

Fate of phthalates in a river receiving wastewater treatment plant effluent based on a multimedia model

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ABSTRACT

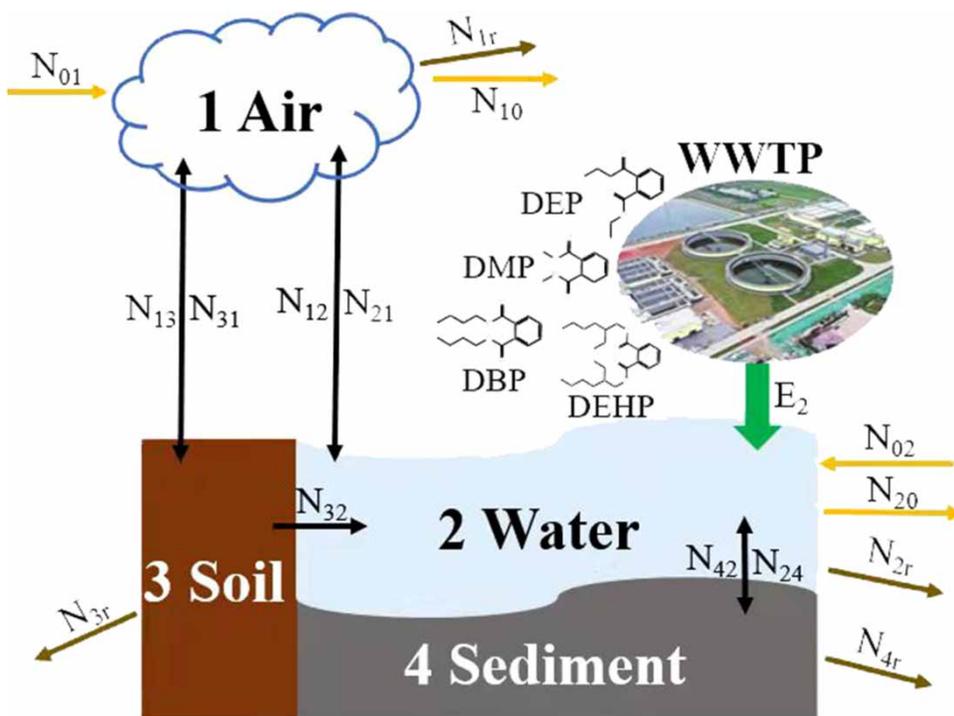
Phthalic acid esters (PAEs) can enter environment media by secondary effluent discharge from wastewater treatment plants (WWTP) into receiving rivers, thus posing a threat to ecosystem health. A level III fugacity model was established to simulate the fate and transfer of four PAEs in a study area in Tianjin, China, and to evaluate the influence of WWTP discharge on PAEs levels in the receiving river. The results show that the logarithmic residuals of most simulated and measured values of PAEs are within one order of magnitude with a good agreement. PAEs in the study area were mainly distributed in soil and sediment phases, which accounted for 84.66%, 50.26%, 71.96% and 99.09% for dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and di-(2-ethylhexyl) phthalate (DEHP), respectively. The upstream advection accounted for 77.90%, 93.20%, 90.21% and 90.93% of the total source of DMP, DEP, DBP and DEHP in the river water, respectively, while the contribution of secondary effluent discharge was much lower. Sensitivity analysis shows that emission and inflow parameters have greater influences on the multimedia distributions of PAEs than physicochemical and environmental parameters. Monte Carlo analysis quantifies the uncertainties and verifies the reliability of the simulation results.

Key words: fate and transfer, level III fugacity model, phthalic acid esters, receiving river, secondary effluent, sensitivity analysis

HIGHLIGHTS

- The fate of PAEs in a river receiving WWTP effluent was simulated by fugacity model.
- DEHP had the highest total amount and residence time in the system.
- Air–soil/water and water–sediment were the main ways of PAEs cross-interface transfer.
- River advection played a principal role in the spatial distribution of PAEs.

GRAPHICAL ABSTRACT



Apply fugacity model to quantify the impact of wastewater treatment plants.

1. INTRODUCTION

Phthalic acid esters (PAEs) are one of the most abundant synthetic organic compounds in the world, which have been widely used as plasticizers in commercial and industrial fields (Gao *et al.* 2019). PAEs accounted for more than 55% of global plasticizer consumption in 2020, which had been expected to grow at an annual rate of about 3.5% in the next few years (Markit 2021). PAEs exist in plastics and other products in a non-chemical bonding way and are easily released into the environment (Chen *et al.* 2019a). At present, PAEs are widely detected in atmosphere, surface water, seawater, stormwater, sediment, and soil around the world, such as China (Gao *et al.* 2019; He *et al.* 2019; Fang *et al.* 2020; Hu *et al.* 2020), Mexico (Quintana-Belmares *et al.* 2018), India (Selvaraj *et al.* 2015; Sampath *et al.* 2017), Iran (Arfaeinia *et al.* 2019), Mediterranean (Paluselli *et al.* 2018), Czech Republic (Růžičková *et al.* 2016), Serbia (Skrbic *et al.* 2016), Sweden (Kalmykova *et al.* 2013), Spain (Dominguez-Morueco *et al.* 2014; Bolivar-Subirats *et al.* 2021), and South Korea (Heo *et al.* 2019; Kim *et al.* 2020) and considered to be the second most important category of global pollutant following polychlorinated biphenyls (PCBs) (Li *et al.* 2019). PAEs have significant endocrine disrupting properties, and may lead to carcinogenesis, teratogenesis and mutagenesis (Fang *et al.* 2020). Six PAEs have been identified as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) and the European Union (EU) in view of their environmental persistence and ecological effects (Kashyap & Agarwal 2018), including dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DnOP), among which the former three PAEs are also listed in China's Environmental Quality Standards for Surface Water (Chen *et al.* 2021).

Traditional wastewater treatment processes are mainly used to remove conventional pollutants such as suspended solids, COD_{Cr}, nitrogen and phosphorus, but not designed to remove trace refractory pollutants, resulting in that effluent from wastewater treatment plant (WWTP) becomes an important source of PAEs in the water environment (Zheng *et al.* 2016). For example, the removal rate of PAEs in two WWTPs in Harbin was only about 30% by using Anoxic/Oxic (A/O) and Anaerobic/Anoxic/Oxic (A/A/O) processes (Gao *et al.* 2014). PAE concentrations in treated wastewater from 15 WWTPs in India

ranged from 1.3 µg/L (DBP) to 2.6 µg/L (DEHP) (Gani *et al.* 2016). The natural attenuation pathways of PAEs in water environment include biological enrichment, biodegradation, volatilization, adsorption, hydrolysis and photolysis, etc. (Net *et al.* 2015). Studies have shown that biodegradation and adsorption are the main removal mechanisms of PAEs in sewage treatment process (Gao *et al.* 2014; Gani *et al.* 2016; Guo *et al.* 2022). The remaining PAEs that are not biodegraded either enter the environment by adsorption on the sludge surface or are discharged with the wastewater (Dargnat *et al.* 2009). PAEs have been detected in WWTP effluent and the receiving water environments worldwide (Dargnat *et al.* 2009; Deng *et al.* 2018). Some studies have found that the discharge of PAEs from WWTP has a strong impact on the water quality of receiving water environments such as the WWTPs receiving rivers in South Africa (Salaudeen *et al.* 2018) and Portugal (Homem *et al.* 2022) and the Songhua River (Gao *et al.* 2014), while others believe that PAEs discharged from WWTP has a mild impact on water quality of receiving water environments such as the Marne River (Dargnat *et al.* 2009) and a receiving river of WWTP in Wuxi (Zheng *et al.* 2016), and even has a slight dilution effect. These studies are based on the comparison of detected PAEs concentration at the upstream river and the discharge outlet to determine the impact of WWTP discharge on its receiving river, rather than quantitatively explaining the impact of sewage discharge and determining influencing factors from the perspective of transport mechanism.

On the other hand, previous studies have shown that most refractory organics in the environment are exported through air or river advection, but residual refractory organics do transfer cross-interfaces to a certain extent, thus accumulating in soil or sediments for a long time (Zhang *et al.* 2018; Chen *et al.* 2019a). Therefore, if only the main sources and outputs of PAEs in the system are considered, the analysis of PAEs output pathways accumulated in soil and sediment in small amounts but difficult to degrade will be ignored, which is of great significance for accurate assessment and control of PAEs pollution. Fugacity models have proved to be a useful tool for a comprehensive and systematic understanding of the concentration and persistence of chemicals in multiple environmental compartments, as well as the partition and transport between the interfaces of these compartments (Di Guardo *et al.* 2018; Chen *et al.* 2019b; Huang *et al.* 2019; Li *et al.* 2020). According to the multimedia environment, multimedia models can be divided into four levels: I, II, III and IV, as proposed by Mackay (2001). The level III fugacity model is closer to the actual environmental system than level I and level II models do, and more simplified than level IV model, which is favored by many scholars (Li *et al.* 2020, 2021). The receiving river of WWTP effluent in our study has a slow flow rate with stable secondary effluent discharge. Therefore, the level III fugacity model has been employed to simulate the transfer and fate of PAEs in the environmental system, aiming to achieve three objectives: (1) to quantitatively determine the impact of secondary effluent discharge on PAEs level in its receiving river; (2) to clarify the environmental fate and transfer processes of PAEs within and between each bulk compartment (air, water, soil and sediment); and (3) to identify the key factors that have great influence on these processes by sensitivity analysis and quantify their uncertainties by Monte Carlo analysis.

2. MATERIALS AND METHODS

2.1. Study area and sampling points

The study area includes three tributaries (T1, T2, and T3) of Beiyun River and its surrounding area (Fig. S1), which is located in Wuqing District of Tianjin, China (117°3'3.76"E ~ 117°3'10.58"E, 39°21'31.13"N ~ 39°21'54.52"N). T1 and T2 converge to T3 downstream and then flow into Beiyun River. T1 is blocked at position W0 in the upstream and receives secondary effluent from a WWTP (at position W1) as its water source, which treats domestic sewage with an average daily volume of 27,600 m³/d. As shown in Fig. S1, four water sample sites (W0, W1, W2 and W3) are set along the canal section, where W0 and W1 are located at the blocked upstream of T1 and the WWTP outlet, with W2 in the T2, and W3 in the T3, respectively. In consideration of the requirements of model input and validation combined with actual sampling conditions on site, a total of nine samples (four water samples respectively at W0-W3, three soil samples at E1-E3 and two sediment samples at S1 and S2) were collected on October 16, 2021. Water samples at sampling point W0 were used to verify that T1 was blocked upstream and that there was no other PAE input, and the PAE input from T1 was only derived from WWTP. The study area is surrounded by residential areas with a population density of 684 persons/km² and no other point pollution emissions exist.

2.2. Sample collection, pretreatment and analysis

Water samples of 1.5 L were collected at 0.5 m below the water surface with a portable water sampler, stored in covered brown glass bottles, separated by tinfoil between the mouth and the cap, and placed upright. After being transferred to the

laboratory, the samples were filtered with 0.45 μm glass fiber filter as soon as possible and stored in a refrigerator at 4 °C. The sediment samples and soil samples were collected by stainless-steel grab sampler and stainless-steel scoop, respectively, and stored in aluminum foil envelopes. After being transferred to the laboratory, the samples were dried by a freeze dryer as soon as possible, then screened by a screen (100 mesh) and stored in the refrigerator below -20 °C. Referring to our previous study (Wang *et al.* 2021), the glass bottles were washed with ultrapure water (Millipore, Molsheim, France) and dried in the oven at 105 °C for 2 h before sampling. The stainless-steel scoop and grab were washed with ultrapure water and dried at room temperature (20 °C). When sampling, the glass bottles were rinsed three times with water samples.

Six priority PAEs including DBP, DMP, DEHP, DEP, DnOP, and BBP have been selected for detection in this study (Kashyap & Agarwal 2018). The single and mixed standard solutions of the six PAEs (1,000 mg/L, dissolved in n-hexane) were purchased from AccuStandard (Connecticut, USA). The surrogate standard of dibutyl phthalate-D4 (D4-DBP) (100 mg/L, dissolved in n-hexane) and the internal standard of diethyl phthalate-D4 (D4-DEP) (100 mg/L, dissolved in n-hexane) were purchased from Tanmo Quality testing technology Co., Ltd (Beijing, China). Dichloromethane (pesticide grade), n-hexane (pesticide grade) and methanol (chromatography grade) were purchased from ANPEL Laboratory Technologies (Shanghai, China). The solid phase extraction (SPE) method established by our research group was adopted for the pretreatment of water and sediment samples (Wang *et al.* 2021), and the pretreatment of soil samples was the same as that of sediment. PAEs in samples were quantitatively analyzed by gas chromatography mass spectrometer-TQ8040 (GCMS-TQ8040, Shimadzu, Japan) with a DB-5MS capillary column (30 m \times 0.25 mm \times 0.25 μm , Agilent) run in a selective ion monitoring mode. The detailed operational procedures of the GC-MS were detailed in our previous work (Wang *et al.* 2021). The internal standard method was adopted based on a five-point calibration curve with correlation coefficient (R^2) \geq 0.998.

2.3. Quality control and quality assurance

During the sample collection and pretreatment procedure, plastic material was strictly avoided. To eliminate any PAEs residual, all glassware was soaked in $\text{K}_2\text{CrO}_4\text{-H}_2\text{SO}_4$ solution for 12 h, thoroughly cleaned with ultrapure water (Millipore, Molsheim, France), then dried at 450 °C for 4 h, and finally sealed with aluminum foil (to avoid contamination of laboratory air). Glass fiber membranes (Navigator, Tianjin, China) wrapped in aluminum foil were heated at 400 °C for 4 h prior to use.

Quality control and quality assurance of water, sediment and soil samples were carried out strictly. Random duplicate samples, program blanks and spiked matrixes were processed, respectively. The relative standard deviations (RSD) of parallel samples were all less than 5%. Pretreatment and GC-MS analysis of the program blanks for water, sediment, and soil samples were identical to those of their respective samples, respectively. The concentration of PAEs detected in this study were obtained by subtracting the program blank value. Before PAEs extraction, 100 μL of 1.0 mg/L surrogate standard D4-DBP was added to 1 L water sample, 3 g soil sample and sediment sample, respectively, and the recoveries ranged from 96.87% to 125.39%. The recoveries of the standard-spiked samples (i.e. water matrix, sediment matrix, and soil matrix) were $98.34\% \pm 11.95\%$ (DnOP) $\sim 126.68 \pm 10.70\%$ (DEHP), $97.41 \pm 16.36\%$ (DEP) $\sim 128.60 \pm 7.27\%$ (DEHP) and $101.55 \pm 12.19\%$ (DEP) $\sim 124.71 \pm 11.27\%$ (DEHP), respectively. The limit of detection (LOD) was quantified as three times of the standard deviation of blank samples concentrations. The limit of quantitation (LOQ) calculated as three times of LOD, were 4.02 (DEP) ~ 25.92 (DBP) ng/L for water samples, 0.29 (DEP) ~ 1.70 (DEHP) ng/g for sediment samples, and 0.35 (BBP) ~ 29.39 (DEHP) ng/g for soil samples. Specific information about standard-spiked recoveries and LOQ for each PAE have been provided in Table S1 of the Supplementary Materials.

2.4. Level III fugacity model

The level III fugacity model describes the steady-state, non-equilibrium and flow system, and divides the study area into four main bulk compartments: air, water, soil and sediment. It is available free of charge from the Canadian Environmental Modelling Centre (CEMC) website (<https://www.trentu.ca/cemc>) (Mackay & Paterson 1991; Net *et al.* 2015). The four PAEs (DMP, DEP, DBP and DEHP) commonly detected in all matrixes were taken as target chemicals for simulation. The input parameters of the model include physicochemical properties of PAEs, environmental parameters, emission and inflow data, and specific input parameter values are presented in Tables S2–S4 in the Supplementary Materials. The output results describe the environmental fate and transfer processes of target substances through three key variables, i.e., fugacity (f , Pa), fugacity capacity (Z , mol/ $\text{m}^3\cdot\text{Pa}$) and transfer rate coefficient (D , mol/ $\text{Pa}\cdot\text{h}$).

In the constructed level III fugacity model, the measured PAEs concentrations of W1 at T1 and W2 at T2 were input into the model as the point source emission values of PAEs and upstream advection input values, respectively. The logarithmic difference between the model output value and the downstream measured concentration of W3 at T3 was used to verify the model. In view of the immobility of sediment and soil (unlike water, which is a mobile phase), the mean values of measured concentrations of PAEs in sediments (S1 and S2) and soil (E1–E3) were used for validation.

2.5. Sensitivity analysis

Sensitivity analysis was performed to identify the most influential parameters for the model output, i.e., the key factors which have great influence on the transport and fate of PAEs. The sensitivity coefficient (S) was calculated by the following formula (Xu *et al.* 2013):

$$S = \frac{(Y_{1.1} - Y_{0.9})}{0.2 \times Y}$$

where $Y_{1.1}$ and $Y_{0.9}$ respectively represent the simulated concentration when the tested parameter was changed at +10% and -10%. Positive and negative sensitivity coefficients represent the positive and negative correlation between output results and input parameters, respectively. The greater the absolute value of the sensitivity coefficient is, the more sensitive the parameter is.

2.6. Uncertainty analysis

Monte Carlo analysis was performed for parameters with high sensitivity to quantify their uncertainties and verify the reliability of the model. It was assumed that all the sensitive parameters except temperature were in line with lognormal distribution. The simulation was run repeatedly for 10,000 times by Crystal Ball 11.1.2.4 software, and the model output was statistically analyzed. The maximum, 95 percentiles, median, 5 percentiles, minimum values and coefficients of variation (CVs) for the simulated PAE concentrations were used to describe the uncertainty of model outputs and verify the accuracy of the model by comparing with measured values.

3. RESULTS AND DISCUSSION

3.1. Measured concentrations of PAEs

The detected concentrations of PAEs in the sampled water, sediment and soil are shown in Figure 1. DMP, DEP, DBP and DEHP were detected in all water and sediment samples, while BBP was not detected; DMP, DEP, DBP, BBP and DEHP were detected in all soil samples; and low concentration of DnOP was only detected in the sediment sample at S1. The type and

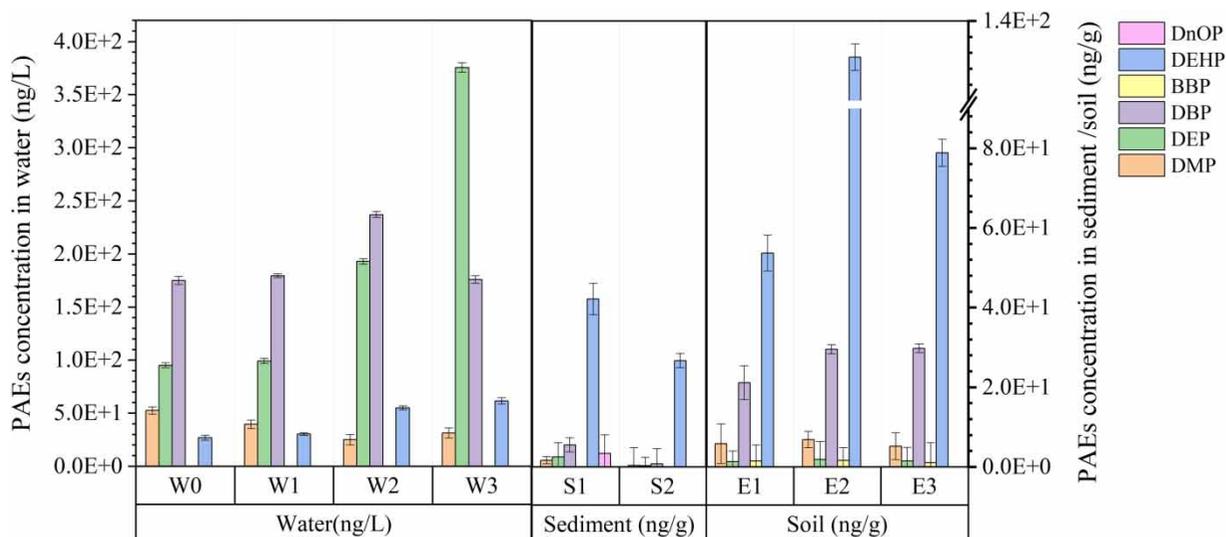


Figure 1 | Detected concentration of PAEs in water (ng/L), sediment (ng/g), and soil phases (ng/g).

concentration levels of PAEs in this study are different from those in other studies (Dargnat *et al.* 2009; Gao *et al.* 2014; Gao & Wen 2016; Zheng *et al.* 2016) due to a variety of factors including local industrial use, individual activities and wastewater treatment processes.

Among the four PAEs in water samples, only the concentration of DMP in W1 at the WWTP outlet (39.59 ± 2.19 ng/L) was slightly higher than that in the receiving river (25.10 ~ 31.92 ng/L). The DBP concentration in the WWTP effluent (179.49 ± 2.63 ng/L) was close to that of the river (175.86–237.02 ng/L). The concentrations of DEP and DEHP in the WWTP effluent were 99.24 ± 2.39 ng/L and 30.38 ± 4.47 ng/L, respectively, which were lower than those in the river (DEP: 193.00–375.49 ng/L; DEHP: 55.12–61.67 ng/L), indicating that there were other sources of PAE pollution in the sampled reach, such as inputs from river upstream and atmosphere. It should be noted that DEP concentration increased significantly from 193.00 ng/L at W2 upstream to 375.49 ng/L at W3 downstream, which might be related to the different land use types adjacent to the upstream and downstream. Both sides of the upstream river were tarmac roads equipped with guardrails, which reduced non-point source pollution to a certain extent. However, the downstream was adjacent to farmland without fences, and there was frequent fishing along the tributary T3, resulting in the downstream inevitably polluted by non-point sources such as the leaching of planting plastic films, pesticides and human activities. In addition, the concentration levels of PAEs for W0 and W1 were very close, which proved that there was no other source of PAEs pollution in the blocked upstream of T1, so it is reasonable to consider T2 as the only upstream of the reach and T1 (where the WWTP is located) as the PAEs emission for subsequent modeling. Different from the distribution of PAEs in water samples, DEHP was the most abundant in sediment (26.70–42.18 ng/g) and soil samples (53.70–130.95 ng/g), followed by DBP in sediment (0.89–5.57 ng/g) and soil phase (21.17–29.79 ng/g), while the concentration levels for the other PAEs were much lower. Some studies also showed that DBP and DEHP were the most abundant PAEs in sediment and soil (Zeng *et al.* 2009; Teng *et al.* 2015; Arfaeina *et al.* 2019).

Overall, the concentrations of PAEs in the WWTP effluent met the limit values of the Tianjin Local Standard – Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (DB12599-2015) (DBP: 3 µg/L; DOP: 8 µg/L) and Chinese Pollutant Discharge Standard for Urban Sewage Treatment Plants (GB 18918-2002) (DEP: 100 µg/L; DnOP: 100 µg/L); and DBP and DEHP values in all the water samples were lower than their limit values of Chinese Surface Water Environmental Quality Standard (GB 3838-2002) (DBP: 3 µg/L; DEHP: 8 µg/L). Furthermore, the PAEs levels in various media in our study were lower than those reported in many countries and regions such as Spain (Bolivar-Subirats *et al.* 2021) and Iran (Arfaeina *et al.* 2019), even lower than those previously reported by Kong *et al.* (2012) in Tianjin. The great reduction of the PAE discharge from WWTPs might owe a big deal to the establishment of the Tianjin Local Standard (DB12599-2015) possessing much stricter limits for PAEs than those in the original – the national standard (GB 18918-2002). Nevertheless, studies have shown that even low concentrations of PAEs in the environment pose potential ecological risks (He *et al.* 2013; Liu *et al.* 2016). Therefore, it is necessary to use fugacity model to quantitatively determine the source and fate of PAEs in the system and to explain the influence of sewage discharge on the receiving river from the perspective of transport mechanism, so as to provide an overall judgment for PAEs pollution control.

3.2. Predicted concentrations and multimedia fates of PAEs

We modeled and analyzed the transport and fate of DMP, DEP, DBP and DEHP in this area by taking the WWTP drainage (at W1), the upstream (at W2) and downstream (at W3) of the receiving river as the emission source, advective inflow and advective outflow, respectively. Fugacity model outputs for the four PAEs are provided as PDF files in supplementary materials. The deviations between measured and simulated concentrations of DMP, DEP, DBP, and DEHP were 0.01, 0.26, 0.17 and 0.04 logarithmic units for the downstream river, 0.56, 0.37, 0.72 and 0.99 logarithmic units for the sediment, and 0.01, 0.33, 0.83 and 0.02 logarithmic units for the soil, respectively, as shown in Figure 2(a). These deviations were mainly caused by the complexity of PAEs sources and the uncertainty of environmental and physicochemical parameters, while the model ignored rainfall runoff, agricultural non-point sources and nearby human activities, and adopted the assumption of steady state and homogeneity. Nonetheless, they were all less than one order of magnitude, indicating preferable agreements (Kong *et al.* 2018; Du *et al.* 2020).

Figure 2(b) shows the highly different distribution patterns of the four PAEs in the air, water, soil and sedimentary phases based on the simulation results. The proportion of PAEs in the sediment phase increases with the rise of molecular weight. The high octanol–water partitioning (K_{ow}) values ($\log K_{ow} > 1$) of the four PAEs indicate these substances are very hydrophobic and more easily adsorbed by the organic matters in soil and sediment phase (Cousins *et al.* 2003). Therefore, these

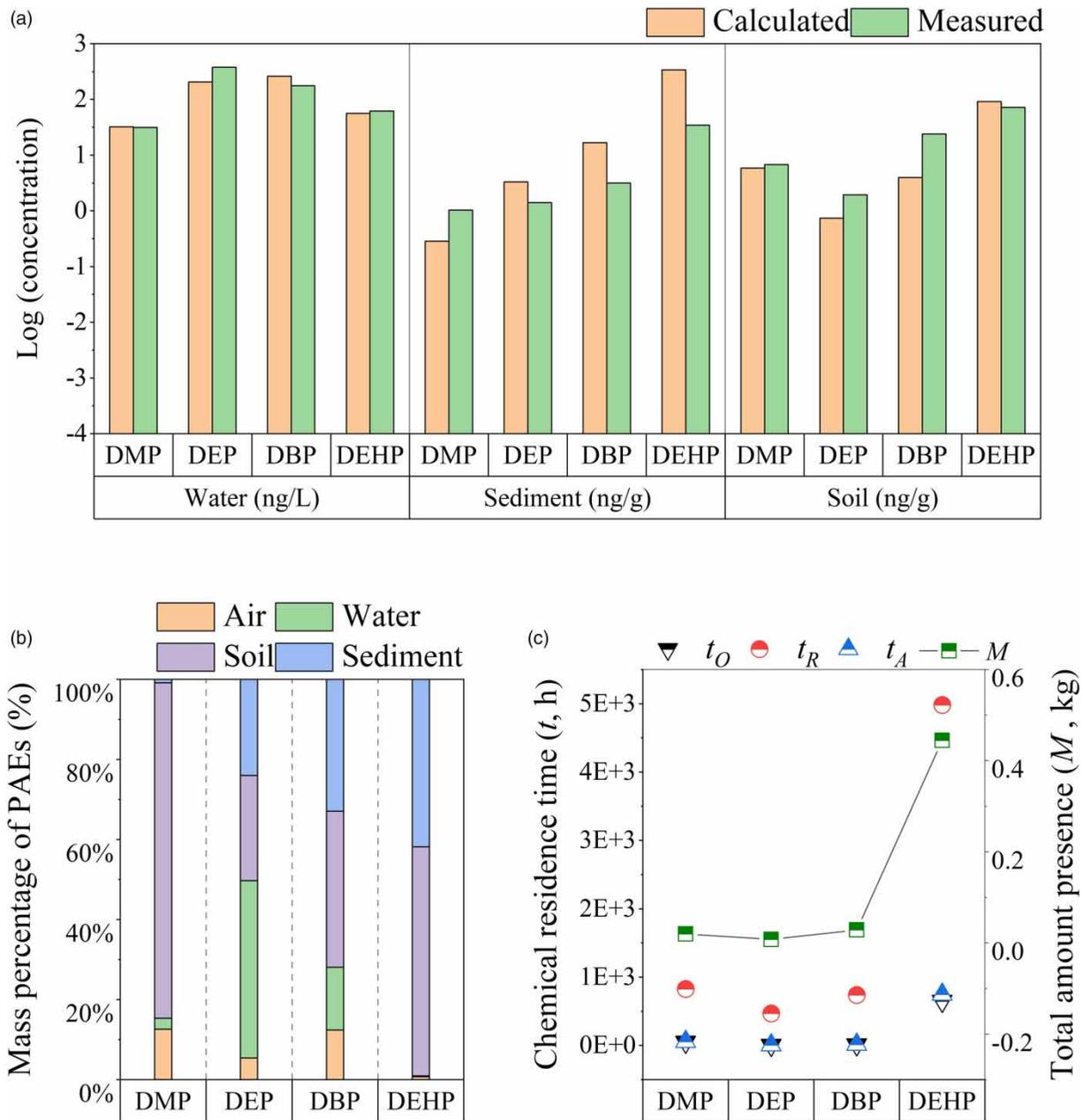


Figure 2 | The simulation results of the environment fates for the four PAEs by level III fugacity model. (a) Comparison of simulated and measured concentrations of PAEs in water, sediment and soil phase; (b) the mass percentage (%) of PAEs in various environmental media; and (c) total amount, reaction, advection and overall residence time of PAEs in the system. *Note:* The overall residence time (t_o , h), reaction residence time (t_R , h), and advection residence time (t_A , h) of PAEs were calculated by: $t_o = M/(N_A + N_R)$, $t_R = M/N_R$, $t_A = M/N_A$, and $1/t_o = 1/t_R + 1/t_A$, where M , N_A , and N_R were obtained by the fugacity model (Mackay & Paterson 1991).

PAEs in the environmental system of this region were mainly distributed in soil and sediment phases, which accounted for 84.66%, 50.26%, 71.96% and 99.09%, respectively for DMP, DEP, DBP and DEHP. This means that most of the PAEs that enter the environment through sewage discharge, river transport and volatilization will eventually migrate to soil and sediment, which has been proved by some studies (Net *et al.* 2015).

The total amount (M , kg) reaction residence time (t_R , h), advection residence time (t_A , h) and overall residence time (t_o , h) of the four PAEs in the system are shown in Figure 2(c), where the t_R and t_A stands for the time required to remove all chemicals from the system by degradation or advection, respectively. The overall residence time of PAEs in the system is positively

correlated with the total amount of PAEs M , and negatively correlated with the total advective output rate N_A (kg/h) and total degradation rate N_R (kg/h). The total amount of DBP in the system was slightly higher than that of DMP. However, as DMP had a much higher proportion in soil phase, it was difficult to be exported from the system through advection, resulting in that the overall residence time of DMP in the system was higher than that of DBP. The t_o , t_R and t_A of DEHP were higher than those of the other three PAEs, because DEHP had the largest total amount in the system, and the highest proportion in soil and sediment phases, resulting in the lowest N_R and N_A . This could explain that DEHP was the dominant phthalate type in environmental media in many countries and regions (Sampath *et al.* 2017; Kim *et al.* 2020). Advection residence time of PAEs in the system was much lower than reaction residence time, which was related to degradation properties of PAEs and frequent hydrodynamic disturbance of water flow (Liu *et al.* 2014). In addition, overall residence time of the system was close to advection residence time, suggesting that the main output pathway was advection output.

3.3. Net fluxes of PAEs

Figure 3(a) shows the inter-media transport processes of PAEs among air, water, soil and sediment phase. In the air phase, atmospheric advection input (N_{01}) was the main source of PAEs, accounting for more than 98% of the total source. The main output pathway of DMP, DEP, DBP and DEHP was atmospheric advection output (N_{10}), accounting for 75.18%, 84.81%,

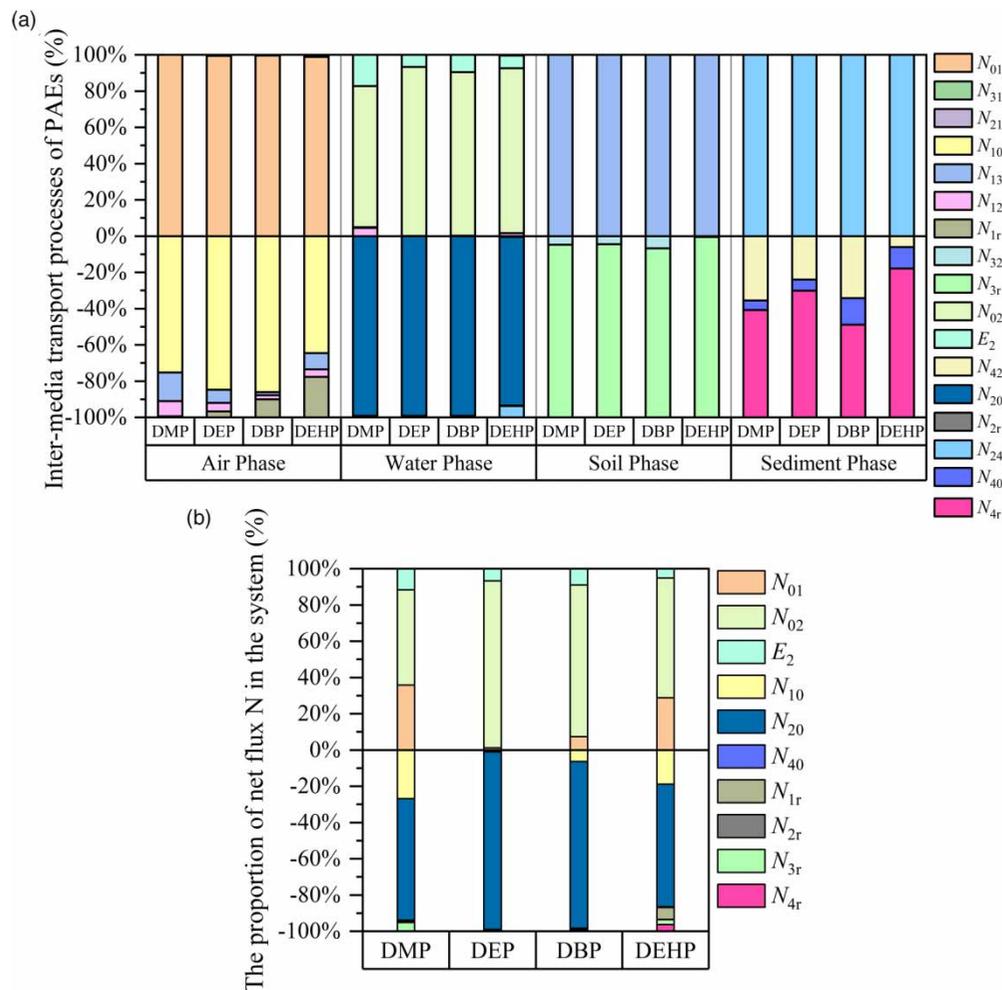


Figure 3 | Inter-media transport processes (a) and spatial transferring fluxes of PAEs (b). Note: N_{ij} - Net flux from i to j ($i, j = 1, 2, 3, 4$); N_{0i} , N_{i0} - i advection input/output rate ($i = 1, 2, 4$); N_{ir} -degradation rate in i ($i = 1, 2, 3, 4$); E_2 -discharge rate from secondary effluent of WWTP; and subscript numbers 1, 2, 3, and 4 respectively represent air, water, soil, and sediment phases. Positive values indicate input of PAEs, and negative values indicate loss of PAEs. The net flux of the detailed inter-media transport process is shown in Table S6 of the Supplementary Materials.

86.11% and 64.61% of the total output, respectively, which implies that air advection was the most important driving force for PAEs transfer in the air phase. With the increase of molecular weight, the reaction half-lives of PAEs in the air phase decreased (Stales *et al.* 1997), and the more easily PAEs were removed by degradation (N_{1r}).

In the water phase, the main input pathway of PAEs was upstream advection input (N_{02}), accounting for 77.90% (DMP) ~ 93.20% (DEP) of the total sources, while discharge of secondary effluent from WWTP (E_2) was much less, accounting for 6.72% (DEP) ~ 17.84% (DMP) of the total sources. The main output pathway of PAEs was downstream advection output (N_{20}), accounting for 92.99% (DEHP) ~ 99.13% (DMP) of the total output, which implies that river advection was the most important driving force for PAEs transfer in the water phase, and the secondary effluent discharge from the WWTP had minor influence. For air–water interface processes, the net transfer direction of DMP (1.17×10^{-5} kg/h), DEP (8.77×10^{-7} kg/h), DBP (3.08×10^{-6} kg/h), and DEHP (5.94×10^{-6} kg/h) was all from air to water, indicating that air phase was a source of PAEs in water phase. Since most PAEs have low vapor pressure (P^s) and high K_{ow} , PAEs in water phase were more likely to diffuse into sediment phase rather than into air phase, and diffusion from water to sediment (N_{24}) was 1.61 (DBP) ~ 13.91 (DEHP) times of diffusion from water to air (N_{21}). With the increase of molecular weight, PAEs were more easily adsorbed by sediments, and N_{24} increased accordingly.

In the soil phase, N_{13} was the only source of PAEs, and the main output pathway was degradation in soil (N_{3r}), accounting for more than 93.0% of the total output pathway. The half-lives of PAEs in soil reported in the literatures vary greatly with PAEs types, soil types and environmental conditions (Zhu *et al.* 2018; Zhu *et al.* 2019). For air–soil interface processes, the net transfer fluxes for DMP (2.22×10^{-5} kg/h), DEP (1.51×10^{-6} kg/h), DBP (2.84×10^{-6} kg/h), and DEHP (1.77×10^{-5} kg/h) were all from air to soil, indicating that the soil would serve as the sink of PAEs in atmosphere. Atmospheric deposition has been recognized as an important sources of PAEs in soil, as well as sewage sludge used as soil amendment and agricultural plastic films (Net *et al.* 2015; Li *et al.* 2016).

In the sediment phase, N_{24} was the only source of PAEs. The main output pathway of PAEs was degradation in sediment (N_{4r}), accounting for 51.04% (DBP) ~ 82.14% (DEHP) of the total output. Some studies have indicated that the kinetics of anaerobic degradation of PAEs in river sediment depends on a variety of factors including pH, temperature, surfactants, pollutants, or microbial inhibitors, and the action of microorganisms is considered to be the principal mechanism for PAEs degradation in both aquatic and terrestrial systems (Stales *et al.* 1997; Net *et al.* 2015). For water–sediment interface processes, the net transfer direction for DMP, DEP, DBP, and DEHP (4.37×10^{-8} kg/h, 4.78×10^{-7} kg/h, 8.37×10^{-7} kg/h, and 2.95×10^{-5} kg/h) was all from water to sediment, indicating that the sediment phase was an important sink of PAEs in water phase. DEHP had the largest net transfer flux from water to sediment because of its high K_{ow} coefficient.

Without considering cross-interface transfer, the input and output fluxes of PAEs in the study area were analyzed, as shown in Figure 3(b). The main input pathway of PAEs in the system was the upstream advection, accounting for 52.59%, 92.14%, 83.79% and 66.09% of the total input of DMP, DEP, DBP and DEHP, respectively, while the effluent from WWTP accounting for only 11.64%, 6.65%, 8.90% and 5.11%, respectively. The main output pathway of the system was downstream advection output, accounting for 66.92%, 97.98%, 92.01% and 67.58% of the total output of DMP, DEP, DBP and DEHP, respectively. In other words, river advection played a dominant role in the spatial migration of PAEs in the study area, which also explains why the overall residence time of PAEs was close to their advection residence time. It also indicates that effluent discharge from WWTPs has been no longer the main source of PAEs in the environment of this region with the upgrading of the WWTPs in the aspect of PAE level's further reducing in the sewage effluent, which might be attributed to the more stringent standard promotion.

3.4. Parameters sensitivity and model uncertainty

In order to identify the key factors affecting the fate and distribution of PAEs in the receiving river, sensitivity analysis was performed on all input parameters, and the results are shown in Supplementary Materials Table S5. The influence degree of parameters on the simulated concentration of PAEs in various environmental media is expressed by the absolute value of sensitivity coefficient, and the parameter whose absolute value of sensitivity coefficient is greater than 0.5 is considered to have a great influence on the model output (Xu *et al.* 2013). The positive and negative sensitivity coefficients respectively indicate that the parameters have a positive or negative influence on the simulation results. Figure 4 demonstrates that the concentration distributions of PAEs in air, water, soil and sediment phases have been influenced considerably by 19 parameters, including two emission and inflow data of PAEs (C_{01} and C_{02}), four physicochemical parameters of PAEs (H , $T_{1/23}$, $T_{1/24}$, K_{oc}), and 13 environmental parameters (X_{33} , X_{43} , A_2 , A_4 , h_3 , h_3 , ρ_{23} , ρ_{33} , ρ_{43} , Φ_{23} , U_R , U_D , Q).

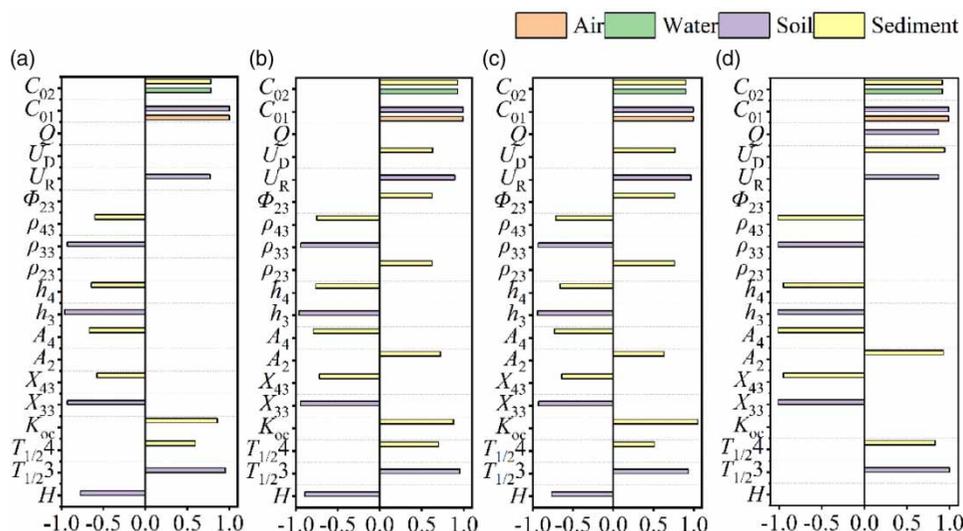


Figure 4 | Sensitivity coefficients of model parameters on the simulated concentration of DMP (a), DEP (b), DBP (c), and DEHP (d) in various environmental media. Note: C_{01} : atmospheric advection input concentration; C_{02} : river advection input concentration; H : henry's law constant ($\text{Pa}\cdot\text{m}^3/\text{mol}$); $T_{1/23}$: reaction half-life in soil (h); $T_{1/24}$: reaction half-life in sediment (h); K_{oc} : carbon – water partition coefficient; X_{33} : volume fraction of solids in soil; X_{43} : volume fraction of solids in sediment; A_2 : water area (m^2); A_4 : sediment area (m^2); h_3 : soil depth (m); h_4 : sediment depth (m); ρ_{23} : suspended particle density in water (kg/m^3); ρ_{33} : solid density in soil (kg/m^3); ρ_{43} : solid density in sediment (kg/m^3); Φ_{23} : advection residence time of suspended particles (h); U_R : rain rate (m/h); U_D : sediment deposition (m/h); Q : scavenging ratio (unitless).

Among these parameters, the emission and inflow data represented by C_{01} and C_{02} had the most significant influence on the model outputs. The air advection input concentrations C_{01} was the most influential parameter for the concentrations of PAEs in air and soil phases (with the same sensitivity), and its sensitivity coefficients were 1.00, 0.99, 1.00 and 0.99 for DMP, DEP, DBP, and DEHP, respectively. The river advection input concentration C_{02} was the most influential parameter for the concentrations of PAEs in water and sediment phases (with the same sensitivity), and its sensitivity coefficients were 0.78, 0.93, 0.90 and 0.91 for DMP, DEP, DBP, and DEHP. This also indicates that source control is the most important way to reduce the PAEs pollution levels in the environment. In addition, the main input pathway of PAEs in air and water phases were atmospheric advection and river advection, respectively, which were little affected by interphase diffusion, therefore, C_{01} and C_{02} were the only highly sensitive parameters of PAEs in air and water phases, respectively. On the contrary, as the sinks of PAEs in air and water phases, PAEs in soil and sediment phases mainly came from interphase diffusion, which were jointly influenced by physicochemical parameters, environmental parameters, emission and inflow parameters. Specifically, the physicochemical parameters $T_{1/24}$ and $T_{1/23}$ represent half of the degradation duration of PAEs in the sediment and soil, respectively, which positively affected their concentrations in the corresponding phases. The physicochemical parameter K_{oc} affected the distribution of PAEs between water and sediment phase, and had a positive effect on the concentration of PAEs in sediment phase. The environmental parameters X_{33} , X_{43} , ρ_{33} , and ρ_{43} had negative effects on the concentration of PAEs in soil and sediment phases by affecting the distribution of PAEs between water and suspended particles in these two phases. The environmental parameters h_3 , h_4 , and A_4 negatively affected the concentration of PAEs in soil and sediment phases by affecting the volume of soil and sediment phases. The environmental parameter U_D represents the rate of water deposition into sediments, which had a positive effect on PAEs in sedimentary facies. In addition, the physicochemical parameter H represents the tendency of compounds to escape from water into air, which indirectly affected the concentration of PAEs in the soil phase by affecting their levels in air phase. The environmental parameters A_2 , ρ_{23} , Φ_{23} and U_R also had a positive indirect effect on the concentration of PAEs in sediment phase by affecting their levels in air phase.

The Monte Carlo simulation results are shown in Fig. S2. Most of the measured values fall between the maximum and minimum values of the simulation, indicating that the model has good reliability and stability. The uncertainty for the predicted PAE concentrations in water phase ($\text{CV} = 0.16\% - 0.19\%$) were lower than those for sediment phases ($\text{CV} = 0.40\% - 0.53\%$) and soil phases ($\text{CV} = 0.49\% - 0.53\%$). With the increase in molecular weight, the simulation results of PAEs in sedimentary phase tended to be overestimated, probably due to the stronger lipophilicity of high molecular weight PAEs, resulting in more

significant cumulative effect in aquatic organisms which were ignored in the model. The simulated concentrations of DEP in water and soil phase were underestimated to some extent, possibly due to high uncertainties in input parameters or ignoring potential sources as proposed in 3.1. In addition, the physicochemical parameters of PAEs were obtained according to literatures, which might not be exactly the same as the actual environment conditions in our study area and to some extent lead to the uncertainty of the simulation results.

4. CONCLUSIONS

In this study, the level III fugacity model performed well for simulating the transfer and fate of PAEs in the environmental system, and the uncertainty analysis verified its reliability. The simulation results reveals that river advection played a dominant role in the spatial migration of PAEs in the study area, much greater than the WWTP discharge. The upstream advection contributed 52.59%, 92.14%, 83.79% and 66.09% of the total input of DMP, DEP, DBP and DEHP in the system, respectively, while the WWTP effluent only contributed 11.64%, 6.65%, 8.90% and 5.11%, respectively. The downstream advection contributed 66.92%, 97.98%, 92.01% and 67.58% of the total output of DMP, DEP, DBP and DEHP from the system, respectively. In addition, air diffusion to soil and water phases and water diffusion to sediment phase were the main ways of PAEs cross-interface transfer, resulting in the accumulation of PAEs in soil and sediment phase, which accounted for 84.66%, 50.26%, 71.96% and 99.09% of the total DMP, DEP, DBP and DEHP in the environmental system of this region, respectively. Among the four PAEs, DEHP had the highest total amount presence and residence time in the system. Sensitivity analysis shows that the emission and inflow parameters had the most significant influence on the environmental multimedia distribution of PAEs.

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AUTHOR CONTRIBUTIONS

Chenchen Wang: Investigation, software, formal analysis, data curation, writing – original draft, and visualization; Yaqi Guo: Conceptualization, methodology, writing – review and editing, resources, and funding acquisition; Lixia Feng: Investigation, resources, and visualization; Weiliang Pang: Investigation and resources; Jingjie Yu: Supervision; Shaopo Wang: Project administration; Chunsheng Qiu: Validation; Chaocan Li: Writing – review and editing; Yufei Wang: Writing – review and editing.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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