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A Mechanistic Model to Assess the Fate of Naphthalene and Benzo(a)pyrene in a Chilean WWTP

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) are a family of organic compounds of widespread presence in the environment. They are recalcitrant, ubiquitous, prone to bioaccumulation, and potentially carcinogenic. Effluent from wastewater treatment plants (WWTPs) constitutes a major source of PAHs into water bodies, and their presence should be closely monitored, especially considering the increasing applications of potable and non-potable reuse of treated wastewater worldwide. Modeling the fate and distribution of PAHs in WWTPs is a valuable tool to overcome the complexity and cost of monitoring and quantifying PAHs. A mechanistic model was built to evaluate the fate of PAHs in both water and sludge lines of a Chilean WWTP. Naphthalene and benzo(a)pyrene were used as models of low-MW and high-MW PAHs. As there were no reported experimental data available for the case study, the influent load was determined through a statistical approach based on reported values worldwide. For both naphthalene and benzo(a)pyrene, the predominant mechanism in the water line was sorption to sludge, while that in the sludge line was desorption. Compared to other studies in the literature, the model satisfactorily describes the mechanisms involved in the fate and distribution of PAHs in a conventional activated sludge WWTP. Even though there is evidence of the presence of PAHs in urban centers in Chile, local regulatory standards do not consider PAHs in the disposal of WWTP effluents. Monitoring of PAHs in both treated effluents and biosolids is imperative, especially when considering de facto reuse and soil amendment in agricultural activities are currently practiced downstream of the studied WWTP.

Keywords: fate of PAHs in WWTP; mechanistic model of xenobiotics in WWTP; PAHs is wastewater reuse; PAHs in biosolids for agriculture

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants formed during the incomplete combustion of organic materials [1]. They are hydrophobic, with low solubilities in water and low vapor pressure [2]. They can be classified as low molecular weight (LMW—two or three fused benzene rings) or as high molecular weight (HMW—four or more rings). As their molecular weight increases, their hydrophobicity increases, and their water solubility and vapor pressure decrease, which makes these compounds more recalcitrant [3]. Due to their persistence in the environment, and the carcinogenic and mutagenic effects of some PAHs, they are listed as US-EPA and EU priority pollutants to be monitored in the urban water cycle [4,5].

Even though their sources into the environment can be both natural and anthropogenic, the major source of PAHs into water bodies in urban areas are wastewater treatment plants (WWTPs) [6,7]. Several authors have studied and measured PAHs in WWTP [8–12], reporting a wide range of both influent and effluent concentrations (Table 1). In these studies, LMW PAHs were in most cases present in higher concentrations in both influent and effluent in the dissolved phase only, whereas HMW PAHs tended to sorb to particulate matter present in the sewers, thus entering the WWTP sorbed to particles [9,13]. Evidence suggests that the removal of PAHs depends on the treatment train and/or technology of the WWTP, as well as its operational parameters, influent wastewater composition, and seasonal/climatic conditions [7,14]. Thus, the influent concentrations are highly variable and inherent to each specific case study.

In conventional activated sludge plants, the main removal mechanisms of PAHs are adsorption to sludge, volatilization, and biotransformation [14,15], while abiotic degradation mechanisms such as photolysis and hydrolysis are not effective removal mechanisms [16]. The physicochemical properties of PAHs can also impact their removal. For instance, highly hydrophobic HMW PAHs are expected to be removed by sorption to sludge at higher rates than LMW PAHs [17], while it is expected that LMW PAHs are removed at higher rates by volatilization and biodegradation [14].

Understanding and quantifying PAH removal in WWTPs can provide a better awareness of their presence in the environment, especially when considering reuse applications for the treated wastewater and biosolids. However, testing and monitoring PAHs in WWTPs is not always feasible due to the costs and complexity associated with the experimental methods for their detection in the water and sludge matrices [18]. Whenever experimental data are unavailable, using modeling tools to assess the fate of PAHs in WWTP can be quite valuable [18,19]. To date, several authors have developed models to predict the fate of micropollutants in wastewater treatment. Although models can differ in their complexities (e.g., different number of state variables and treatment units), most of those applicable to PAHs consider two phases for the fate of micropollutants in the water matrix: as dissolved and as sorbed to particles. Models for the fate of PAHs in the sludge matrix consider either two or three phases: freely dissolved, sorbed to dissolved and colloidal matter (DCM), and sorbed to sludge particles. Table 2 summarizes some studies focusing on modeling the fate of different micropollutants in wastewater treatment. The available models for the water line are extensive, considering various treatment units such as conventional activated sludge, membrane bioreactors, and primary clarifiers. For the sludge treatment, however, available models are limited.

In this study, we constructed a mechanistic model to assess the presence and removal of PAHs in a Chilean WWTP. Naphthalene and benzo(a)pyrene were used as model contaminants to evaluate the fate of LMW and HMW PAHs. Results were compared to those obtained by different experiences available in literature, and the potential implications of the presence of PAHs for the reuse of the treated wastewater and biosolids are also discussed.

Table 1. Summary of influent and effluent concentration of PAHs in WWTPs worldwide. For WWTPs with industrial inputs, the percentage of domestic/municipal WW is provided.

Location	Inflow and Population Served	Treatment Technology	Naphthalene [ng/L]		Benzo(a)pyrene [ng/L]		∑LMW PAHs [ng/L]		∑HMW PAHs [ng/L]		∑PAHs [ng/L]		Reference
			Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
Belo Horizonte, Brazil	290,000 m^3/d 1,600,000 PE	CAS	114.3	46.1	25.8	27.6	290.7	183.9	50.3	54.4	553.5	483.7	[20]
	155,000 m^3/d 1,100,000 PE	UASB with trickling filters	217.5	102.8	26.3	25.4	483.5	270.3	50.8	50	699.6	472.4	
	1600 m^3/d 30,000 PE	WSP	435.8	61.4	25.1	27.4	996	219.8	69.4	54.9	1210.8	431.1	
Konya, Turkey	200,000 m^3/d 1,300,000 population Unknown content of industrial input	4 stage Bardenpho	2282	560	72	46	2386	594	229	183	2615	777	[21]
	16,500 m^3/d 110,000 population	WSP	1429	370	39	43	1509	436	193	181	1702	617	
	210 m^3/d 2000 people	CW	360	103	42	36	444	161	197	173	641	334	
Guangzhou, China	220,000 m^3/d Municipal ww	Inverted A2/O	435.5	80.1	ND	ND	551.1	143.8	99.0	79.9	650.1	223.8	[17]
Harbin, China	650,000 m^3/d 80% domestic	A/O and BAF	882	471	100	ND	1866.3	859.6	1039.9	114.1	2906.2	973.7	[12]
Hefei, China	300,000 m^3/d 60% municipal ww	A/O	1437.3	924.4	1383.5	380.4	2073	1327.6	3685.8	912.8	5758.8	2240.4	[22]
Tai'an, China	50,000 m^3/d 60% municipal ww. In autumn	A2/O	971.1	207.9	ND	ND	1129.4	258	27.5	3.1	1156.9	261.1	[23]
	50,000 m^3/day 60% municipal ww. In spring		205.6	56.7	ND	ND	659.5	123.7	488.9	5.5	1148.4	129.2	
Italy	25,000 m^3/d 30% municipal	CAS	250	56	16	ND	735	133	215	90	950	223	[9]
	15,000 m^3/d 100% municipal	CAS	96	73	ND	ND	307	127	56	12	363	139	
	19,500 m^3/d 100% municipal	CAS	113	43	ND	ND	195	43	8	7	203	50	

Table 1. *Cont.*

Location	Inflow and Population Served	Treatment Technology	Naphthalene [ng/L]		Benzo(a)pyrene [ng/L]		∑LMW PAHs [ng/L]		∑HMW PAHs [ng/L]		∑PAHs [ng/L]		Reference
			Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	
	118,000 m^3/d 60% municipal	CAS	634	74	14	ND	1315	131	356	37	1671	168	
	21,000 m^3/d 90% municipal	CAS	103	37	20	ND	324	83	189	ND	513	83	
Norway	106,750 m^3/d Domestic ww	A/O	315	26	13	ND	558	30	242	1	800	31	[24]
	35,450 m^3/d Domestic ww	Chemical treatment	325	445	7	ND	721	815	198	40	925	855	
	21,050 m^3/d Domestic ww	Chemical treatment	84	105	16	ND	245	145	225	5	470	150	
	23,125 m^3/d Domestic ww	Chemical treatment	250	170	8	ND	388	215	157	17	545	232	
	10,150 m^3/d Domestic ww	Mechanical treatment	122	105	ND	ND	175	145	72	55	250	190	
Venice, Italy	100,000 m^3/d 90% municipal	Denitrification, oxidation + nitrification	18	5	17	2	90	35	121	41	211	76	[8]
Thessaloniki, Greece	40,000 m^3/d Municipal ww	CAS	7300	5000	22	4.8	10,490	5547	1023.7	137.8	11,513.7	5684.8	[10]
Montreal, Canada	1,300,000 m^3/d 85% municipal 1,400,000 population	Coagulation-flocculation	147	88	48	1	582	231	603	60	1185	291	[11]

CAS—Conventional Activated Sludge, UASB—Up-flow sludge blanket reactor, WSP—Waste stabilization pond, CW—Constructed wetland, A/O—anaerobic-oxic reactor, BAF—Biological Aerated Filter, A2/O—Anaerobic-anoxic-oxic, ∑LMW PAHs: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene; ∑HMW PAHs: fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i,)perylene, dibenzo(a,h)anthracene, indenol(1,2,3-c,d)pyrene; ∑PAHs: ∑LMW PAHs and ∑HMW PAHs. Ref. [20] does not consider benzo[k]fluoranthene. Ref. [21] only considers ∑PAHs: naphthalene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i,)perylene, indenol(1,2,3-c,d)pyrene.

Table 2. Summary of studies focusing on modeling the fate of different micropollutants in wastewater treatment.

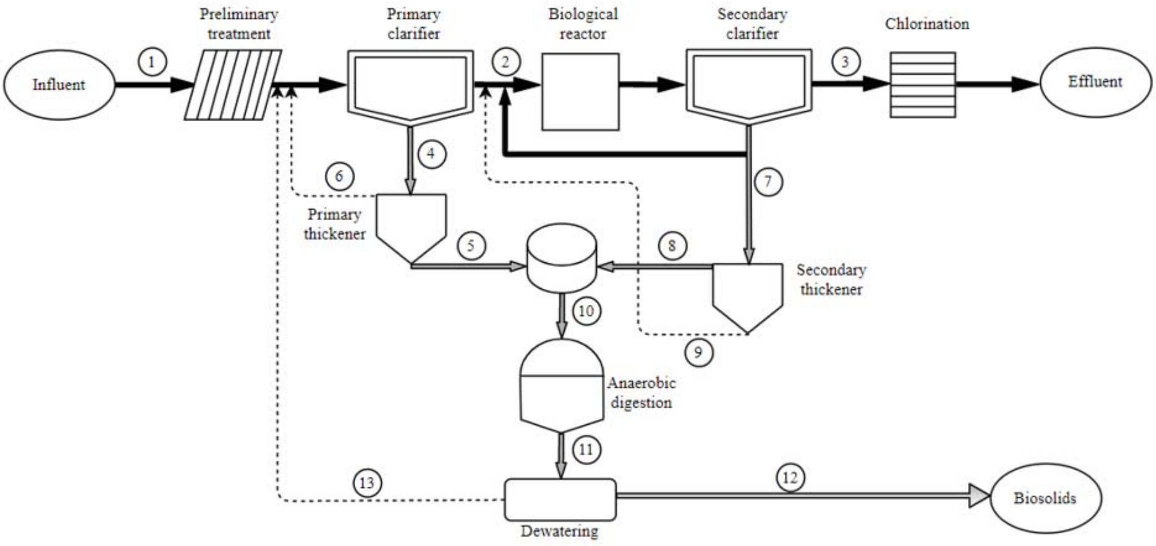
Description	Modeled Treatment Stages	Modeled Micropollutants	Processes	Reference
Studies using the 2-phase approach to model the fate of micropollutants				
Fate of organic micropollutants in novel WWTPs	CEPT, HRAS, RBF, PN-AMX	Pharmaceuticals	Sorption, biodegradation (pseudo-first-order reaction)	[25]
Modeling of micropollutant removal in full-scale MBRs	MBR	51 MPs: 24 metals, 10 beta blockers, 8 pharmaceutical products, 2 alkylphenols, 3 PAHs, and 4 pesticides	Biodegradation (dissolved and particulate phase) in oxic and anoxic conditions and sorption/desorption	[26]
Mechanistic modeling approach to anaerobic systems	AD	20 OMPs	Sorption, desorption, biotransformation in the liquid and solid phase	[27]
Fate of micropollutants in aeration tank and secondary clarifier	AS + SC	MPs (androstenedione, ibuprofen, triclosan, and caffeine)	Biological degradation (first-order reaction) and sorption	[28]
Activated Sludge Model for Xenobiotics (ASM-X)	AS	Pharmaceuticals	Co-metabolic biotransformation, retransformation in oxic and anoxic conditions and sorption/desorption	[29,30]
Dynamic transport and fate of micropollutants in integrated urban wastewater and stormwater systems	Sewers; WWTPs (PR, AS, SC, F, ST, AD, SD; river (water, sediment)	MPs	Settling, resuspension, volatilization, filtration/separation, sorption, desorption, hydrolysis, photolysis, biological biodegradation (aerobic, anoxic/anaerobic)	[31]
Model for co-metabolic biotransformation of organic micropollutants in NAS reactors	NAS	Pharmaceuticals	Co-metabolic biotransformation, sorption/desorption and volatilization	[32]
Mechanistic model for fate of estrogens in inverted A/O reactors	Anoxic/aerobic reactor	Estrogens	Cleavage, adsorption, desorption, aerobic biodegradation, anoxic biodegradation	[33]
Micropollutant fate in SBRs during startup and steady state	SBR	Cadmium and lead	Adsorption	[34]
Steady-state model for the fate of hydrophobic and volatile compounds in activated sludge	PR, AS	VOCs	Biodegradation, bubble and surface volatilization, sorption to particles	[35]
Studies using the 3-phase approach to model the fate of micropollutants				
Modelling PAHs removal in activated sludge process: effect of disintegration	AS	PAHs	Biodegradation, volatilization, sorption/desorption to particulate matter and sorption/desorption to DCM.	[15]
Dynamic model for bioavailability and co-metabolism of micropollutants during anaerobic digestion	AD	PAHs	Co-metabolic biodegradation, volatilization, sorption/desorption to particles and DCM	[36]
A three-compartment model for micropollutants sorption in sludge	AD	PAHs	Biodegradation, sorption to particles and DCM	[37]

PR—primary, AS—activated sludge, SBR—sequencing batch reactor, MBR—membrane bioreactor, SC—secondary clarifier, F—filtration, CEPT—chemically enhanced primary treatment, HRAS—high-rate activated sludge, RBF—rotating belt filter, PN-AMX—partial nitritation unit, NAS—nitrifying activated sludge, ST—sludge thickener, SD—sludge dewatering, AD—anaerobic digestion. DCM—dissolved and colloidal matter.

2. Materials and Methods

2.1. Model Treatment Plant

The model WWTP is a conventional activated sludge plant located in Santiago, Chile. It has a influent flow of 8.8 m^3/s, treating approximately 50% of the city's domestic wastewater (equivalent to a population of 3.7 million people) [38]. The treated effluent is discharged to the Mapocho river, downstream from the WWTP, where it is further used for agricultural irrigation (de facto reuse). The plant's biosolids (digested and stabilized sludge) are disposed either in agricultural lands or in designated landfills [39]. A simplified schematic of the treatment process and the plant's data are presented in Figure 1.

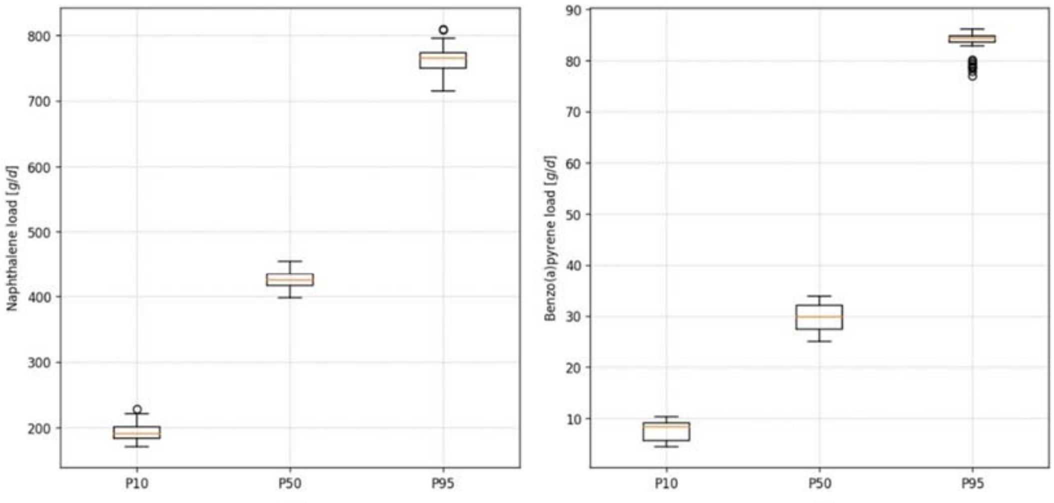


	1	2	3	4	5	6	7
Q [m³/d]	771,539	732,171	732,171	33,091	2405	30,479	40,877
TSS [mg/L]	273	120	20	4861	56,079	390	2913
	8	**9**	**10**	**11**	**12**	**13**	
Q [m³/s]	2866	38,010	5273	5274	463	463	
TSS [mg/L]	35,310	597	44,245	25,796	280,631	1308	

Figure 1. Schematic of the model WWTP. Data correspond to flow rates (Q) and total suspended solids (TSS) concentration between treatment stages. The black arrows represent the water line (wastewater treatment units), the gray arrows represent the sludge line (sludge treatment units), and the dashed arrows represent return flows.

2.2. PAH Influent Loads

Due to the lack of available experimental data, and to represent the variability in the influent wastewater characteristics, a bootstrap or resampling approach (n = 50,000) was applied to influent loads of PAHs from WWTPs around the world (Table 1). Naphthalene and benzo(a)pyrene were used as models of LMW and HMW PAHs. Naphthalene is usually found in higher concentrations in WWTPs and, due to its high vapor pressure, it can be used as a control compound to verify if volatilization occurs in the treatment process [9,12,22,23]. On the other hand, benzo(a)pyrene is considered among the IARC's Group 1 carcinogens; its presence in WWTP has been reported in many studies and it can be used as a control compound to verify if sorption occurs [9,12,14,22]. Population served (>100,000 PE) and content of industrial waste (<50% of the influent flow) were the main criteria for data selection. Resulting loads of PAHs in the 10%, 50%, and 95% probability percentiles of occurrence were grouped, and the minimum, median, and maximum values of each group were used as inputs for the modeled WWTP. For the 95% percentile, these values correspond to 715.3, 760.1, and 795.4 g/day for naphthalene, and 82.9, 84.4, and 86.2 g/day for benzo(a)pyrene, respectively. Input loads resulting from the bootstrap are summarized in Figure 2. Additional data from the bootstrap calculations are provided in Tables S1 and S2.



(a) (b)

Figure 2. Input loads of (**a**) naphthalene and (**b**) benzo(a)pyrene for 10%, 50%, and 95% probability percentiles.

2.3. Mechanistic Model for the Fate of PAHs in the WWTP

The constructed mechanistic model was based on a steady-state mass balance for each of the treatment stages. The mass balance equations for each of the phases in a treatment stage were solved simultaneously using a commercially available solver. The overall model was used to determine the mobility of the studied PAHs through the WWTP. The general mass balance equation can be expressed as

$$V\cdot\frac{\partial C_i}{\partial t} = F_{in} - F_{out} \pm \sum r_i, \tag{1}$$

where V is the reactor volume (L), C_i is the PAH concentration in the treatment stage (ng/L), F_{in} is the inlet PAH load (ng/day), F_{out} is the outlet PAH load (ng/day), and r_i is reaction rate (ng/day). For each treatment stage, r_i was modified to include the processes and/or partitioning mechanisms considered in the stage. Table 3 presents a summary of the selected models and transport/partitioning processes used in each of the treatment stages. Additional considerations and assumptions are itemized below:

- According to different authors, the removal of micropollutants during preliminary treatment is close to null [40,41]. Moreover, experimental sampling by Manoli et al. (1999) reported negligible removal of PAHs by chlorination [10]. Thus, preliminary treatment and chlorination are not considered in the current model.
- For the water line (Figure 1), PAHs were assumed to be distributed between the dissolved and sorbed-to-particle phase, and only the dissolved phase was bioavailable [42]. For the sludge line (Figure 1), three phases were considered: freely dissolved, sorbed to DCM, and sorbed to particles. In this case, only the PAHs freely dissolved and sorbed to the DCM were bioavailable [36].
- Throughout all the treatment units, sorption was assumed to occur onto the total suspended solids fraction.

Table 3. Summary of the selected models and processes for each of the treatment stages.

	Treatment Stage	Modeled Processes	Reference
Water line	Primary treatment: Gravitational sedimentation	Advection, adsorption, surface volatilization,	[35]
	Secondary treatment: Conventional activated sludge	For PAHs: advection, adsorption, biodegradation as co-metabolism (oxic and anoxic conditions), surface and bubble volatilization For BOD: Activated Sludge Simple Model (ASSM)	[30,35,42,43]
Sludge line	Primary gravitational thickener Secondary thickener (flotation) Mixing chamber	Advection	[37]
	Anaerobic digestion	Advection, sorption/desorption to particles, sorption/desorption to DCM, volatilization, biodegradation as co-metabolism	[36]
	Dewatering with centrifuges	Advection	[37]

The removal efficiency of each treatment stage was determined by

$$R\% = \frac{(F_{in} - F_{out})}{F_{in}} \cdot 100, \tag{2}$$

where R% is the removal efficiency, F_{in} is the inlet PAH load (ng/day), and F_{out} is the outlet PAH load (ng/day).

Details about the model equations are available in Tables S3–S7, as well as the summary of the parameters used in the model.

2.4. Sensitivity Analysis

The analysis was carried out as a function of parameters defining the governing partitioning mechanisms in each treatment stage. For the water line, the predominant mechanism was adsorption to sludge; thus, the solid–liquid partition coefficient (K_d) was used in the analysis for primary and secondary treatment. SRT was also considered in the latter. On the other hand, in the anaerobic digestion, the predominant mechanism is desorption from particles. Therefore, the first-order kinetic constant of sorption to particles (k_1) and the equilibrium constant for PAH sorption to particle (K_P) were evaluated.

3. Results

3.1. Fate of PAHs in a Chilean WWTP

Tables 4 and 5 present the model results for the fate and distribution of naphthalene and benzo(a)pyrene throughout the treatment train. Results are presented for the 10%, 50%, and 95% probability percentiles of occurrence. For naphthalene in the water line, the influent load was 760.1 g/day, and the resulting effluent load was 238.9 g/day, predominantly in the dissolved phase. The overall removal efficiency of naphthalene from the water phase was 70.2%. In the sludge line, the resulting load to the biosolids (Figure 1, flow line 12) was 293.3 g/day, predominantly sorbed to particles. For benzo(a)pyrene, an influent load of 84.4 g/day resulted in an effluent load of 2.1 g/day, predominantly in the dissolved phase (97.7% overall removal). The resulting load to the biosolids was 80.9 g/day, predominantly sorbed to particles.

Table 4. Fate of naphthalene in the modeled WWTP. Results are presented in g/day for 10%, 50%, and 95% percentiles. Combined values for flows 1, 2, 3, 6, 9, and 13 correspond to the aqueous phase (See Figure 1). Data are shown as min–max; median.

Flow	10%			50%			95%		
	F_{free}	F_{DCM}	F_P	F_{free}	F_{DCM}	F_P	F_{free}	F_{DCM}	F_P
1	170.7–221; 191.4		—	397.9–454; 426.4		—	454–795.4; 760.1		—
2	123.8–160.3; 138.9		14.7–19.1; 16.5	288.7–329.4; 309.4		34.3–39.2; 36.8	329.4–577.1; 551.5		39.2–68.6; 8.2
3	51.5–66.6; 57.7		2.2–2.9; 2.5	119.9–136.8; 128.5		5.1–5.9; 5.5	136.8–239.8; 229.1		5.9–10.3; 9.8
4	1.6–2.0; 1.7	4–5.2; 4.5	22.9–29.6; 25.6	3.7–4.2; 3.9	9.4–10.7; 10.1	53.3–60.8; 57.1	6.6–7.3; 7	16.9–18.8; 17.9	95.8–106.5; 101.8
5	0.1–0.1; 0.1	3.1–4.0; 3.5	21–27.2; 23.6	0.3–0.3; 0.3	7.2–8.2; 7.7	49–55.9; 52.5	0.5–0.5; 0.5	12.9–14.4; 13.7	88.1–97.9; 93.6
6	2.4–3.1; 2.7		1.8–2.4; 2	5.6–6.4; 6		4.3–4.9; 4.6	10.1–11.2; 10.7		7.7–8.6; 8.2
7	0.6–0.8; 0.7	2.3–3.0; 2.6	56.1–72.6; 62.9	1.4–1.5; 1.5	5.3–6.1; 5.7	130.7–149.2; 140.1	2.4–2.7; 2.6	9.6–10.7; 10.2	235–261.4; 249.8
8	—	1.4–1.9; 1.6	45.8–59.3; 51.4	—	3.4–3.8; 3.6	106.8–121.9 114.4	—	6.1–6.7; 6.4	192–213.5; 204
9	1.4–1.8; 1.6		10.3–13.3; 11.5	3.2–3.7; 3.5		23.9–27.3; 25.7	5.8–6.5; 6.2		43.1–47.9; 45.8
10	0.2–0.2; 0.2	4.4–5.6; 4.9	66.3–85.8; 74.9	0.4–0.4; 0.4	10.1–11.6; 10.9	154.4–176.2; 165.6	0.7–0.7; 0.7	18.2–20.3; 19.4	277.6–308.7; 295
11	1.2–1.6; 1.4	5.8–7.5; 6.5	63.4–82.1; 71.1	2.9–3.3; 3.1	13.6–15.5; 14.5	147.7–168.6; 158.3	5.2–5.8; 5.5	24.4–27.1; 25.9	265.6–295.3; 282.2
12	0.1–0.1; 0.1	5.3–6.9; 5.9	59.8–77.4; 67	0.2–0.3; 0.2	12.4–14.1; 13.3	139.4–159.1; 149.4	0.4–0.5; 0.4	22.2–24.7; 23.6	250.6–278.7; 266.3
13	1.6–2.1; 1.8		3.2–4.1; 3.6	3.8–4.3; 4.1		7.4–8.4; 7.9	6.8–7.6; 7.2		13.3–14.8; 14.1

Table 5. Fate of benzo(a)pyrene in the modeled WWTP. Results are presented in g/day for 10%, 50%, and 95% percentiles. Combined values for flows 1, 2, 3, 6, 9, and 13 correspond to the aqueous phase (See Figure 1). Data shown as min–max; median.

Flow	10%			50%			95%		
	F_{free}	F_{DCM}	F_P	F_{free}	F_{DCM}	F_P	F_{free}	F_{DCM}	F_P
1	4.4–10.2; 6.2		—	24.9–33.9; 28.4		—	82.9–86.2; 84.4		—
2	0.4–0.9; 0.5		0–4; 2.5	2.1–2.9; 2.4		9.9–13.4; 11.2	7.1–7.4; 7.2		32.8–34.1; 33.4
3	1.7–0.2; 0.1		—	0.5–0.7; 0.6		0.1–0.1; 0.1	1.7–1.8; 1.8		0.3–0.3; 0.3
4	—	2.7–6.3; 3.8	—	15.3–20.8; 17.4	—	50.9–53; 51.9	—	—	2.7–6.3; 4.2
5	—	2.5–5.8; 3.5	—	14.1–19.2; 16.1	0–0.1; 0.1	46.9–48.7; 47.7	—	—	2.5–5.8; 3.5
6	—		0.2–0.5; 0.3	0–0.1; 0.1		1.2–1.7; 1.4	0.1–0.1; 0		4.1–4.3; 4.2
7	—	2.4–5.6; 3.4	—	13.8–18.9; 12.8	—	45.9–47.7; 46.7	—	—	2.4–5.6; 3.4
8	—	2–4.6; 2.8	—	11.3–15.3; 12.8	—	37.5–39; 38.1	—	—	2–4.6; 2.8
9	—		0.4–1; 0.6	0–0.1; 0.1		2.5–3.4; 2.9	—		8.4–8.7; 8.6
10	—	4.4–10.3; 6.2	—	25–34.1; 28.6	—	83.4–86.7; 85.9	—	—	4.4–10.3; 6.2
11	—	4.1–9.5; 5.8	0.1–0.1; 0	23.2–31.6; 26.4	0.3–0.3; 0.3	77.2–80.3; 79.6	—	0.3–0.8; 0.5	4.1–9.5; 5.8
12	—	3.9–9; 5.5	—	21.9–29.8; 25	—	72.9–75.8; 75.1	—	0.3–0.7; 0.4	3.9–9; 5.5
13	0–0.1; 0		0.2–0.5; 0.3	0.3–0.3; 0.3		1.2–1.6; 1.3	0.8–0.8; 0.8		3.9–4; 4

3.1.1. Distribution in the Water Line

Figures 3 and 4 show the model results for the distribution of naphthalene and benzo(a)pyrene throughout the water line. Results are presented for the median input loads of the 95% percentile.

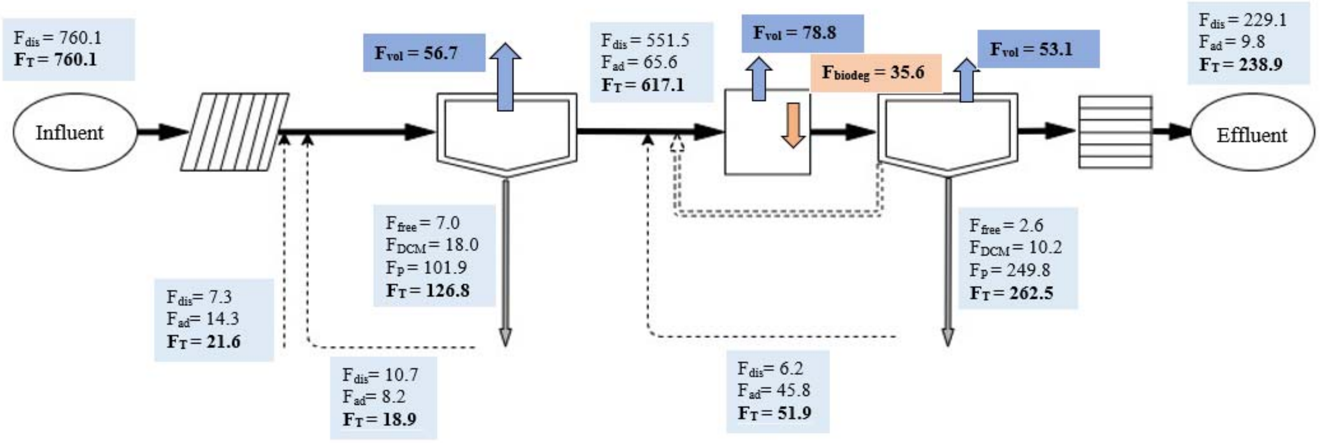


Figure 3. Fate of naphthalene in the water line. Results are presented in g/day. F_{dis} is the resulting load in the dissolved phase, F_{ad} is sorbed to particles in the water line, F_{free} is freely dissolved, F_{DCM} is sorbed to the dissolved and colloidal matter (DCM), and F_p is sorbed to particles going to the sludge line.

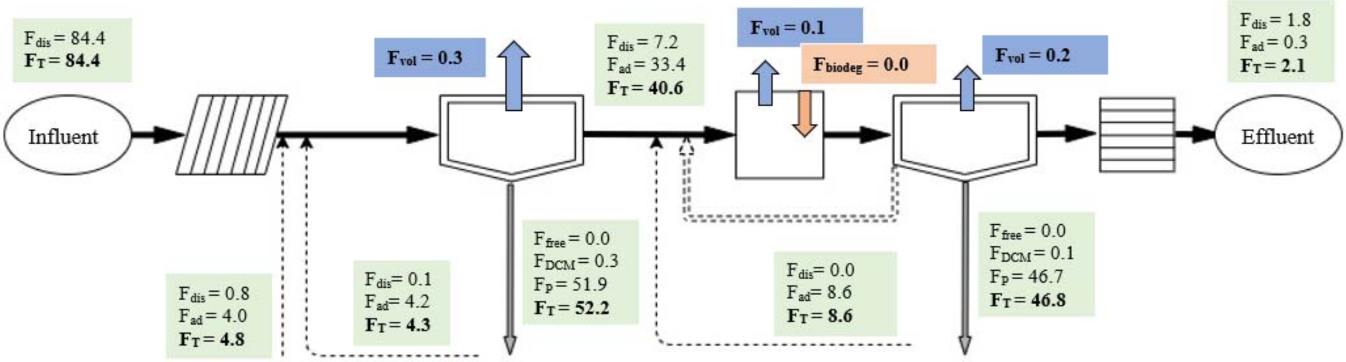


Figure 4. Fate of benzo(a)pyrene in the water line. Results are presented in g/day. F_{dis} is the resulting load in the dissolved phase, F_{ad} is sorbed to particles in the water line, F_{free} is freely dissolved, F_{DCM} is sorbed to the dissolved and colloidal matter (DCM), and F_p is sorbed to particles going to the sludge line.

Considering each of the treatment units, the removal efficiencies were 22.9% for naphthalene and 56.5% for benzo(a)pyrene during primary treatment. For naphthalene, transport and sorption to sludge removed 15.8%, while volatilization removed 7.1%. In contrast, benzo(a)pyrene transport and sorption to sludge removed 55.8%, whereas volatilization was close to null (0.3%). The differences in the impact of sorption in the removal of naphthalene and benzo(a)pyrene can be explained by the solubility of PAHs. As their molecular weight increases, their solubility decreases; thus, they tend to adsorb at a higher rate [14]. For volatilization, the differences between the results obtained for naphthalene and benzo(a)pyrene can be explained by the differences in their Henry's constant. Byrns et al., (2001) reported that compounds with log K_{ow} between 3.3–5 present removal by sorption to sludge of 15–50%. They also reported that volatilization has a low impact on primary treatment removal rates, but is maximum for compounds with log K_{ow} of 2 [44]. In the present study, results for naphthalene (log K_{ow} = 3.36) and benzo(a)pyrene (log K_{ow} = 5.97) agree with previous reports.

For naphthalene, 77% of the influent load went to secondary treatment units, most of which was in the dissolved phase, while 16% of the influent load went to the primary thickener, predominantly in the sorbed to particles phase. For benzo(a)pyrene, 43% of the influent load was transported to secondary treatment, while 56% was transported to primary thickener; in both cases, the sorbed to particle phase was predominant.

During secondary treatment, 64.3% of naphthalene and 95.7% of benzo(a)pyrene were removed. Once again, the predominant mechanism was adsorption to sludge for both PAHs. For naphthalene, volatilization removed 19.7% while biodegradation removed only 5.8%. In contrast, benzo(a)pyrene was hardly removed by biodegradation (0.4%) or volatilization (0.2%). Low biodegradation rates can be explained by two factors. First, naphthalene was more bioavailable than benzo(a)pyrene (61.3 g/day and 7.2 g/day in the dissolved phase, respectively). Second, as naphthalene is a shorter molecule (two benzene rings), its biodegradation rates are higher than benzo(a)pyrene (four-ringed molecule) [45].

3.1.2. Distribution in the Sludge Line

Figures 5 and 6 show the model results for the distribution of naphthalene and benzo(a)pyrene along the sludge line. Results are presented for the median input loads of the 95% percentile.

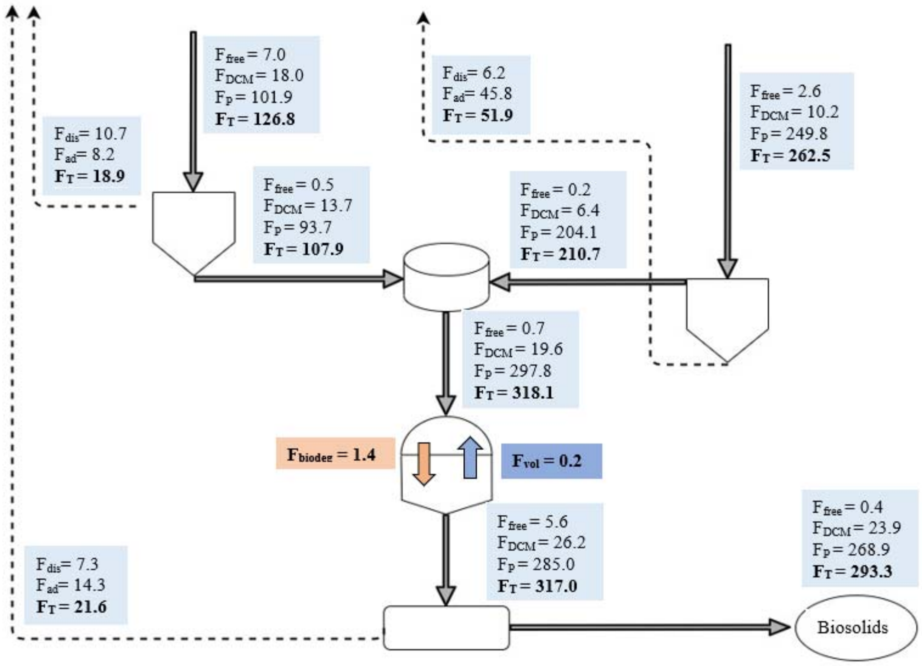


Figure 5. Fate of naphthalene in the sludge line. Results are presented in g/day. F_{dis} is the resulting load in the dissolved phase, F_{free} is the freely dissolved, F_{DCM} is sorbed to the dissolved and colloidal matter (DCM), and F_P is sorbed to particles.

Overall, naphthalene and benzo(a)pyrene removed in the sludge line (25.4% and 19.3%, respectively) were mostly returned to the water line. PAHs were not removed by the thickeners and dewatering units due to the model's assumptions (See Table 3).

In the anaerobic digester, the removal efficiencies obtained for both PAHs were negligible (0.5% and 0.1%). Removal by volatilization for both PAHs was also negligible (less than 0.1% for both), in accordance with results obtained by other studies [36,37,46]. As for the biodegradation rates in the AD, naphthalene and benzo(a)pyrene were barely removed by this process (0.4% and 0.1%, respectively). These results can be explained because the influent load to AD (flow line 10, Figure 1) was predominantly sorbed to particles and, therefore, unavailable for biodegradation.

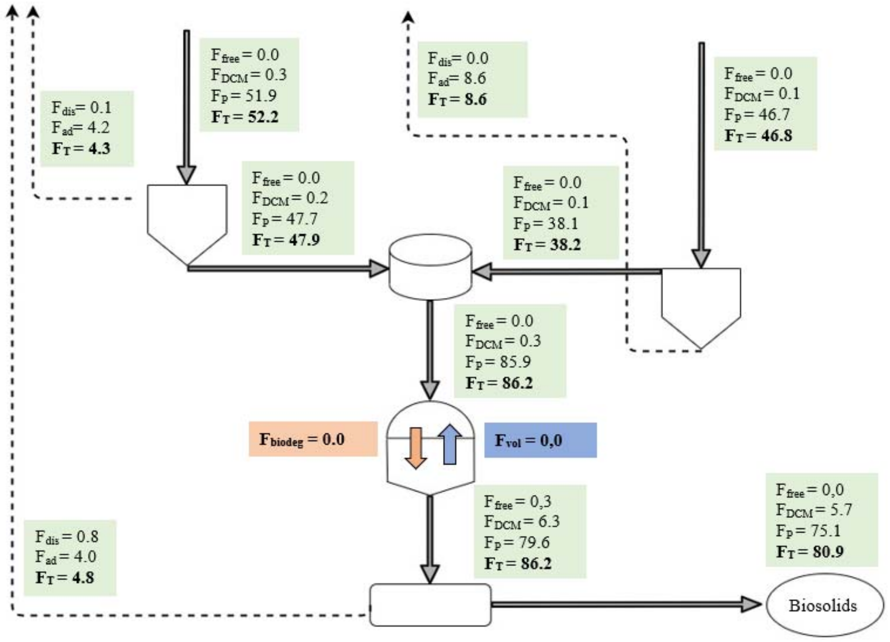


Figure 6. Fate of benzo(a)pyrene in the sludge line. Results are presented in g/day. F_{dis} is the resulting load in the dissolved phase, F_{free} is the freely dissolved, F_{DCM} is sorbed to the dissolved and colloidal matter (DCM), and F_p is sorbed to particles.

3.2. Sensitivity Analysis

Figure 7a,b present the results for the sensitivity analysis using the median of the 95th percentile influent load. The complete analysis is provided in Tables S8 and S9. Response variables include naphthalene loads in WWTP effluent and biosolids. Results are shown only for naphthalene because the model's sensitivity to changes in benzo(a)pyrene parameters was similar to that to changes in naphthalene parameters (data not shown). Moreover, volatilization was more evident in the latter. Figure 7 shows that the parameter with greatest impact was the solid–liquid partitioning coefficient in the secondary treatment ($K_{d,sec}$). An increase in $K_{d,sec}$ had the greatest impact on the load to the biosolids as the sorption to sludge increased. Furthermore, biodegradation and volatilization were negatively affected by less naphthalene present in the dissolved phase. Changes in SRT also affect the removal efficiencies described in the model. For a 50% increase in SRT, effluent loads of naphthalene decreased by approximately 12%. In contrast, a 50% decrease in SRT increasing the effluent load by approximately 19% (Table S8). Other studies also reported a direct correlation between SRT and PAH removal [9,46]; however, it is important to consider the feasibility of varying SRT during the operation. Increasing SRT decreases the frequency of sludge wasting, which potentially decreases the load of PAHs entering the AD unit. Longer SRTs could also promote changes in the mixed liquor (old sludge), thus promoting growth of undesired microorganisms and accumulation of extra polymeric substances. Changes in the chemical characteristics of the mixed liquor could potentially affect the partitioning coefficients (e.g., $K_{d,sec}$) and removal mechanisms of PAHs in the secondary treatment [47].

As for K_p and k_1 (which determine sorption to particles during AD), results showed that these parameters impact naphthalene's distribution in the sludge (e.g., F_{free}, F_{DCM}, and F_p), but do not alter the total load in the biosolids or in the water exiting the plant (Figure 7b). They could, however, impact the bioavailability and further biodegradation of naphthalene during anaerobic digestion.

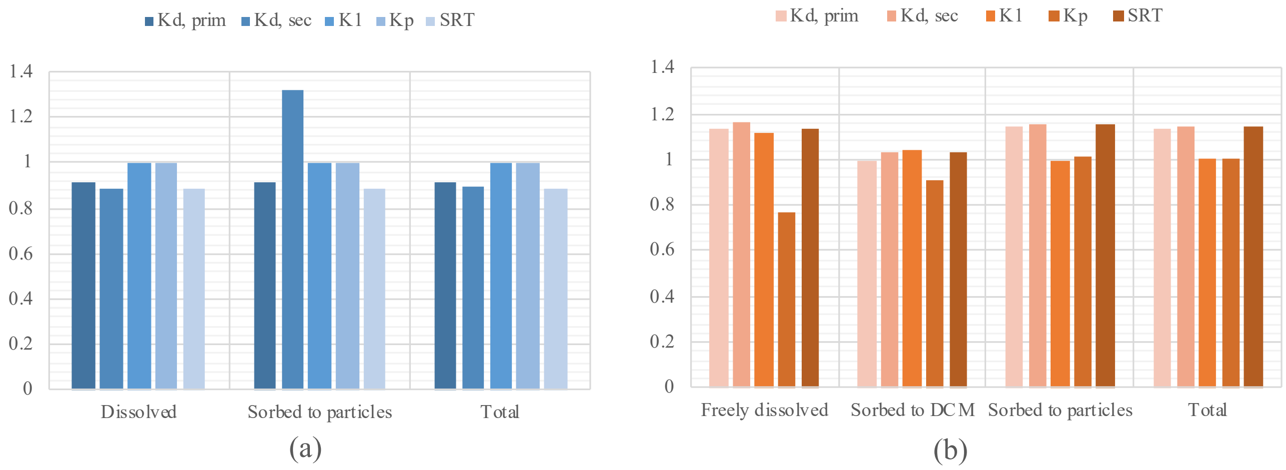


Figure 7. Sensitivity analysis for a 50% increase in $K_{d,prim}$, $K_{d,sec}$, k_1, K_p, and SRT. Response variables include naphthalene loads in WWTP (**a**) effluent and (**b**) biosolids.

4. Discussion

4.1. Fate of PAHs in a Chilean WWTP

Some clear differences could be observed in the behavior of the studied PAHs, mainly attributed to their physicochemical properties and associated partitioning, transport, and removal mechanisms in each treatment unit. Overall removal efficiencies for naphthalene and benzo(a)pyrene in the water line were 70.2% and 97.7% respectively, where volatilization removed 26.8% and 6.1% mostly in secondary treatment. Similar to other studies in WWTPs worldwide (Table 6), high sorption rates promoted their predominant transport to the sludge treatment units.

Biodegradation did not play an important role in the removal of PAHs in the modeled WWTP. When comparing the results obtained in the secondary treatment to other studies, Manoli et al., (2007) only obtained a 1–4% removal by biodegradation, while Byrns et al., (2001) obtained 80% removal for compounds with log K_{ow} of 3.6 [1,44]. An important distinction, however, is that Byrns et al., (2001) considered both the dissolved and sorbed to particles phases as bioavailable. In this study, 36% of the naphthalene load in the activated sludge influent (Flow 2, Figure 1) was transported in the water line effluent (Flow 3, Figure 1), predominantly in the dissolved phase, while 39% was transported to secondary thickener (Flow 7, Figure 1). For benzo(a)pyrene, 4% of the influent load was transported in the water line effluent (Flow 2, Figure 1), while 95% was derived into the sludge line (Flow 7, Figure 1).

The predominant fate mechanism of PAHs in AD was desorption from sludge particles, while biodegradation was negligible. For example, even though the bioavailable fraction of naphthalene was 6.4% of the AD influent load, less than 1% was biodegraded. The remaining was sorbed to particles in this treatment stage and went back to the water line by desorption. Other available studies did not show a clear tendency in biodegradation of PAHs in AD. While some presented removal efficiencies on the order of 38% to 73% [36,48], other studies presented low or null removals in this stage [10,49,50]. Semblante et al. (2015) suggested that the inconsistency occurs because high removal rates are often obtained in pilot-scale studies [51].

In summary, for both naphthalene and benzo(a)pyrene, the predominant mechanism in the water line was sorption to sludge, while, in the sludge line, desorption was identified as the predominant mechanism. Higher removal efficiencies of benzo(a)pyrene in the water line by sorption to the sludge were expected due to its lower solubility in water. Compared to other studies in the literature, the model satisfactorily describes the mechanisms involved in the fate and distribution of PAHs in a WWTP [1,35,44].

4.2. Impacts on Reuse in Chile

Quality standards must be ensured in order to reuse both treated wastewater and biosolids; however, information is scarce regarding established regulatory standards worldwide. In Chile, PAHs are not included in the current regulation related to the disposal of treated effluents and/or biosolids [52]. For example, the DS 90/2000 regulates the discharge of treated effluent to marine and continental surface waters and does not include organic contaminants of any kind. Other related regulations, such as the NCh1333, which sets water quality requirements for different uses (including irrigation), only consider basic parameters for soil maintenance. Regarding reuse applications, the Ley 21.075/2018 regulates the collection and disposition of gray water in urban and rural areas, while it does not include emerging or persistent pollutants. In this case, international regulations/recommendations should be followed when considering water reuse or biosolids disposal projects in Chile.

Standards for PAH concentration in drinking water are variable across the world, but only a few organizations have set maximum concentrations for different micropollutants for direct potable reuse applications. For benzo(a)pyrene, WHO's maximum concentration in water is 0.7 μg/L, which is based on their recommended drinking water standards [53]. The European Union, Council Directive 2008/105/EC on the quality of water intended for human consumption established a maximum limit for benzo(a)pyrene of 0.01 μg/L, and a maximum of 0.10 μg/L for the sum of benzo[b]fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indenol(1,2,3-cd)pyrene [54]. The US federal government established regulatory standards and guidelines to protect people from potential health effects caused by eating, drinking, or breathing PAHs. Under the Safe Drinking Water Act, the US-EPA sets legal maximum limits on the level of benzo(a)pyrene in drinking water at 0.2 μg/L [55]. In Latin America, only a few countries have regulations for PAHs in water, specifically for benzo(a)pyrene: Brazil, with a maximum limit of 0.7 μg/L concentration in drinking water [56], and Argentina, with a maximum of 0.04 μg/L in water sources for human consumption [57].

In the case of Naphthalene, the US-EPA has defined a maximum concentration in surface runoff and in groundwater at a Health Reference Level (HRL) of 140 μg/L. Furthermore, the agency states that naphthalene is infrequently detected in public water supplies. When detected, naphthalene rarely exceeds the HRL or a value of one-half the HRL [55].

When considering other water reuse applications, such as irrigation of crops, no limit concentration of PAHs has been established, even though evidence suggests that PAH-contaminated water may lead to bioaccumulation of these compounds in crops [58,59].

A common practice worldwide is the disposal of stabilized biosolids for soil amendment in agriculture. Most international entities focus on establishing a limit concentration for heavy metals or pathogens and do not establish a maximum concentration of PAHs for soil amendment [60]. Only a few countries such as France and Italy have established maximum concentrations for benzo(a)pyrene and for the total concentration of PAHs as 2 μg/gDM and 6 μg/gDM, respectively [61].

Even though there is evidence of the presence of PAHs in Chilean urban centers [62–67], local regulations do not consider PAHs in the disposal of WWTP effluents, potential reuse scenarios, or biosolid use in agriculture. Monitoring of PAHs in both treated effluents and biosolids is imperative, especially when considering that de facto reuse in agricultural activities currently takes place downstream of the studied WWTP.

Table 6. Summary of PAHs presence in sludge/biosolids from literature.

Location	Sludge Type	Naphthalene [µg/kgDM]	Benzo(a)pyrene [µg/kgDM]	Reference
Thessaloniki, Greece	2ary	190	66	[10]
	Mixed (1ary + 2ary)	900	140	
	Thickened	340	140	
	Stabilized	800	240	
	Dehydrated	1.000	240	
Venice, Italy	2ary	31	87	[8]
	Stabilized	28	86	
Beijing, China	2ary	1.100	5.000	[68]
Wuxi, China		500	24	
Dapu, China		310	7	
Yuanlang, China		120	480	
Shatian, China		240	33	
GBD, China	2ary	98	395	[69]
BXH, China		23	327	
Sibao, China	2ary	16.320	4.540	[70]
Ningbo, China		140	3.700	
Spain	2ary	197	34	[71]
Spain		27	522	
Lombardy, Italy	1ary	259	56	[50]
	2ary	277	36	
	Thickened	279	44	
	Stabilized	254	62	
Guadalete, Spain	1ary	776	115	[72]
	2ary	707	87	
	Stabilized	539	170	
This study	1ary	1.270	271	
	2ary	2.140	378	
	Thickened (1ary + 2ary)	1.646	318	
	Stabilized	2.692	503	
	Dehydrated	2.658	498	

4.3. Limitations

The results of this study present a first approach to quantifying the presence of PAHs in a Chilean WWTP. However, as experimental samples were unavailable, it is recommended to validate the model with in situ measurements. It is important to notice that the mechanistic model considers only influent PAHs loads in the dissolved phase. However, evidence suggests that, as urban wastewater takes hours to reach the WWTP, a sorption equilibrium condition is likely to be reached and PAHs could be found in the particulate phase [10]. Further studies should incorporate the particulate phase in the influent load.

The results also highlight the importance of estimating (or measuring) relevant parameters considered in the model (e.g., K_d), as they show how possible variations in them can impact the obtained concentrations. Calibration of these parameters is also recommended using current measured data.

5. Conclusions

The present study provides a modeling tool to estimate the presence and fate of PAHs in a conventional activated sludge WWTP in Chile, including both water and sludge lines. Despite the inherent variability of the treated wastewater, represented here by an influent concentration of 95% probability of occurrence, the model satisfactorily describes the main partitioning mechanism of PAHs. For instance, adsorption to sludge was the predominant mechanism in the water line, while desorption from particles was identified as the predominant mechanism in the sludge line. Clear differences could be established between naphthalene and benzo(a)pyrene mainly due to the differences in their physicochemical properties. Even though biodegradation and volatilization had negligible influence in the removal of benzo(a)pyrene during the treatment process, volatilization was an important removal mechanism of naphthalene in the secondary treatment. Further studies should include current in situ measurements to validate the model for the Chilean scenario.

Chilean regulatory standards for the disposal of WWTP's effluents or biosolids do not consider maximum concentration for PAHs (or any other micropollutant). However, PAH's presence in treated wastewater and biosolids should be monitored in order to ensure human and environmental safety, as evidence suggests that PAH accumulation in wastewater-irrigated soil and crops can occur. Considering the growing market for potable and non-potable reuse of treated effluents in Chile, this topic should be a matter of urgent concern.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9081313/s1, Table S1: Influent naphthalene loads (g/d) obtained through the bootstrap for the 10%, 50% and 95% probability percentiles, Table S2: Influent benzo(a)pyrene loads (g/d) obtained through the bootstrap for the 10%, 50% and 95% probability percentiles, Table S3: Assumptions for each treatment stage in the PAH model, Table S4: Rate equations for the processes considered in the water line, Table S5: Parameters used in the water line, Table S6: Rate equations for the processes considered in the sludge line, Table S7: Parameters used in the sludge line, Table S8: Variations in the PAH load present in the effluent for variations of ±25%, ±50%, and ±75%, Table S9: Variations in the PAH load present in the biosolids for variations of ±25%, ±50%, and ±75%.

Author Contributions: A.A., methodology, investigation, formal analysis, and writing—original draft preparation; F.P., methodology, investigation, and formal analysis; M.R., methodology, investigation, and resources; A.L.P., conceptualization, data curation, writing—review and editing, supervision, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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