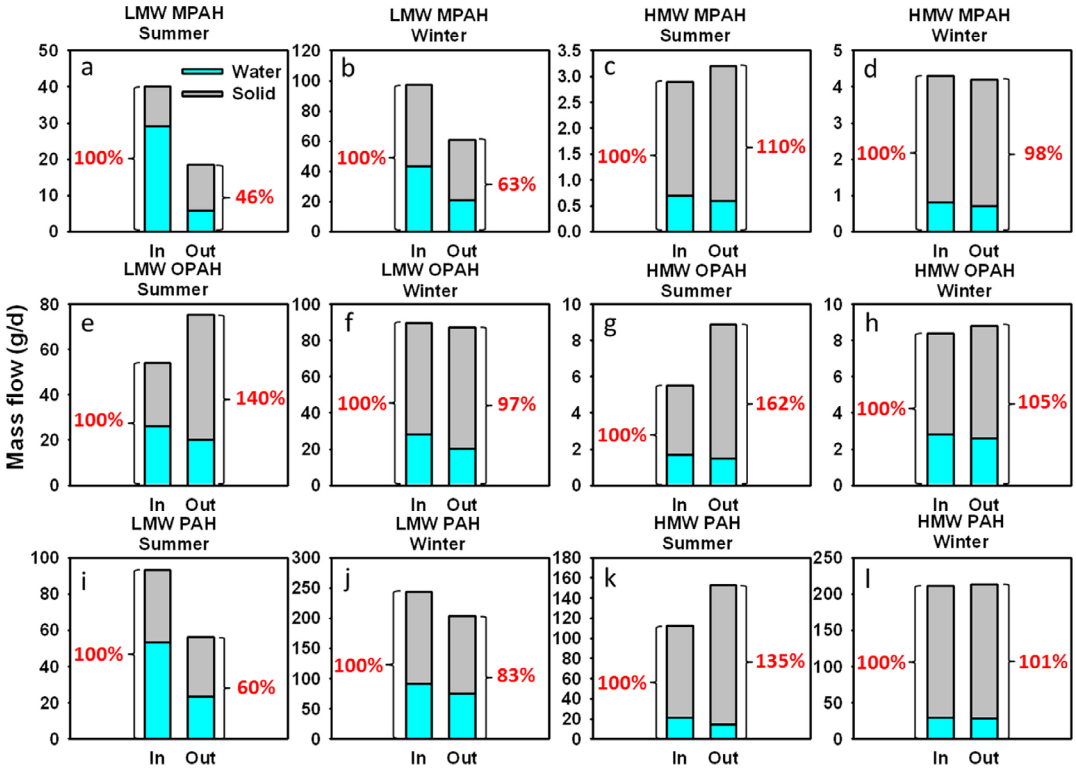


EXHIBIT 6 The presence of PAHs and their substitutions at different seasons, which are in summer and winter adapted from Qiao et al. (2014a). It is noted that a, b, e, f, i, and j refer to LMW compounds and others refer to HMW compounds [Color figure can be viewed at wileyonlinelibrary.com]

EXHIBIT 7 The existence of SPAHs in WWTPs effluent in several regions

Country	ΣMPAHs (ng/L)	ΣOPAHs (ng/L)	ΣClPAHs (ng/L)	ΣOHPAHs (ng/L)	Reference
Venice, Italy	–	–	–	15–69	Pojana and Marcomini (2007)
Beijing, China	208 ± 30	192 ± 19	–	–	Qiao, Qi, Zhao, Liu, and Qu (2016)
Tianjin, China	40–4,300	80–4,430	–	–	Qiao et al. (2014b)
Beijing, China	29.6–56.3	69.9–109	–	–	Qiao et al. (2014a)
Beijing, China	65 ± 33 to 147 ± 56	199 ± 67 to 264 ± 35	33 ± 4 to 44 ± 3	–	Qiao et al. (2017)
Beijing, China	271.8	312.3	–	–	Cao et al. (2018)
Beijing, China	49 ± 18	192 ± 54	60 ± 13	–	Qiao et al. (2018)
Guangdong, China	13–36	114–154	2		Qiao et al. (2019)

13–36, 114–154, and 2 ng/L, respectively. Transformation from parent PAHs to OPAHs in the atmospheric environment can be achieved via photochemical transformation. During the summer, the ratios of OPAHs/PAHs in the atmosphere can achieve 20 times higher compared to during the winter (Walgraeve, Demeestere, Dewulf, Zimmermann, & Van Langenhove, 2010).

Temporal variation of SPAHs in influent and effluent (treated and sludge) was observed by Qiao et al. (2014a). The study found that the total effluents of LMW MPAHs have been observed to decrease compared to the influent in the summer and winter. For LMW OPAHs, the output was found to be high compared to the input, which is possible due to the formation of OPAHs. For HMW OPAHs, their concentrations in the effluent were higher compared to the influent both in the summer and winter. In general, findings of the study can be observed in Exhibit 6.

The existence of NPAHs was inspected in biological WWTPs in Shangdong, China (Zhao et al., 2019). The ∑NPAHs in the WWTPs were 1,143.9–1,193.2 ng/L in the influent while 195.6–725.5 ng/L in the effluent. In addition, the ∑NPAHs in the sludge samples were found to be 483.5 to 2763.0 ng/g. The study proposed the removal mechanism of these SPAHs as follows. The transformation from PAHs to NPAHs can be associated with the mass surplus in WWTPs. Removal of NPAHs in the existing system was carried out in primary and secondary stages. Interestingly, the A^2O method was highly effective

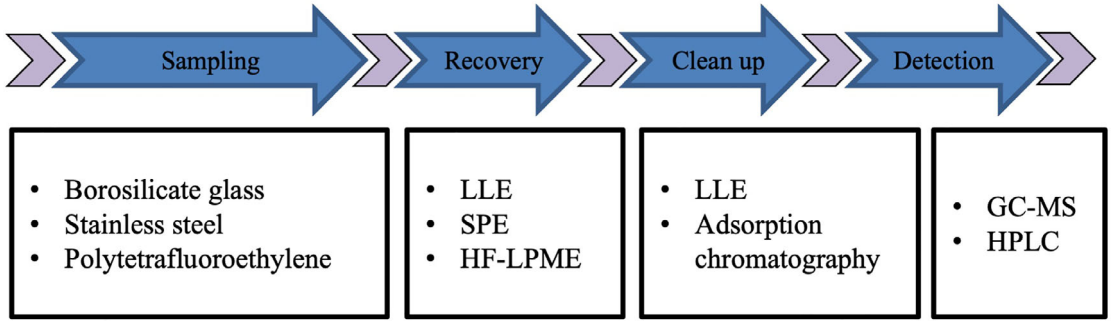


EXHIBIT 8 Summary of analytical procedures for sampling, recovery, cleanup, and quantification of PAHs [Color figure can be viewed at wileyonlinelibrary.com]

in the removal capacity of NPAHs and it was found to be less influenced by seasonal variations. However, the study also found that the existing treatment at the tertiary stage was ineffective in the removal of NPAHs. Moreover, the study also found that the transformation from PAHs to NPAHs was observed in the aqueous phase, mainly in the summer. This was confirmed by an increase in concentrations of NPAHs not only in the aqueous phase but also in the particulate phase. During the summer, this transformation was more preferable because of higher temperatures compared to winter.

4 | ANALYTICAL TECHNIQUES: SAMPLING, RECOVERY, CLEANUP, AND QUANTIFICATION ANALYSES

Exhibit 8 shows steps for monitoring and identifying PAHs in WWTPs including water and sludge samples. It can be initiated by sampling procedure for collecting water and sludge samples before it ends up with the quantification analyses using established analytical techniques. The first step in the field measurement is how wastewater and sludge samples can be representative of the matrix being sampled and how to maintain sample integrity before further analysis in laboratory. Thus, it needs a strategy to cope with temporal and spatial heterogeneity of the targeted organic compounds. In addition, it is also critical to plan the sampling at different periods such as winter or summer when the estimation of discharge loads of PAHs in WWTPs is necessary. This is essential to estimate the temporal variation of PAHs from baseline values.

For the sampling procedure, determination of storage materials to handling organic compounds such as PAHs is important because unreliable storage materials can interact chemically with targeted PAHs or they can release some chemicals, which probably affect further chromatographic analysis. Commonly recommended storage materials are borosilicate glass, stainless steel, and polytetrafluoroethylene (PTFE). In general, amber glass containers are normally recommended as storage materials for handling wastewater and sludge samples (Busetti, Heitz, Cuomo, Badoer, & Traverso, 2006; Charalabaki, Psillakis, Mantzavinos, & Kalogerakis, 2005; Chen et al., 2019; Liu et al., 2017b, Tian, Bai, Liu, Sun, & Zhao, 2012). The reason for this is as follows. The use of plastics such as polyethylene or polypropylene can probably release plasticizers to samples and potentially lead to some complicated problems during chromatographic analysis. In addition, some plastics are porous to organic compounds. This has the potential to loss of the targeted compounds during transportation and storage before the analysis. Since the plastic surface is commonly associated with the presence of microbes, this has the potential for the enhancement of degradation of PAHs. Hence, the use of the glass has been widely popular in various studies (Busetti et al., 2006; Charalabaki et al., 2005; Chen et al., 2019; Jiries, Hussain, & Lintelmann, 2000; Liu et al., 2017b; Manoli & Samara, 1996, 2008; Pérez, Guillamón, & Barceló, 2001; Tian et al., 2012).

Recovery and preconcentration of PAHs from wastewater samples are also crucial in the determination of PAHs. Several approaches such as liquid– extraction (LLE) (Manoli & Samara, 1996, 2008), solid phase extraction (SPE) (Busetti et al., 2006), and hollow fiber liquid-phase microextraction (HF-LPME) (Charalabaki et al., 2005) have been widely implemented. It is noted that LLE has several drawbacks such as large volumes of toxic organic solvents requirement, emulsion formation, contamination from glassware, and the involvement of toxic chemicals as the extracting solvent. The advantage of LLE is related to low equipment costs. SPE could eliminate these problems. By using this method, extraction conditions can be carried out at different variations leading for the achievement of the desired separation and preconcentration (Brouwer, Hermans, Lingeman, & Brinkman, 1994). Alternatively, the recovery and preconcentration of PAHs from wastewater samples can be achieved via HF-LPME (Charalabaki et al., 2005). Charalabaki et al. (2005) claimed that the method was powerful, and it is relatively simple and low cost.

Cleanup procedure is crucially needed before the analytical determination of PAHs in the samples since wastewater samples can be considered as a relatively complex matrix. The most commonly used cleanup procedures are simple SPE (Manoli & Samara, 1996, 2008). Alternatively, it can also be carried by using adsorption chromatography (Jiries et al., 2000). It is noted that the degree of cleanup involvement depends highly on the selectivity of the further detection step (Wise, Sander, & May, 1993).

Determination and quantification of PAHs in wastewater and sludge samples can be carried out using some analytical methods. For instance, PAHs can be investigated by gas chromatography coupled with mass spectrometric detection (GC-MS). Alternatively, it can also

EXHIBIT 9 Analytical techniques used for the determination of PAHs wastewater samples

Analytical technique	Detection limit	Reference
GC-MS	0.2–0.4 ng/L	Pham and Proulx (1997)
HPLC	0.52–1.2 ng/L	Busetti et al. (2006)
HPLC	0.17—30 ng/L	Manoli and Samara (2008)
GC-MS	0.01—0.59 μg/L	Zhang et al. (2012a)
GC-MS	–	Zhang et al. (2012b)
GC-MS	0.01—0.58 μg/L	Zhang et al. (2013)
GC-MS	–	Sun, Tian, and Wang (2013)
GC-MS	0.01—0.59 μg/L	Zhang, Wei, and An (2015)
HPLC	0.5–3.0 ng/L	Yan, Zhang, Wu, Yang, and Wang (2016)
GC-MS	–	Gong et al. (2017)
GC-MS	–	Zhao, Sui, and Huang (2018)
GC-MS	0.7 to 1.1 ng/L	Sun et al. (2018)
GC-MS	0.02–0.45 μg/L	Ren, Li, Li, Chen, and Cheng (2019)
GC-MS	0.02—12.49 ng/L	Zhao et al. (2019)
GC-MS	0.07—11 ng/L	Berardi et al. (2019)
GC-MS	–	Sun et al. (2019)

be carried out via liquid chromatography (LC). These techniques are capable of detecting PAHs, but MS can perform well compared to FL or UV. This is very crucial as the detection of PAHs in wastewater and sludge samples can be challenging and complex. In general, the use of LC techniques needs less intensive sample cleanup processes compared to the GC method since LC techniques are operated with guard precolumns (Marcé & Borrull, 2000). In addition, LC techniques are possible for the injection of higher sample volumes compared to GC, which is only a few microliters. As a result, the use of GC techniques requires sample preparation, which is usually preconcentrated by volatilization of the solvent. In general, detection and quantification of PAHs and their substitutions can be carried out by using high-pressure liquid chromatography (HPLC) or GC-MS as listed in **Exhibit 9**. A comprehensive overview, summary of analytical procedures for sampling, recovery, cleanup, and quantification of PAHs is presented in Exhibit 8.

5 | FULL-SCALE PERFORMANCES OF BIOLOGICAL TREATMENT METHODS

Performance of WWTPs employing biological treatment process has been evaluated in the full-scale. The treatment is considered as an acceptable and effective approach for organic compounds in WWTPs. A mechanism in the removal of PAHs and their substitutions in WWTPs can be possible by volatilization by aeration, biodegradation by microorganism, and adsorption on sludge. In the conventional WWTPs, the contribution of volatilization in the removal process is only below 2% (Sponza & Gök, 2010). In addition, the contribution of biodegradation can be minor unless specific microorganisms were inoculated for the enhancement of PAHs removal (Chen, Wang, & Hu, 2010). Moreover, the adsorption acts as the main mechanism for removing PAHs in WWTPs (Lei, Hu, Wong, & Tam, 2007). This is because PAHs have high affinity for particulate matter.

The activated sludge method is a biological treatment that has capability to remove PAHs in WWTPs. The removal process can occur via biodegradation by existing microorganism or by adsorption on sludge. For instance, WWTP in the East Norway employing activated sludge as the biological treatment combined with precipitation mechanism has successfully removed 16 PAHs ranging from 94 to 100% (Vogelsang, Grung, Jantsch, Tollefsen, & Liltved, 2006). The biological treatment performance was compared with WWTPs in other east and west locations employing coagulation as the chemical treatment, which can only achieve the removal ranging from 61 to 78%. It was noted that the chemical treatments removed 82–100% and only 29–70% of the 4, 5, 6 PAHs (log P_{ow} 4.9–6.8) and 2, 3 PAHs (log P_{ow} 3.3–4.5), respectively. As a comparison, the removal of 2, 3 PAHs using the biological treatment can achieve 91–100%, indicating these PAHs can be biodegraded and/or evaporated during the process. This is scientifically evidenced by the previous study who observed that some PAHs can be biodegraded in the biological treatment (McNally, Mihelcic, & Lueking, 1998).

The performance of activated sludge in the removal of 16 PAHs was also evaluated in the WWTPs in Korea (Lee, Sim, Kim, Chang, & Oh, 2011). The removal efficiency of PAHs by the activated sludge process was 80.6 ± 6.6%. The adsorption was proposed as the main mechanism due to the free-floating and aerated microorganisms. A similar finding was also observed in WWTP in Xi'an, China, for the investigation of eight PAHs (Liu, Wang, & Fan, 2011). The removal of these PAHs ranged from 75% to 97% with an average of 85.7%. The removal of 16 PAHs in WWTPs employing activated sludge as the biological treatment in Beijing, China, was investigated (Cao et al., 2018). The removal of 16 PAHs in the WWTPs was observed in the range of 59.2% to 68.4%. To clarify the possible mechanism, the study then investigated the removal efficiencies in the dissolved and adsorbed phase. It was found that the removal of these PAHs in the WWTPs can be found ranging from 43.7% and 58.2% (in dissolved phase), while between 60.6% and 80.7% was confirmed in the adsorbed phase. It was clear that the removal efficiencies in the adsorbed phase are high compared to in the dissolved phase, suggesting the adsorption of PAHs in the activated sludge is more favorable.

The removal of eight SPAHs (MPAHs and OPAHs) in the biological treatment of WWTPs in Beijing, China, was examined (Cao et al., 2018). The study observed that the removal of these SPAHs can be archived up to 65.1%. The removal efficiencies were slightly lower than for PAHs that ranged from 59.2% to 68.4% in the same WWTPs. This is possibly due to the lower log K_{ow} of the SPAHs compared to PAHs. This is also possible since biotransformation of the PAHs to SPAHs in the WWTPs. By analyzing their removal efficiencies in the dissolved (45.8–52.1%) and adsorbed phase (67.1–75.4%), the study proposed that the adsorption was the main process for the removal of SPAHs in the WWTPs.

EXHIBIT 10 Biological treatment methods at full-scale WWTPs for the removal of PAHs

Biological treatment method	Location	Finding	Reference
Activated sludge	Umeå, Sweden	Successfully removed five MPAHs ranging from 84 to 100%	Bergqvist et al. (2006)
	East Norway	Removed 16 PAHs ranging from 94 to 100%	Vogelsang et al. (2006)
	Thessaloniki, Greece	Removed in the range of 37% for F to 89% for B[α]An	Manoli and Samara (2008)
	Korea	Removed 16 PAHs by 80.6 $\pm$ 6.6%	Lee et al. (2011)
	Xi'an, China	Investigation of eight PAHs with removal performance ranging from 75% to 97% for CHRY and PYR, respectively, with an average of 85.7%	Liu et al. (2011)
	Hiroshima Prefecture, Japan	Half of the PAHs (63%) were biologically or chemically transformed or removed	Ozaki et al. (2015)
	Lombardy, Italy	Removed PAHs up to 97 and 90% for Alto Seveso and Nosedo, respectively	Mezzanotte et al. (2016)
	Beijing, China	The removal efficiencies of 16 PAHs by the three WWTPs were observed in the range of 59.2% to 68.4%	Cao et al. (2018)
	Beijing, China	Removed eight SPAHs including four MPAHs and four OPAHs with the removal efficiencies ranging from 58.3 to 65.1%	Cao et al. (2018)
Bioreactor	Granada, Spain	Removal efficiencies: Phenanthrene (82%), Fluoranthene (91%), and Pyrene (92%)	González-Pérez et al. (2012)
	Italy	Could remove 16 PAHs up to 64%	Fatone et al. (2011)

Investigation of removal efficiencies of SPAHs was also carried out in WWTP in Umea, Sweden (Bergqvist, Augulytė, & Jurjonienė, 2006). The biological treatment method employed in the WWTP can successfully remove these five MPAHs ranging from 84 to 100%. The study proposed that the biodegradation mechanism was the main process.

An evaluation of full-scale performance of WWTP in Italy employing a membrane bioreactor for the removal of 16 PAHs was carried out (Fatone, Di Fabio, Bolzonella, & Cecchi, 2011). The WWTP can perform the removal efficiencies up to 64%. Alternatively, González-Pérez et al. (2012) performed full-scale evaluation of the removal capability of WWTP in Granada, Spain. The WWTP uses membrane bioreactor as the biological treatment method for the removal of detected three PAHs. The study found that the WWTP can remove PAHs up to 92% with individual removal as follows: Phe (82%), Flua (91%), and Pyr (92%). It was proposed that the main mechanism was air stripping. This process can reduce establishment of microorganisms that are responsible for the biodegradation of PAHs in the WWTP. Some biological treatment methods at full-scale WWTPs for the removal of PAHs and their substitutions are listed in **Exhibit 10**.

6 | FEASIBILITY OF FULL-SCALE TREATMENT METHODS: TECHNICAL, SOCIAL, ADMINISTRATIVE, ECONOMIC, AND ENVIRONMENTAL ASPECTS

Feasibility evaluation is an efficient approach for the determination of the best option compared with available alternatives. For the current context, this analysis shows the effectiveness of the treatment system used in WWTPs for the removal of particular pollutant. Therefore, it is noted that WWTPs are a positive process not only from an environmental point of view but also economically and technically. Therefore, this review focuses on the feasibility analysis between full-scale activated sludge and membrane bioreactor methods in WWTPs.

Recently, membrane bioreactors have been more popular for the treatment of wastewater as they become alternative to activated sludge process. By an annual growth rate ranging from 10 to 20%, they become the fastest growing treatment system used for treating wastewater (Wozniak, 2012). When an advanced biological treatment is considered, membrane bioreactors are probably the best option since they have capability for the complete suspended solid removal in the effluent of WWTPs (Bis, Montusiewicz, Piotrowicz, & Łagód, 2019). The drawbacks of membrane reactors are the high cost related to operation and high energy consumption, high sludge production related to retention of suspended solid, and fouling problem in the membrane. The above discussions showed that both biological treatments are capable of the removal of PAHs in WWTPs.

To assess the feasibility of both treatment systems, some holistic comparisons have been carried out and reported in the literature. Based on long-term cost and footprint analyses, membrane bioreactors system was the best option for long-term operation (longer than 67 years) while activated sludge system was the best for the operation less than 67 years (Karim & Mark, 2017). Although activated sludge system was also designed for enhanced nutrient removal or water reuse, its capital and overall 20-year present worth costs is still equal compared to membrane bioreactors system (Young, Muftugil, Smoot, & Peeters, 2012).

A comparative assessment for full-scale WWTPs found that activated sludge system was more preferable essentially due to lower energy consumption and cost (Bertanza et al., 2017). However, the study exhibited that membrane bioreactors system has a bet-

EXHIBIT 11 Scores range comparison between full-scale activated sludge (AS) and membrane bioreactors (MBR) (Bertanza et al., 2017). Scores equal to 0 and 2 reflect the worst and best ranking, respectively

Aspect	Parameter	AS (Score)	MBR (Score)
Technical	Reliability	1.67	1.67
	Flexibility	1.75	1.75
	Complexity	1.20	0.80
Social	Economic Impact	2.00	1.00
	Effluent quality	0.00	1.00
	Odor emissions	0.00	0.00
	Skyline modification	0.00	1.00
	Soil consumption	0.00	1.00
	Others	2.0	2.0
Administrative	Complexity of the authorization	2.00	2.00
Economy	Total cost under the favorable conditions	2.00	0.00
	Total cost under the worst conditions	2.00	1.00
Environment	Global warming potential	2.00	2.00
	Acidification potential	2.00	2.00
	Eutrophication, fresh water	2.00	0.00
	Eutrophication, marine	1.00	2.00
	Eutrophication, terrestrial	2.00	2.00
	Photochemical oxidant formation potential	1.00	2.00
Final score		1.58	1.32

ter social acceptance compared to the activated sludge system. In general, technical, social, administrative, economic, and environmental aspects of both treatment system are presented in **Exhibit 11**, which shows scores range comparison between full-scale activated sludge and membrane bioreactors. Scores equal to 0 and 2 reflect the worst and best ranking, respectively. Currently, a plant-wide modeling comparison revealed some better findings for the activated sludge system compared to membrane bioreactors. Specifically, the activated sludge system had lesser direct and indirect greenhouse gas emissions than membrane bioreactors (Mannina, Cosenza, & Rebouças, 2020).

7 | MATHEMATICAL MODELING

Employing mathematical model is useful to comprehensively understand the fate and treatability of the pollutants in WWTPs. Since this review has focused on full-scale WWTPs, this section provides the knowledge not only on the overview of pollutant behaviors but also the treatment performance, which are beneficial to designing the further improved full-scale engineered bioremediation systems. Although several mathematical models such as Byrns' model (Byrns, 2001) and STP-WIN model (a version of the Toronto STP model present in the Estimation Programs Interface Suite™) (Clark, Henry, & Mackay, 1995) were used for the modeling the fate and treatability of some pollutants in WWTPs, the majority of studies reported in literature employed the fate and treatability estimator (FATE) model for the modeling of PAHs in full-scale WWTPs. Hence, this section is focused only on the discussion of application of the FATE model.

The FATE model is more popular for the prediction of removal of PAHs in WWTPs.

Currently, the FATE model is more popular for the prediction of removal of PAHs in WWTPs in several regions. FATE is known as a user-friendly computerized model that has capability for the estimation of pollutants released to a conventional activated sludge process. It was proposed by the Industrial Technology Division of the U.S. Environmental Protection Agency. It basically involves two separate models that can evaluate the removal of pollutants (organics and inorganics). In relation to the current focus, this paper only focuses on the application of the organic submodel. At a steady state, a mathematical equation for this model for the description of the pollutant concentration exiting the primary clarifier is given as

$$S_0 = \frac{QS_{\text{in}}}{Q + Q_p X_p \left(4.1 \times 10^{-5} K_{\text{ow}}^{0.35}\right)}. \quad (1)$$

At the secondary clarifier, the pollutant concentration is estimated as

$$S = \frac{Q_0 S_0}{Q_0 + (GH/RT)\, Q_w X_v \left(3.06 \times 10^{-5}\right) K_{\text{ow}}^{0.67} + k_1 X_a V}, \quad (2)$$

where S_0 is the concentration of pollutant outgoing from primary sedimentation, $Q = Q_0$ is the incoming flow rate = the outgoing flow rate from a secondary stage (Q_c water + Q_w), S_{in} is the incoming pollutant concentration, Q_p is the sludge flow rate extracted from primary sedimentation, Q_w is the sludge flow rate extracted from secondary sedimentation, X_p is the dry substances concentration in primary sedimentation, S is the organic pollutant concentration outgoing from secondary sedimentation, X_v is the concentration of pollutant in secondary sludge, X_a is the concentration of active cells in the reactor, G is the air flow rate in an aeration compartment, T is the aeration compartment temperature, and k_1 is the first-order biodegradation coefficient. In addition, constants of the model are H and R, which refer to Henry's constant and 8.206×10^5 (m^3 atm K^{-1} mol^{-1}).

Successful evaluation of the model in the full-scale WWTPs has been intensively reported. For instance, PAHs removal efficiencies at Varese Olona WWTPs, Italy, were reported (Torretta, 2012). The study found that the percentage removal efficiency can be well predicted using the model for five PAHs (Ant, Flt, Pyr, Chry, BaA) with the percentage differences between the model and field data ranging from 0.01 to 0.03%. However, the model underestimated the removal efficiencies for other detected PAHs.

Another report also confirmed the success of the model for the estimation of percentage removal efficiency of WWTP in northern Greece

(Manoli & Samara, 2008). The study exhibited that the model was capable of predicting for the full process (in the primary and secondary stages). The drawback was observed when the model was used for the prediction at an individual treatment stage, which is only in individual primary or in individual secondary stage. In the primary stage, lower underestimations in the range of 5 for B[α]An to 30% for B[ghi]Pe were observed compared to the field data. In the secondary stage, the model achieved well predicted only for N_p, while for other detected PAHs the model overestimated (28% for B[ghi]Pe –64% for F) compared to the field data.

The inaccuracy of the model can be probably explained as follows: (i) the model does not include the volatilization and adsorption rate coefficients, which is likely unrealistic since the removal is controlled not only by biodegradation but also by volatilization and adsorption, (ii) the model does not consider the possible effect from dissolved organic carbon, which favors removal mechanism in the dissolved phase compared to that occurs via sorption on sludge, (iii) the proposed mathematical model is a combination of kinetic model and hydraulic model with the assumption of a well-mixed reactor, which in the real WWTPs, the well mixed is possibly not achieved, and (iv) since a functional condition of the FATE model is limited by the minimum concentration for each compound in the influent to the primary clarifier by more than 0.1 μg/L, this model possibly perform low accuracy as in the field condition, much lower concentration of PAHs (far below 0.1 μg/L) can be found in WWTPs.

8 | CHALLENGES AND FUTURE OUTLOOK

This review has clarified that PAHs can be produced during the combustion process and can be transferred into surface runoff by the atmospheric deposition mechanism before reaching WWTPs through drainage networks. Fate and behaviors of PAHs and their substitutions in WWTPs are complex phenomena depending on their physiochemical properties and environmental conditions. For instance, LMW PAHs are dominant in the aqueous phase (wastewater samples) while HMW PAHs are dominant in the solid phase (sludge samples). The possible explanation for this can be correlated to the low solubility of HMW PAHs in water due to their high log K_{ow}. In addition, LMW PAHs with two or three rings (more than 30% each) are dominant in influent of WWTPs while only LMW PAHs with two rings (more than 60%) are dominant in the effluent of WWTPs (Zhang et al., 2019). It seems to be logic since the HMW PAHs are deposited to the solid phase (sludge) rather than passing and diluting in the aqueous phase. Therefore, most of LMW PAHs can be released into water bodies such as river via the effluent from WWTPs while HMW PAHs can reach the environment via the application of sewage sludge as a fertilizer for agriculture. A similar mechanism is also valid for the fate and behaviors of SPAHs in WWTPs, which shows that SPAHs with higher molecular weight are favorable to be deposited to sludge compared to aqueous phase (Qiao et al., 2014a). It has also been established that the current WWTPs are not specifically designed for the removal of PAHs via biodegradation. As a result, most of them are concentrated in sludge by the adsorption mechanism because of their high hydrophobicity and recalcitrance. Most of the studies presented in this review showed the use of activated sludge and membrane bioreactor in full-scale WWTPs operation.

The use of activated sludge and membrane bioreactor in full-scale WWTPs operation is common.

This review has also shown that PAHs and their substitutions are present in the influent, effluent, and sludge of full-scale WWTPs. In the near future, studies on PAHs in WWTPs should be focused on several topics including the enhancement of method for the detection not only for PAHs but also for their substitutions PAHs since WWTPs are a complex system. For instance, the accurate identification of trace nitro-PAHs in complicated matrices and biological samples is still a challenge (Sun et al., 2020). In addition, more studies are needed for further clarification of the effects of the presence of PAHs in WWTPs since Luo, Chen, and Feng (2016) reported the impact of PAHs on the performance of biological wastewater and sludge treatments. This information is useful to explore and clarify whether the presence of PAHs can affect functional microorganisms and can modify the fundamental mechanism. This is also to note that some WWTPs with the existing treatment system possibly meet with the requirement, but in some cases, they do not meet the allowable limit. It is noted that the European Commission has regulated an allowable limit by 6000 ng/g of PAHs before sludge spreading. In the future, study on the enhancement of existing treatment system and its effects on the removal of PAHs is needed.

Although several methods are possible in the removal of PAHs and their substitutions from WWTPs, the current trend is focused on how it can be carried out in an inexpensive way using green technology. Hence, biological treatment methods seem to be a sustainable and greener approach compared to chemical and physical methods. It is noted that biological treatment methods for the removal of PAHs and their substitutions from WWTPs depend highly on the microbial activities. Although biological systems such as anaerobic and anoxic can be used to remove PAHs in WWTPs, further studies are needed for the improvement of their performance particularly for the removal of LMW PAHs. For instance, the anaerobic and anoxic treatments can only achieve the removal efficiency around 35% of LMW PAHs (Qiao et al., 2014a). Other studies also found the similar findings for different PAHs, which is below 40% (Yao, Zhang, & Lei, 2012) and Liu et al. (2017a) found that the removal of LMW PAHs was only 52.9%. In addition, water composition, the temperature, extension of aeration, and loading rate can affect the treatment efficiency. Biological treatment methods are also susceptible to seasonal changes and the occurrence of toxic substances in WWTPs. Problems such as fouling are commonly experienced in bioreactors. This must be considered in

the near future biological treatment technology since the problems can decrease treatment performances.

The selection of treatment system can be carried out by the evaluation of removal performance, economic, social, and environmental aspects. This review exhibited that both full-scale activated sludge and membrane bioreactors performed quite similarly in the removal of PAHs (above 90%). In some aspects, full-scale activated sludge is preferable than membrane bioreactors or vice versa. Also, these aspects are site specific and depend highly on local situations as well as a particular goal. In the future, study on the evaluation of socioeconomic and environmental aspects of these treatments specifically designed for considering the removal of PAHs and their substitutions is recommended because such study has not been carried elsewhere.

Due to its simplicity, molecular diagnostic ratios are commonly used as a basis to distinguish between PAHs from pyrogenic and petrogenic origins based on the basis of their composition and distribution pattern. It is noted that two- to three-ringed and some alkyl-SPAHs are used to distinguish their petrogenic origins whereas four- to six-ringed PAHs are used for their identification from pyrogenic origins. In addition, several studies have questioned the validity of this approach as a source identification tool since some assumptions for the analysis are sometimes contradictory with the real phenomena (Katsoyiannis & Breivik, 2014; Katsoyiannis, Terzi, & Cai, 2007). For instance, this method assumes that (i) paired chemicals are diluted to a similar extent and (ii) the ratios are speculated to be constant during their transportation from sources to receptors, which have been proven that they do not happen (Zhang et al., 2005). Further studies are needed to address a more realistic and reasonable method for describing the origin of PAHs.

9 | CONCLUSIONS

This review paper highlighted the current state of knowledge concerning PAHs and their substitutions in full-scale WWTPs including their fate and behaviors, analytical techniques, biological treatments, feasibility examination, and modeling. Study on the evaluation of fate and mechanism of PAHs substitutions in WWTPs needs more research as only a few reports can be found in the literature. Evaluation and modification of the FATE model for the removal of PAHs in full-scale WWTPs needs to be carried out as some studies reported several shortcomings.

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