Transfer and migration of polycyclic aromatic hydrocarbons in soil irrigated with long-term wastewater

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Abstract: In order to investigate the transfer and migration behavior of polycyclic aromatic hydrocarbons (PAHs) in soil with long-term wastewater irrigation, Groundwater Ubiquity Score (GUS) and fugacity method were respectively used to assess the potential entry into the groundwater and transfer capacity of PAHs. The results of assessment using GUS show that there is significant correlation between the GUS and organic carbon sorption coefficient (K_{OC}) for PAHs and a simple assessment method with K_{OC} was referred to evaluate contamination of groundwater. Applying fugacity method, evaluation results of transfer and migration of PAHs in soil suggest that the PAHs accumulation in the soil through long-term wastewater irrigation could be re-volatilized as secondary emission sources to atmosphere for the Low Molecular Weight (LMW) PAHs, in contrast to High Molecular Weight (HMW) PAHs for which the soil remains a sink that could absorb more PAHs. The net volatilisation flux was 0.39 g/d in upland and 0.32 g/d in paddy for LMW Nap (Naphthalene), and 0.97×10^{-3} g/d in upland and 0.37×10^{-3} g/d in paddy for LMW Phe (Phenanthrene). The net deposition was 0.72×10^{-4} g/d in upland and 0.10×10^{-3} g/d in paddy for HMW Fla (Fluoranthene), and 0.22×10^{-4} g/d in upland and 0.20×10^{-4} g/d in paddy for HMW Bap (Benzo[a]pyrene). Sensitivities of the model estimates to input parameters were tested, and the sensitivity coefficient was defined for the test. The most influential parameters were the volumes of the air, water, and organic carbon fractions in soil and the thickness of the soil.

Keywords: wastewater irrigation, polycyclic aromatic hydrocarbons, transfer and migration, groundwater contamination, groundwater ubiquity score

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) consist of two or more fused aromatic rings. They are extensively distributed in natural ecological environments due to their low solubilities, moderate vapour pressures, low reactivities, and widespread source[1,2]. They are generally the by-products of industrial processes, mainly from the incomplete combustion of organic materials such as coal, or from oil spills, vehicle exhausts, fossil fuels, industrial discharges, and agricultural activity processes, such as biomass burning[3].

With the growing of population, the rapid industrialization and urbanization in China have created severe environmental issues over the past several decades, e.g., municipal sewage and industrial effluent were discharged into the river or urban drainage channels, along with the flow of water, which will lead to a lot of pollutants, changing their spatial locations. Nowadays,

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the discharge amount of wastewater is about 80 billion tons each year in China. Due to the scarcity of water resources and the abundant availability of untreated wastewater, therefore, the use of wastewater for irrigation has had a huge impact, causing serious soil contamination by heavy metals and PAHs[4,5]. The accumulation of PAHs in the soil has aroused interest and concern because of their leachability and transfer through the food chain, which can impact groundwater safety, food quality, and potential human health[6]. Urban wastewater has been an important source of irrigation water in China since the 1950s due to the disproportionate distribution and relative shortage of water resources[7-9]. The wastewater has effectively increased the supply of water resources for agricultural irrigation and has also supplied large amounts of nutrients such as phosphorus, nitrogen, potassium, carbon, and macro- and micronutrients to the soil, which can increase agricultural production[10]. Wastewater irrigation, however, also adds organic pollutants that can accumulate in the soil and cause eco-environmental risks[11,12]. The soils are particularly polluted by PAHs, which have attracted considerable attention due to their toxicity, mutagenic and carcinogenic properties[13].

The contamination level, source apportionment, and risk assessment of individual and total PAHs have been studied in the historic wastewater irrigation area of Hunpu[4,12,14,15]. This area is located in southwest Shenyang, Liaoning Province, Northeast China and has been irrigated for more than 40 years. Shenyang is an industrial city that has discharged its wastewater into the Xihe River, the major drainage channel for the city's industrial and municipal sewage. Approximately 30% of the wastewater is municipal sewage, and 70% is industrial effluent containing organic chemicals and heavy metals[9]. Wang et al.[12] suggested that PAHs entered agricultural soils by atmospheric deposition rather than by groundwater irrigation after wastewater irrigation was banned in 2002. All of these previous studies, however, mainly focused on the environmental monitoring or risk assessment based on toxicology of PAHs in wastewater irrigation area. The environmental behaviour and transition mechanism of PAHs in soil, e.g., assessing likelihood of groundwater contamination or vertical transfer and migration ability in different soil layers are usually considered more important for environmental management and agricultural production practices.

The dissipation of the PAHs has mostly been attributed to biodegradation, volatilisation, irreversible sorption, leaching, and untaken by plants[16]. Information for the environmental sources, distributional characteristics, and fates of the PAHs is thus necessary for understanding their environmental behaviour and effective exposure and for assessing their risks[17]. The objectives of this study were to: (1) identify the leaching potential of individual PAHs to the groundwater in agricultural soils, (2) evaluate the transfer and migration capabilities of individual PAHs including low molecular weight (LMW) and high molecular weight (HMW) between air and soil or adjacent soil layers.

2 Methodology

2.1 Data compilation

2.1.1 Study area

The Hunpu irrigation area is a typical wastewater irrigation area of approximately 41000 hm^2. The annual mean temperature is 7.8°C, and the annual mean precipitation is 734.4 mm. The wind is predominantly from the north in winter and from the south in the other seasons[4,15]. Data for the concentrations of PAHs in the air and soil have been compiled from various studies (Table 1).

Table 1 Concentration of PAHs in soil (μg·kg^{-1}) and air (ng·m^{-3})

	Naphthalene		Phenanthrene		Fluoranthene		Benzo[a]pyrene	
	upland	paddy	upland	paddy	upland	paddy	upland	paddy
Soil concentration [4]								
Layer 1 (0-2 cm)	90	100	62	35	122	75	25	28
Layer 2 (2-5 cm)	110	50	70	32	128	65	29	18
Layer 3 (5-10 cm)	28	27	45	18	71	35	23	8
Air concentration[18]	4.15		81.3		166.1		18.8	

Paddy fields and upland fields are the predominant land used in this region, which have been contaminated by long-term irrigation with wastewater. The amounts of the individual PAHs and the environmental monitoring equipment used to collect the data varied among the studies, which may affect comparisons, but we expect that these data are comparable to some degree.

2.1.2 Collection of physicochemical data

Experimental values of organic carbon sorption coefficient (K_{OC}), half-life in soil (DT_{50}), octanol-water partition coefficient (K_{OW}), and aqueous solubility (S) were derived from the Mackay[19] and US EPA EPI Suite™ [20]. The EPI Suite™ is facilitated by a database of more than 40 000 chemicals derived from the PHYSPROP© database[21]. Approximately 20% of the compounds in PHYSPROP© have multiple values for one or more property, so the inner connection value for physicochemical property, which means the values derived from the same research group, was selected when multiple values were available. The properties were measured at 25°C.

2.2 Groundwater ubiquity score

The Groundwater Ubiquity Score (GUS), proposed by Gustafson[22], is frequently used to evaluate the potential of chemicals to move toward groundwater. Chemicals known to leach can be distinguished from those that do not by the use of a hyperbolic function:

$$\mathrm{GUS} = \log_{10}(DT_{50}) \times (4 - \log_{10}(K_{\mathrm{oc}})) \tag{1}$$

where, DT_{50} is the half-life in soil (days), and K_{OC} is the sorption coefficient (mL/g), used to compare the relative sorption of chemicals. GUSs≥2.8 generally represent a potential to leach to the groundwater, GUSs<1.8 represent no leaching, and GUSs between 2.8 and 1.8 represent an uncertain potential to leach.

2.3 Transfer and migration model

Soil is an important reservoir for many organic compounds in terrestrial environments due to their abundant organic matter in comparison to other environmental phases such as air and water. Soil can act as a long-term or a temporary storage medium depending on its physicochemical properties and on environmental factors. Chemicals, however, can escape from surface soils when their concentrations in soil are higher than their atmospheric concentrations to maintain equilibrium between the soil and air. This diffusion can be assessed by a transfer-rate coefficient usually used to represent exchange potentials or diffusion capacities between air and soil or between soil layers.

The transfer-rate coefficient for diffusion (D_v, mol/h·Pa) between the soil exchange layer (the first soil layer) and the atmosphere is calculated as following[23,24]:

$$D_v = \frac{1}{\dfrac{1}{D_a + D_w} + \dfrac{1}{D_e}} \tag{2}$$

where, D_a, D_w, D_e are the chemical diffusions in air, soil water, and the boundary layer, respectively (mol/h·Pa). The chemical diffuses in air (D_a) and in water (D_w) are defined by

$$D_a = A_r B_{ae} \frac{Z_a}{Y_d} \tag{3}$$

$$D_w = A_r B_{we} \frac{Z_w}{Y_d} \tag{4}$$

where, A_r is the area of study region; Z_a and Z_w are the chemical capacity for air and water compartment (termed the fugacity capacity), and has units of mol/m^3·Pa. Y_d is the log mean diffusion distance in soil (Layer 1, 2, and 3), defined by (5).

$$Y_d = \frac{dep_{\mathrm{lo}} - dep_{up}}{\ln(dep_{lo} / dep_{up})} \tag{5}$$

where, dep_{lo} and dep_{up} are depth of lower and upper for soil layer. B_{ae} and B_{we} in Equations (3), (4) are effective diffusivity in air and water, respectively. B_{ae} is given by

$$B_{ae} = \frac{B_a \phi_{sa}^{10/3}}{(\phi_{sa} + \phi_{sw})^2} \tag{6}$$

in which the molecular diffusivity in air is expressed as:

$$B_a = \frac{0.186 \times 10^{0.0283T}}{V_m^{\ 0.213}} \tag{7}$$

where, ϕ_{sa} is the volume fraction of air in soil; ϕ_{sw} is the volume fraction of water in soil. V_m is the molar volume.

The effective diffusivity in water B_{we} is defined by

$$B_{we} = \frac{B_w \phi_{sw}^{\ 10/3}}{(\phi_{sa} + \phi_{sw})^2} \tag{8}$$

in which the diffusivity in water can be expressed by

$$B_w = \frac{4.864 \times 10^{-3}}{\mu^{0.905} V_m^{\ 1.32}} \tag{9}$$

where, μ is molecular viscosity in water.

The chemical diffuse in the boundary layer is given by

$$D_e=A_rK_vZ_a \tag{10}$$

where, the boundary-layer mass transfer coefficient can be expressed by

$$K_v=\frac{B_a}{0.00475} \tag{11}$$

in which B_a is given in Equation (7).

Transfer rate coefficient of diffusions between soil layers n and n+1 are defined by

$$\frac{1}{D_{v,(n,n+1)}}=\frac{1}{D_{a,n}+D_{w,n}}+\frac{1}{D_{a,n+1}+D_{w,n+1}} \tag{12}$$

where, D_a and D_w are given by Equations (3), (4).

The diffusion flux (N, mol/m^2·h) usually represents the net migration of chemicals between soil and air or between soil layers when the concentrations differ. N is calculated as:

$$N=D_v(f_s-f_a) \tag{13}$$

$$N=D_{v,(n,\,n+1)}(f_{n+1}-f_n) \tag{14}$$

where, f_s (Pa) and f_a (Pa) are the fugacity of a chemical in soil and air, respectively, and f_{n+1} (Pa) and f_n (Pa) are the fugacity of a chemical in lower and upper soil layers, respectively. The concentration of a chemical (mol/m^3) was calculated as $Z\times f$. We used an area of 1 m^2, because the flux N has unit of mol/m^2·h.

2.4 Method of sensitivity analysis

The transfer and migration of a chemical in an environment can be modelled, but not all input parameters can produce influential outputs. The sensitivities of the modelled results must thus be tested for all variable input parameters. The most sensitive components of the model, though, can be determined by sensitivity analysis. To compare the influence of the input parameters on GUS and transfer diffusion flux, we conducted a sensitivity analysis by varying the parameters and recording the corresponding responses[25,26]. We selected changes of ±10% and calculated the sensitivity coefficient (C_s), the ratio of the relative variation of the estimated concentration to that of the input parameter, as following[27]:

$$C_s=A\text{bs}\left(\frac{C_{1.1}-C_{0.9}}{0.2\times C_{1.0}}\right) \tag{15}$$

where, $C_{0.9}$, $C_{1.0}$, and $C_{1.1}$ are the estimated GUS or diffusion flux when the tested parameter was multiplied by a factor of 0.9, 1.0, or 1.1, respectively. The absolute values were taken for an easy comparison of the extent of the influence.

3 Results and discussion

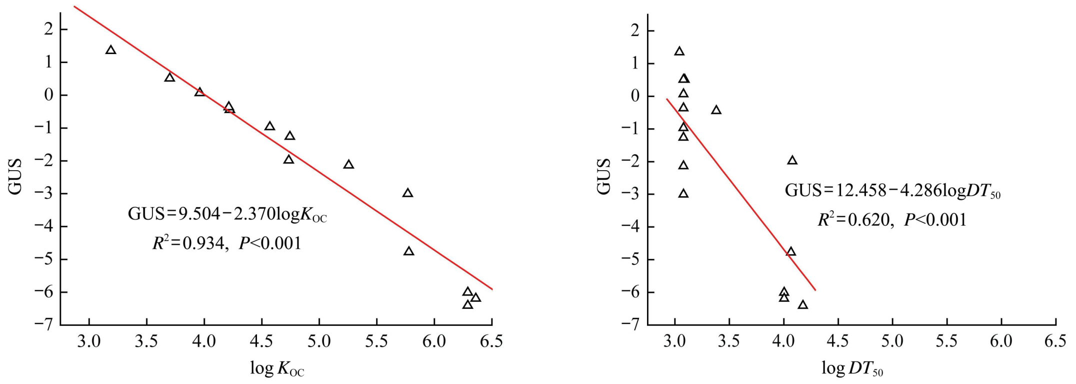
3.1 PAH leaching potentials

Many factors can influence the potential for contamination of groundwater by chemicals, such as the properties of the soils and the physicochemical properties of the chemical. The properties of the chemicals, however, will mainly affect their distributional behaviour and fate in the environment for the same soil type and characteristics. PAHs are generally retained in soils for many years due to adsorption or absorption by soil organic carbon and may even enter the aquatic environment, inducing further hydrospheric pollution because of their hydrophobicity[28,29], so that soil can be a secondary emission source or the final sink of PAHs[30]. In other words, the K_{OC} is a fraction of organic carbon normalized sorption coefficient, which can reflect the sorption capability of the soil to chemicals. Higher K_{OC} indicates stronger sorption and less mobile PAHs[31].

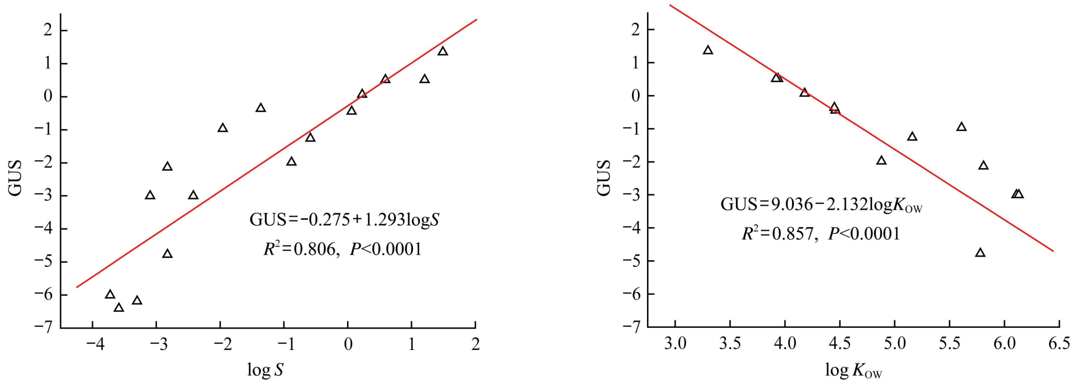
The GUSs of all 16 PAHs calculated using Equation (1) were less than 1.8 (Table 2), indicating that the PAHs were unlikely to leach to the groundwater. To further investigate the main factor affecting the leaching capacity of the PAHs, we analysed the correlations between the GUSs and log DT_{50}, log K_{OC}, log S, and log K_{OW}. K_{OC} was the most important factor, with a significant correlation between GUS and log K_{OC} (R^2=0.934, p<0.0001), followed by log K_{OW}, log S, and log DT_{50} (Figure 1). K_{OC} was thus generally used to assess the adsorption of organic pollutants in soil and was the most important factor influencing the leaching and migration of chemicals to the groundwater. The calculated GUSs indicated that the PAHs were not contamination risks to the groundwater. Higher PAH concentrations, however, were detected at two groundwater sampling sites (24 μg/L and 17 μg/L) in the Hunpu wastewater irrigation area, which may be caused by long-term wastewater irrigation or the lower soil organic carbon content ranged 0.0002 to 0.0028 g/g in this study area that could accelerate the transfer rate of PAHs in vertical soil layer.

Table 2 Common name, sorption coefficient (K_{OC}), half-life (DT_{50}), octanol-water partition coefficient (K_{OW}), water solubility (S), and GUS for 16 PAHs

PAH	Abbr.	Molecular weight	Log K_{OC}	DT_{50}/d	Log K_{OW}	S/mg·L^{-1}	GUS
Naphthalene	Nap	128	3.19	46	3.30	31	1.478451
Acenaphthylene	Acy	154	3.70	51	3.94	16	0.290648
Acenaphthene	Ace	152	3.70	50	3.92	3.8	0.356784
Fluorene	Flu	166	3.96	50	4.18	1.9	−0.25485
Phenanthrene	Phe	178	4.22	100	4.46	1.1	−0.44
Anthracene	Ant	178	4.21	50	4.45	0.045	−0.69658
Fluoranthene	Fla	202	4.74	50	5.16	0.26	−1.25724
Pyrene	Pyr	202	4.74	500	4.88	0.132	−2.21316
Benzo[a]anthracene	BaA	228	4.57	50	5.61	0.011	−2.82029
Chrysene	Chr	228	5.26	50	5.81	0.0015	−2.32759
Benzo[b]fluoranthene	BbF	252	5.78	485	5.78	0.0015	−5.07605
Benzo[k]fluoranthene	BkF	252	5.77	50	6.11	0.0008	−3.21105
Benzo[a]pyrene	BaP	252	5.77	50	6.13	0.0038	−2.90524
Indeno[1,2,3-cd]pyrene	IcdP	276	6.29	420	6.70	0.00019	−5.61375
Dibenzo[a,h]anthracene	DahA	278	6.36	420	6.75	0.0005	−5.1678
Benzo[g,h,j]perylene	BghiP	276	6.29	625	6.63	0.00026	−6.15094



a. log K_{OC} b. log DT_{50}



c. log S d. log K_{OW}

Figure 1 Correlations between the GUS

As mentioned above, the physicochemical properties of the PAHs, such as K_{OC}, will affect their environmental behaviour in soil. The advantage of K_{OC} is that it represents a soil independent measure of chemical mobility. According to calculation, the relation expression between GUS and K_{OC} for PAHs is:

$$\mathrm{GUS} = -2.370 \log K_{OC} + 9.504 \quad (R^2 = 0.934,\ p < 0.0001) \tag{16}$$

Therefore, the Equation (16) may be a simple method of preliminary assessment for PAHs to contaminate groundwater.

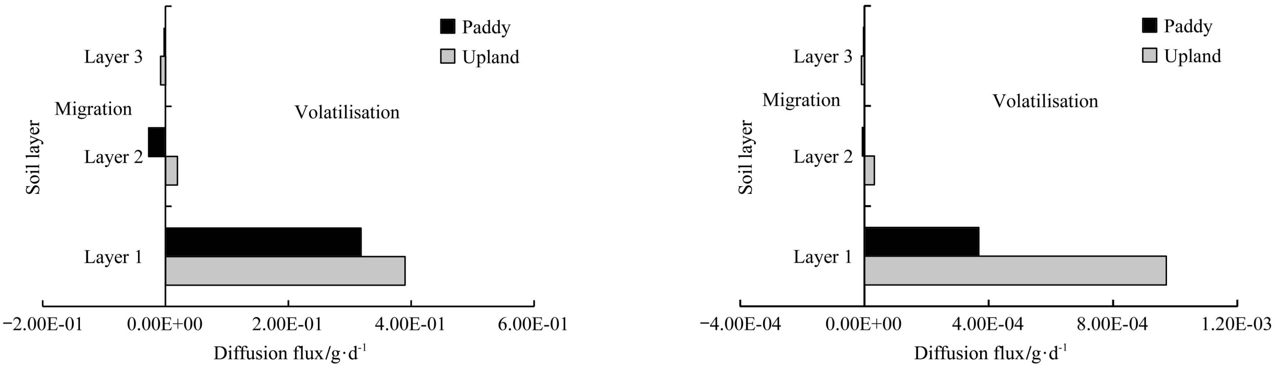
3.2 Transfer and migration capacities of the PAHs

The environmental behaviour of pollutants between compartments generally includes deposition (dry or wet), volatilisation, degradation and leaching. In this study, the transfer and migration of pollutants between air and topsoil or between soil layers was only considered for studying and assessing the transfer and migration capacity of the PAHs. The objectives of this study thus aimed to determine the factors affecting the movement of pollutants and the retardation effect of the soil.

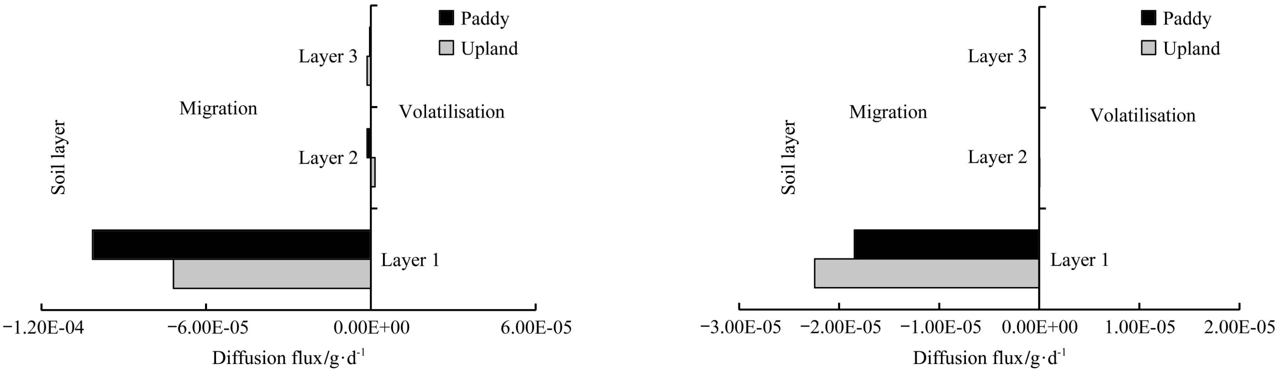
3.2.1 Diffusion flux between soil and air

Nap, Phe, Fla and Bap, as representative PAHs, were also selected for evaluating the capacity of diffusion and migration. The mean concentrations of these four PAHs in 0-2 cm (Layer 1), 2-5 cm (Layer 2), and 5-10 cm (Layer 3) soil layers were also derived from long-term monitored data in the wastewater irrigation area (Table 1)[4]. The proportional volumes of the air and water fractions in the soil were 0.35 and 0.15 for upland field and 0.30 and 0.20 for paddy field, respectively. The concentrations in air were obtained from data for the corresponding period at Shenyang, close to our study area[18]. The soil and air concentrations are presented in Table 1.

The diffusion fluxes calculated in this study enabled us to understand the environmental behaviour of the PAHs between the air and soil. Figure 2 summarises the deposition and migration from air or upper soil and the volatilisation and migration from the topsoil or lower soil layer during the sampling period. The net volatilisation flux was 0.39 g/d in upland and 0.32 g/d in paddy for LMW Nap, and 0.97×10^{-3} g/d in upland and 0.37×10^{-3} g/d in paddy for LMW Phe (Figures 2a and 2b), indicating higher concentrations in the soil than in the air. In contrast, the net deposition was 0.72×10^{-4} g/d in upland and 0.10×10^{-3} g/d in paddy for HMW Fla, and 0.22×10^{-4} g/d in upland and 0.20×10^{-4} g/d in paddy for HMW Bap from air to soil (Figures 2c and 2d), suggesting that the soil was unsaturated and could absorb more pollutants. The diffusion flux differed by approximately five orders of magnitude between Nap and Bap from positive (volatilisation) to negative (deposition) (Figure 2). Whether net volatilisation or deposition, however, the flux gradually decreased from LMW to HMW PAHs, indicating that the LMW PAHs could escape from the surface soil more easily than the HMW PAHs due to their different physicochemical properties.



a. Nap b. Phe



c. Fla d. Bap

Figure 2 Diffusion fluxes between air and soil and adjacent soil layers in two soil types

The tendency of a chemical to evaporate into the atmosphere is generally controlled by its vapour pressure[23], which differs by approximately eight orders of magnitude between Nap and Bap. The vapour pressures for Nap, Phe, Fla, and Bap are 11.3 Pa, 1.61×10^{-2} Pa, 1.21×10^{-3} Pa, and 7.32×10^{-7} Pa (25°C), respectively. The partitioning from soils and other organic media to the atmosphere, however, is controlled by the octanol-air partition coefficient (K_{OA})[23], which differs by approximately five orders of magnitude between Nap and Bap. The K_{OA} values for Nap, Phe, Fla, and Bap are 1.55×10^5, 3.72×10^7, 5.75×10^8, and 7.24×10^{10} (25°C), respectively. Nap is thus the most active PAH in the environment due to its high vapour pressure and low K_{OA}. On the other hand, the net diffusion flux of Nap and Phe was from soil to air, indicating that the accumulated PAHs in the soil from long-term wastewater irrigation can be re-volatilised as a secondary emission source. In contrast to HMW Fla and Bap, however, the soil remains a sink that could absorb more PAHs.

3.2.2 Vertical migration of PAHs

The vertical migration of a chemical in soil in this study was mainly due to diffusion between the upper and lower soil layers, not including the effects of bioturbation, cryoturbation and macropore transport[32]. The maximum mean concentrations of the four PAHs were in the topsoil of the paddy field and just below the soil surface of the upland field, and the concentrations decreased with depth[4]. Diffusion differed between the layers and types of soil (Figure 2). Layer 2 in the upland field served as a storage layer for all PAHs and could provide sufficient material to the top layer for exchange between the soil and air or for migration to the lower soil layer for maintaining balances. In contrast to the upland field, the soil surface of the paddy field has more substance than the second soil layer, which will continuously transport PAHs to the lower soil layer, especially for HMW PAHs where most of the content is from deposition.

The transfer and migration capacity of the PAHs in all soil layers was from strong to weak for LMW (two and three rings) to HMW (four and five rings), particularly for Bap that was poorly exchanged and transported (Figure 2). The evaluation of the PAH diffusion and migration capacities thus further verified the use of the amended GUS index, which could be used to assess the level of contamination of the groundwater.

3.3 Sensitivity analysis

3.3.1 Sensitivity of the GUS index

K_{OC} and half-life (DT_{50}) were used to calculate the sensitivity of the GUS index (Figure 3). K_{OC} was more sensitive than DT_{50} for calculating the GUS especially for the numerical values ranged from 0.49 to 2.9 for K_{OC} and ranged from 0.16 to 0.26 for DT_{50}, which could lead to large fluctuations for LMW PAHs. In contrast, DT_{50} was relatively stable, which is not considered as influential parameter in the GUS index. Figure 3 also depicted that both K_{OC} and DT_{50} could not cause significant change of GUS index for HMW PAHs.

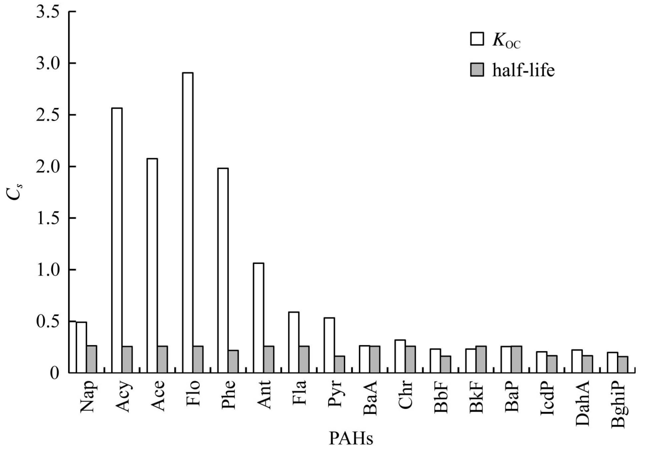
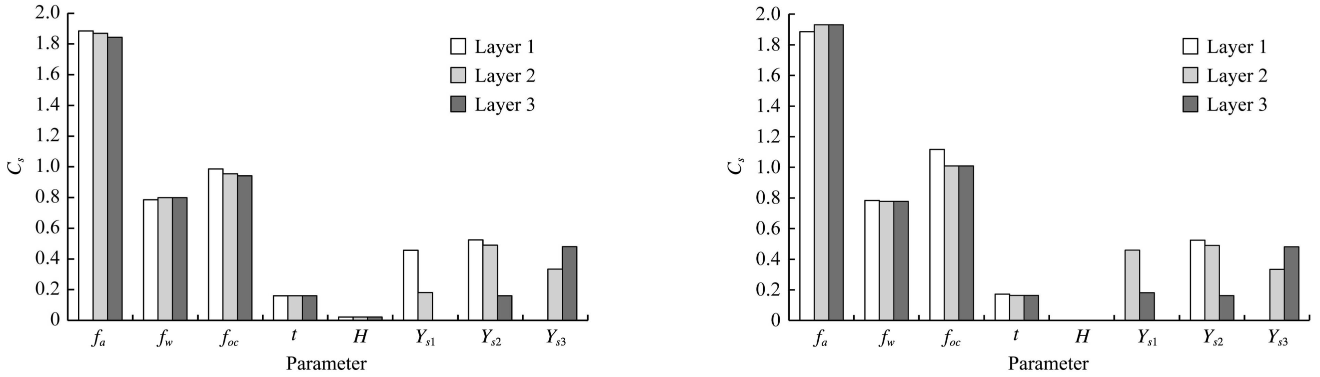


Figure 3 Coefficients of sensitivity (C_s) of the calculated GUS index using K_{OC} and DT_{50}

3.3.2 Sensitivity of the diffusion flux estimates to the input parameters

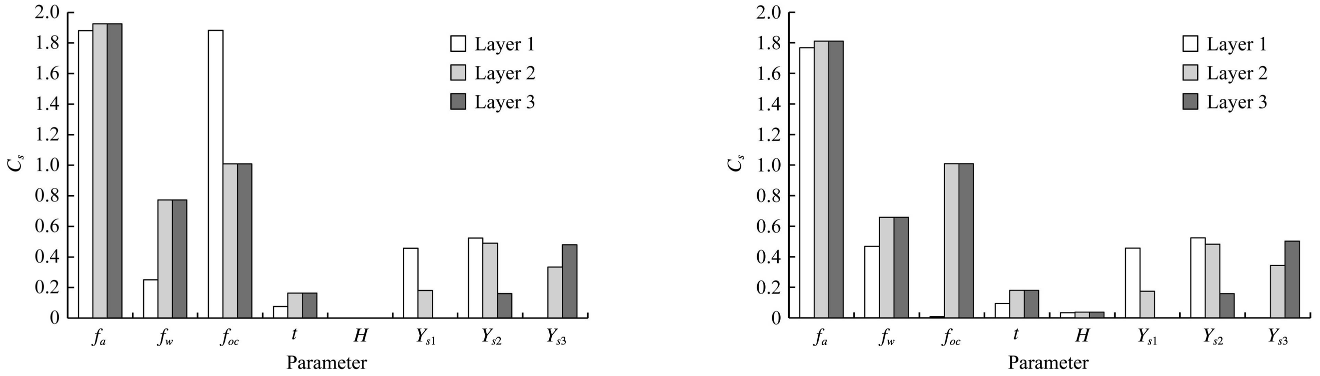
On the basis of the sensitivity coefficients, the influence of the parameters on the estimated diffusion fluxes of the four PAHs in the soil layers of the upland field followed the order $f_a > f_{oc} > f_w > Y_{s2} > Y_{s1} \approx Y_{s3} > t > H$ (see Figure 4 for the definitions of these terms). f_{oc}, Y_{s1}, and Y_{s3} were attentive parameters, and f_{oc} had the most influence on the diffusion flux for Fla in the top soil layer but had little effect on the change of diffusion flux for Bap in the same soil layer. Y_{s1} and Y_{s3} slightly affected their adjacent soil layers.

In summary, the most significant parameters for modelling the diffusion flux of PAHs were the proportional volumes of the air, water and organic carbon fractions in the soil, perhaps due to the physicochemical properties of the PAHs and to the soil properties, because the PAHs are hydrophobic and lipophilic organic compounds that are easily absorbed by organic carbon in soil. The estimates were also very sensitive to the thickness of the soil layer.



a. Nap

b. Phe



c. Fla

d. Bap in the three soil layers

Note: The parameters from left to right are: f_a, volume of the air fraction in the soil; f_w, volume of the water fraction in the soil; f_{oc}, volume of the organic carbon fraction in the soil; t, temperature; H, Henry's constant; Y_{s1}, thickness of the top soil layer; Y_{s2}, thickness of the second soil layer; and Y_{s3}, thickness of the third soil layer.

Figure 4 Coefficients of sensitivity (C_S) to the input parameters of the calculated concentrations

4 Conclusions

The transfer and migration capacities of PAHs were evaluated in an area irrigated with wastewater for more than 40 years. The GUS index was used to assess their potential to contaminate the groundwater. Theoretical calculations, however, differed significantly from monitored data, which may be caused by long-term wastewater irrigation or the lower soil organic carbon content in this study area.

1) A simple assessment method by using K_{OC} was referred to evaluate contamination of groundwater because of the significant correlation between GUS and K_{OC}.

2) LMW PAHs volatilised and migrated to the air and lower soil layers more easily than HMW PAHs, indicating a higher risk of transport into the groundwater. In addition, the soil acted as a secondary source of LMW Nap and Phe and remained a sink for HMW Fla and Bap.

3) The estimates of diffusion flux were sensitive to the proportional volumes of the air, water, and organic carbon fractions in the soil and to the thickness of the soil layer. The environmental behaviour and fate of PAHs in areas of wastewater irrigation requires further research, particularly the mechanisms of exchange and interaction of physical or chemical processes between different environmental phases.

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