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Assessment of the effects of soil organic matter and iron oxides on the individual sorption of two polycyclic aromatic hydrocarbons

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Abstract
Soils are the ultimate sink for environmental pollutants like polycyclic aromatic hydrocarbons (PAHs), but the roles of major soil constituents in this process are still unclear. The fate of PAHs is governed by sorption processes which in turn affect transport, chemical and biological reactivity of these PAHs. Thus, the effects and contributions of two major soil constituents (organic matter-OM and iron oxides-IOs) on pyrene and fluorene sorption on soils were assessed by removal of both constituents. The whole soils had higher sorption than the treated OM/IOs soils. Pyrene sorption on OM-rich soils was high and nearly instantaneous, while on the IOs-rich soils, it was lower with delayed equilibrium. The IOs contributed < 25% to the sorption process while OM contributed ≥ 50%. The extent of PAHs desorption was dependent on the main constituent(s) on each soil; soils with high OM content exhibited lower desorption and high hysteresis. Hysteresis was higher for pyrene, and this was far obvious in the presence of OM; the hysteresis trend is whole > IOR > OMR soils. Though, removal of any of these soil constituents usually reduced sorption and enhanced sorbed PAHs desorption, the presence of IOs masked some PAHs sorption sites, thus its removal resulted in higher sorption. In general, this study highlights the contributions of soil OM and IOs on the sorption of pyrene and fluorene.

Keywords Pyrene · Fluorene · PAHs Sorption · Sub-Saharan soils · Soil iron oxides · Soil organic matter

Introduction

Natural organic pollutants in soils have been enormously supplemented by recent anthropogenic inputs; this is an issue of huge concern because soils and their constituents are vital factors in global development issues, such as global burden of disease and food security (Diagboya 2015; Hamdi et al. 2007; Site 2001). Pollutants of importance include the persistent toxic chemicals and emerging pollutants, such as polycyclic aromatic hydrocarbons (PAHs) (Adesina et al. 2018), pharmaceuticals and personal care products (PPCPs), and agricultural pesticides (Vaikosen et al. 2019). Though soils have long been recognized as the ultimate sink for these pollutants, the roles of major soil constituents on the fates of some of these chemicals are still vague; better

knowledge of their fate is vital if polluted soils are to be managed appropriately.

Polycyclic aromatic hydrocarbons are primary contaminants in several soils and sediments. Sorption processes determine the fate of these pollutants in soils, and these processes affect transport and reduce reactivity (both chemical and biological) of organic pollutants (Amir et al. 2005; Huang et al. 2003). The sorption of hydrophobic organic pollutants in soils has been reported to be controlled mainly by either their organic matter or iron oxide contents (Ahangar 2010; Chilom et al. 2005; Mokwenye et al. 2016; Olu-Owolabi et al. 2014, 2015; Site 2001; Yang et al. 2014). However, none of such reports considered the simultaneous roles and interactions of these major constituents in relation to the whole soil in the sorption process. Contrary to these general reports that soil organic matter is the main contributor to sorption of pollutants, Diagboya et al. (2016) have reported that the presence and interactions of major soil constituents, such as iron oxides with other constituents, play vital roles in anionic pesticides sorption. However, no such report on the simultaneous contributions of major soil constituents to uncharged PAHs sorption on soils has been

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reported. The PAHs are especially important because they are ubiquitous in soils and sediments, and toxic to biota, especially the lower molecular weight members. Hence, pyrene and fluorene are listed as priority PAHs, though not known carcinogens in themselves but some other members (such as benzo[e]pyrene and benzo[c]fluorene) of this group are (ATSDR 1995).

The qualitative and quantitative assessments of soil constituents' contributions to PAHs sorption on soils are vital for predicting the fates and initiating appropriate remediation strategies for PAHs. This is significant because most soil constituents play a contributory role in PAHs and other organics sorption processes (Chilom et al. 2005); thus, direct extrapolation using only soil organic matter content would give a partial detail of PAHs and other organics fate in soils. Current information on these pollutants sorption on soils is still insufficient for these, as well as predicting the possible mechanisms for PAHs sorption. Hence, the objective of this study was to assess the effects and contributions of two major soil constituents (organic matter and iron oxides) on the sorption of pyrene and fluorene on three tropical sub-Saharan soils with varying physicochemical characteristics, as well as describe the data obtained using various adsorption models.

Materials and methods

Soil sampling, treatments, and characterization

Sub-Saharan surface soils (0–30 cm) from three different agro-ecological zones (AEZs) were obtained from locations which are relatively free from anthropogenic contaminations, such as pesticides and fertilizer applications (Table 1). Soil organic matter and iron oxides removal involved using hot (80 °C) hydrogen peroxide (30%) and sodium dithionite in citrate-bicarbonate buffer, respectively; details have been described previously (Diagboya et al. 2016). The whole, organic matter removed (OMR), and iron oxides removed (IOR) soils' characterizations included determination of pH, organic matter, particle size, metals (exchangeable, trace and oxides), cation exchange capacity (CEC) and soil mineralogy (see Supplementary Material–*SM 1* for details).

Sorption studies of pyrene and fluorene

Milli-Q system purified water was used throughout the experiment. Pyrene and fluorene stock solutions (1000 µg/L each) prepared separately in 20% v/v acetonitrile/milipore water and 10% v/v methanol/water, respectively, were employed for the study. Working solutions (100 µg/L each) were prepared from the stock separately in 5% v/v organic solvent/water. Background electrolyte (0.005 M $CaCl_2$) was used, while biocide (0.01 M NaN_3) was employed to eliminate microbial degradation of the PAHs.

Sorption experiments were carried by adding 10 mL of either pyrene or fluorene solution (100 µg/L) into brown glass vials containing of the whole or treated soil sample (0.50 g) and this was sealed with Teflon lined screw caps. The vials were also wrapped in aluminum foil in the dark to reduce possible losses from photochemical degradation and equilibrated at 25 °C by horizontal shaking (100 rpm). Sorption rate experiments were carried out from 10–1440 min (or 4320 min for fluorene), while initial concentration effects and temperature were investigated from 20–100 µg/L at 25 and 40 °C. All studies were carried out at the ambient soil pH except for the effect of pH which was done from pH 3–9 using 100 µg/L of either PAHs. Desorption studies were done right away after the equilibrium experiments via thoroughly

Table 1 Sample soils' characterization

Soil	Sampling coordinate	AEZ[a]	pH H_2O	pH KCl	OM[c] (%)	CEC[d]	BS[e]	Particle size analysis (%)			Oxides (wt %)	
								Sand[f]	Silt[g]	Clay[h]	Fe_2O_3	Al_2O_3
Lokoja (LF)	6° 45′ E; 7°49′ N	Southern Guinea SV[b]	6.73	5.86	6.25	8.29	98.31	48.3	31.1	20.6	0.16	1.69
Gembu (GSF)	11° 15′ E; 6°43′ N	Montane	5.14	4.25	2.80	2.37	98.18	13.9	79.8	6.3	3.90	15.75
Jos (JB)	8° 52′ E; 9°48′ N	Northern Guinea SV[b]	5.17	4.08	3.57	2.98	85.25	42.3	57.1	0.6	3.13	9.12

[a]*AEZ* Agroecological zone

[b]SV savanna

[c]OM Organic matter

[d]*CEC* (cmol kg^{-1}) Cation Exchange Capacity

[e]*BS* Base saturation

[f]% sand (> 50 µm)

[g]% silt (2–50 um)

[h]% clay (> 2 um)

decanting the PAHs solution and swapping with fresh 5% v/v blank (without PAHs) background solution. The sorption and desorption incubation periods were different for pyrene (1440 min) and fluorene (4320 min) studies. All experiments were carried out in duplicate. Control studies without soil samples were done to predict possible losses from sorption on vials' walls and volatilization; these were negligible.

At equilibrium, the vials were centrifuged for 20 min at 4000 rpm, and the concentrations of pyrene in solution were determined using fluorescence spectroscopy (Perkin Elmer model LS 55, USA) in the synchronous mode by scanning at a wavelength difference ($\Delta\lambda$) of 36 nm, from 300 to 400 nm and at a speed of 500 nm/min. The synchronous peak at 335 nm was used to monitor pyrene sorption. Fluorene was also determined in the synchronous mode by scanning at a wavelength difference ($\Delta\lambda$) of 45 nm, from 200 to 350 nm, and at scanning speed of 1000 nm/min while monitoring the synchronous peak at 264 nm.

Data treatment

The amounts of any PAHs removed from solution were calculated from the initial (C_o) and final (C_e) concentrations in solutions after the incubation using $q_e = (C_o - C_e)v/m$, where v, q_e, and m are, respectively, the volume of the solution (mL), amount of PAHs sorbed (μg/g), and mass (g) of sample. The sorption rate data were also explained using the pseudo-first, second order, Elovich and intra-particle diffusion kinetics models; as well as the thermodynamic parameters: entropy change ($\Delta S°$), enthalpy change ($\Delta H°$) and standard free energy ($\Delta G°$) (see SM 2).

Results and discussion

Soil properties

The soils physical and chemical properties have been extensively described earlier (Diagboya et al. 2015, 2016) but results are shown in (Tables 1, 2; SM Tables 1). Briefly, a comparison of these soils with those of reference soils of the moist lowlands in West Africa indicates a neutral pH for the LF (Lokoja) soil and slightly acidic pH for both the GSF (Gembu) and JB (Jos) soils. The organic matter contents could be regarded as high with LF exhibiting the highest compared to GSF and JB. The observed soil minerals, trace elements and heavy metals were within the ranges reported for sub-Saharan soils. The soils' mineralogy (SM Table 1) showed that quartz is a dominant mineral while the carbonate minerals (siderite, calcite, dolomite and aragonite), hematite and kaolinite were main feature components of these soils. The LF and JB soils showed the presence of expansive illite and montmorillonite clay minerals.

The effects of the soil treatments on the OMR and IOR samples were ascertained by comparing the organic matter, CEC and soil pH of both treatments with the whole soils (Table 2). A zero percent organic matter was expected after removal of organic matter in the OMR soils. Though the presence of OM may not be ruled out after the treatment, the low values recorded might be attributed to interference which occurs when the dichromate-ferrous sulphate titration is used in organic matter determination (McLeod 1973). The OMR treatment resulted in reduced pH (tended towards acidic soils) and CEC reduction for LF and GSF. This CEC trend is an indication that the soils exchange cations are linked to the organic matter components, resulting in the lower CEC values after treatment. On the contrary, there was a significant CEC increase for JB ($\approx 29\%$); which has been

Table 2 Selected physicochemical characteristics of whole and treated soils compared

	pH H$_2$O	pH KCl	Ca	Mg	K	Na	BS[a]	CEC[b](cmol kg^{-1})	% Organic matter
LF	6.73	5.86	6.03	1.15	0.21	0.75	98.31	8.29	6.25
LF OMR	6.08	5.57	0.41	2.18	0.30	0.33	98.77	3.26	0.98
LF IOR	7.79	7.01	1.88	0.49	0.15	15.4	99.78	17.9	4.31
GSF	5.14	4.25	1.35	0.07	0.10	0.71	98.18	2.37	2.80
GSF OMR	4.38	3.98	0.44	0.26	0.14	0.24	50.52	2.14	0.83
GSF IOR	8.06	7.26	2.87	0.14	0.42	21.3	99.68	24.8	1.23
JB	5.17	4.08	1.84	0.38	0.23	0.09	85.25	2.98	3.57
JB OMR	4.14	3.63	2.14	0.52	0.31	0.15	80.86	3.87	0.92
JB IOR	8.00	6.98	1.31	0.30	0.38	35.9	99.79	37.9	1.72

[a]*BS* Base saturation

[b]*CEC* (cmol kg^{-1}) Cation Exchange Capacity

attributed to unmasking of soil components like illite and iron oxides, thus exposing their exchangeable cations as the organic matter components were removed (Diagboya et al. 2015). Conversely, iron oxides treatment resulted in slightly alkaline soils and very high CEC values (> 100%). The high CEC values were attributed to increase in exchangeable bases, such as Na^+ ions, associated with organic matter in similar unmasking process as described earlier (Diagboya et al. 2015; Pérez-Novo et al. 2008; Wang et al. 2008). Table 2 also showed that removal of iron oxides resulted in the loss of significant amount of organic matter as well.

Pyrene and fluorene sorption studies

Kinetics studies

Pyrene sorption equilibria on whole soils were attained within 360 min (Fig. 1a–c). The equilibria attainment for fluorene (Fig. 1d–f) was similar at 360 min except for JB soil which was attained at 2880 min. This relatively fast pyrene and fluorene sorption equilibria may be attributed to the presence of high percentage of organic matter/aluminum oxide which exhibit faster equilibrium than other soils components; similar results have been reported earlier (Olu-Owolabi et al. 2014; Weber et al. 1992). The exception

observed in the JB soil (longer equilibrium time) may suggest that at very low amount of soil OM coupled with relatively lower amounts of soil iron and aluminum oxides, sorption rate reduces and equilibrium takes longer.

In verifying this claim, the influences of two main soil components (organic matter and iron oxides) on the equilibrium attainment were examined (Fig. 1a–f). It was observed that pyrene sorption rate became very fast upon removal of iron oxides on all soils (Fig. 1a–c). The rates were high and equilibria were attained within the first 60 min of sorption initiation except for GSF IOR with similar rate but slightly extended equilibrium attainment at 360 min. However, upon removal of organic matter in the soils (the OMR soils), the sorption rates became lower in the first 60 min and equilibria were attained at 360 min (Fig. 1b–c), a similar time as the whole soils. An exception with a significantly reduced rate was observed in the removal of organic matter in the LF OMR where the equilibrium time was doubled to 720 min (Fig. 1a). These trends may be attributed to the contributions of these soil constituents in the pyrene sorption process. For instance, sorption of pyrene on organic matter is nearly instantaneous–this is especially true for the low-polarity organic matter (Weber et al. 1992); thus, upon removal of iron oxides in the IOR samples, sorption rate became high with fast equilibrium. Pyrene sorption rate on iron oxides is
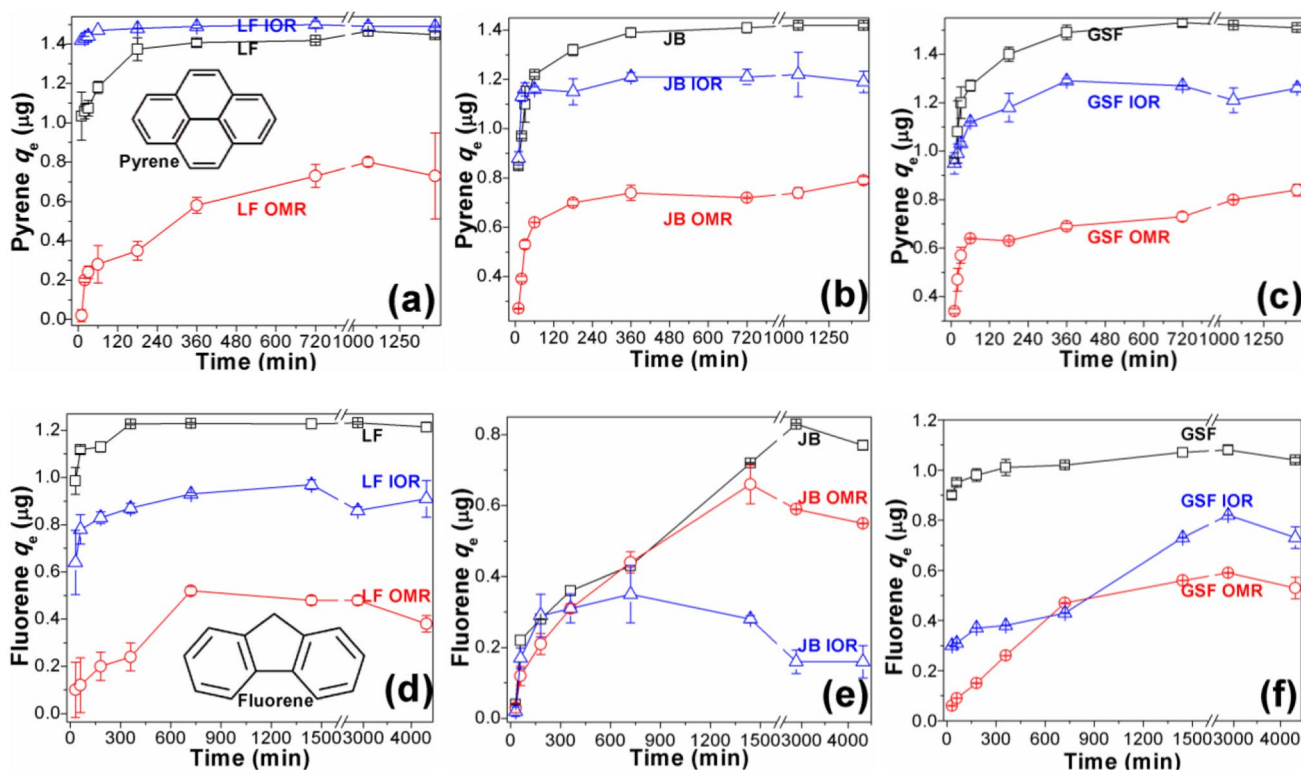

Fig. 1 Effect of soil treatments on the equilibrium attainment time on pyrene sorption by (**a**) LF (Inert: structural formula of pyrene), **b** JB and (**c**) GSF soils, and fluorene sorption on (**d**) LF (Inert: structural formula of fluorene), (**e**) JB and (**f**) GSF soils (*OMR* organic matter treated soils, *IOR* iron oxides treated soils)

not as high as on the organic matter; thus, removal of organic matter resulted in lower sorption rates and slightly delayed equilibrium on the iron oxides-rich soils of JB OMR and GSF OMR (Table 1). The LF soil with lower quantity of iron oxides (Table 1) expressed significantly lower sorption rate and delayed equilibrium upon removal of organic matter (Fig. 1a LF OMR).

Unlike the pyrene, fluorene sorption on whole soils (Fig. 1d–f) exhibited lower and slower sorption rates as well as delayed equilibria. The equilibria for LF and GSF, with higher organic matter and iron oxides, respectively, were recorded at 720 min, while for JB soil (with comparatively lower amounts of both constituents) is 2880 min. Treatment by removal of iron oxides in soils (IOR) resulted in a relatively faster sorption rate and quicker equilibrium (180 min) especially in LF IOR and JB IOR affirming the role of organic matter in fast PAHs sorption as observed above. The GSF IOR with higher iron oxides content had a further delayed equilibrium at 1440 min. On the contrary, removal of organic matter in soils (OMR) resulted in increases in the equilibria times to 720 min in LF OMR, and 1440 min in both JB OMR and GSF OMR soils.

Comparing pyrene and fluorene sorption rates of whole and treated soils indicated that organic matter contributed $\geq 50\%$ of the soils' sorption capacities while iron oxides contributed less: $\leq 20\%$ for GSF and JB soils. An exception is the LF IOR sample which exhibited a slightly different trend: iron oxides removal resulted in $\approx 5\%$ increase in the pyrene sorption, an indication that some of the sorption sites might have been masked by the presence of iron oxides on the whole soil.

In general, the sorption data showed that pyrene and fluorene sorption on the soil aggregates, especially the organic matter, were relatively fast or almost instantaneous. Consequently, removal of organic matter will cause longer sorption time on other soil constituents especially iron oxides, and the expansible and other clay minerals resulting in the increased equilibrium time. Conversely, iron oxide removal made equilibrium faster, and their removal may enhance sorption in cases where they masked the sorption sites before removal. Thus, the role of one soil components in pollutant sorption could be masked by the presence of another soil component.

To predict the mechanisms involved in the sorption processes, the sorption rate data for the whole and treated soils were fitted into four kinetic models (Eq. 1–4) and the models parameters are shown in Table 3. A comparison was done for the pseudo-first and pseudo-second order models' parameters of correlation coefficients (r^2) and estimated model sorption capacity (q_e) for whole and treated soils. It was observed that the r^2 values were closer to unity in the pseudo-second order model (≥ 0.966) than the pseudo-first order model (≤ 0.930), while the pseudo-second order model q_e values were consistent with the experimental values. These good

fittings suggested that the sorption mechanism involved π–π interactions between sorbed pyrene and fluorene and soil surface sites especially those associated with the organic matter (Olu-Owolabi et al. 2015).

Similar to the pseudo-second order model, the Elovich's estimated q_e values were also in agreement with the r^2 values; an indication that the process could be explained by this model. The reaction kinetic suggests that since the Elovich curve did not pass through the graph's origin, boundary layer control played a significant role in the sorption process. In this case, the control was π–π interactions between PAHs molecules in solution and surface sorption sites, and this was the rate controlling mechanism (Olu-Owolabi et al. 2014).

The intra-particle diffusion model (Weber and Morris 1963) parameters are also shown in Table 3 and the values of the parameter C (µg g^{-1}) obtained by a plot of q_t versus $t^{1/2}$ could be used to predict the thickness of the sorbed PAHs boundary layer. If the C value is equal to the overall quantity of sorption (q_e, µg g^{-1}), then the sorption process occurred only on the surface sites and could be regarded as solely adsorption, but when the C value is less than q_e, then the sorption process comprised both surface adsorption and partitioning within interstitial spaces (Abasi et al. 2018; Mohubedu et al. 2019) of the organic matter content, as well as within soil minerals, such as the iron oxides and expansive clays (Illite and montmorillonite). The C values of the study showed that the sorption comprised mainly of surface adsorption and partitioning within various phases in the soils, and this was especially true for the treated soils.

Study of the effect of pH on sorption

A major parameter which affects sorption of PAHs is the soil solution pH; this is due to effects of pH on the soil constituents responsible for the PAHs uptake. For instance, it influences physical and chemical properties of the sorption sites, its surrounding and the pollutant molecules (An et al. 2010; Zeledón-Toruño et al. 2007). Thus, the effect of pH on pyrene and fluorene sorption experiments has been studied from solution pH 3 to 9. The fluorene sorption trends (Fig. 2) were similar to those of pyrene earlier reported (Laor et al. 1998; Olu-Owolabi et al. 2014; Ping et al. 2006) regardless of the soil; the trends showed relatively higher sorption at lower soil pH values and decreasing sorption as the pH value increased. The amount of pyrene or fluorene sorbed at each soil pH was dependent on the soil constituents especially organic matter content: soils with higher organic matter content exhibited higher PAHs sorption.

This sorption trend has been ascribed to the effect of varying solution pH on sorption sites containing phenols and other organic functionalities which may become hydrophobic depending on the ambient pH (An et al. 2010; Zeledón-Toruño et al. 2007). Low soil pH results in high

Table 3 Pyrene and fluorene sorption kinetic model parameters for whole and treated soils

Kinetics model	Model parameters	Soil samples								
		LF	JB	GSF	LF OMR	GSF OMR	JB OMR	LF IOR	GSF IOR	JB IOR
Pyrene sorption										
PFO	q_e (µg g^{-1})	0.318	0.285	0.330	0.59	0.37	0.28	0.06	0.17	0.11
	k_1 (min^{-1})	1.7×10^{-3}	2.5×10^{-3}	1.5×10^{-3}	2.1×10^{-3}	2.0×10^{-3}	2.1×10^{-3}	8.8×10^{-4}	1.3×10^{-2}	1.1×10^{-3}
	r^2	0.783	0.822	0.674	0.768	0.930	0.807	0.525	0.343	0.436
PSO	q_e (µg g^{-1})	1.46	1.43	1.52	0.853	0.838	0.781	1.497	1.252	1.203
	k_2 (g µg^{-1} min^{-1})	0.06	0.07	0.08	0.007	0.032	0.056	1.223	0.173	0.540
	r^2	0.999	1.000	0.999	0.966	0.995	0.998	1.000	0.999	0.999
Elovich	q_e (µg g^{-1})	1.43	1.41	1.43	0.670	0.797	0.752	1.48	1.27	1.18
	β	10.3	9.01	9.01	6.80	12.2	11.1	66.7	15.63	24.4
	r^2	0.948	0.914	0.933	0.952	0.915	0.862	0.911	0.881	0.545
Intra-particle diffusion	C (µg g^{-1})	1.06	1.00	1.10	0.096	0.450	0.425	1.44	1.01	1.06
	k_{id}	0.012	0.013	0.013	0.020	0.011	0.011	0.002	0.008	0.004
	r^2	0.805	0.707	0.735	0.905	0.816	0.651	0.709	0.684	0.358
Experimental q_e		1.44	1.41	1.51	0.75	0.79	0.75	1.49	1.26	1.21
Fluorene sorption										
PFO	q_e (µg g^{-1})	0.07	0.63	0.12	0.30	0.33	0.68	0.15	0.53	0.13
	k_1 (min^{-1})	3.2×10^{-4}	5.1×10^{-3}	3.2×10^{-4}	2.1×10^{-4}	7.4×10^{-4}	2.8×10^{-4}	1.8×10^{-4}	3.9×10^{-4}	1.1×10^{-4}
	r^2	0.249	0.781	0.443	0.211	0.515	0.485	0.137	0.707	0.068
PSO	q_e (µg g^{-1})	1.22	0.88	1.05	0.42	0.60	0.62	0.90	0.62	0.16
	k_2 (g µg^{-1} min^{-1})	0.97	0.00	0.21	0.04	0.01	0.01	3.31	0.01	0.04
	r^2	0.999	0.981	0.999	0.973	0.983	0.983	0.998	0.980	0.975
Elovich	q_e (µg g^{-1})	1.16	0.64	1.02	0.41	0.48	0.65	0.84	0.63	0.21
	β	24.39	6.45	31.25	12.2	8.40	8.13	21.3	9.26	52.6
	r^2	0.724	0.938	0.879	0.744	0.913	0.908	0.665	0.825	0.100
Intra-particle diffusion	C (µg g^{-1})	1.09	0.10	0.94	0.15	0.08	0.10	0.77	0.25	0.22
	k_{id}	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00
	r^2	0.443	0.887	0.672	0.541	0.787	0.748	0.385	0.868	0.000
Experimental q_e		1.23	0.77	1.04	0.47	0.56	0.60	0.91	0.76	0.26

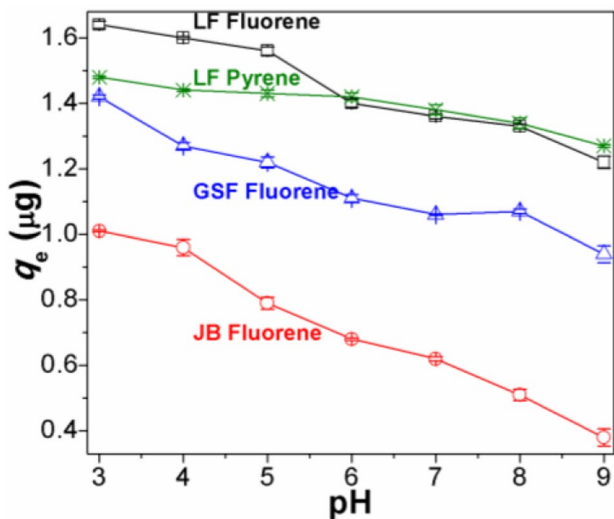*PFO* Pseudo-First Order, *PSO* Pseudo-Second Order

Fig. 2 Effect of soil pH on trends of fluorene and pyrene sorption

proton concentration leading to protonation of negatively charged functional groups especially on organic matter causing reduced ionization and increased hydrophobicity. This increase in hydrophobicity within the soil is what ultimately

results in the higher sorption of pyrene and fluorene especially through π–π interactions. However, at higher soil pH values, sorption could not be attributed to the pH-dependent π–π interaction between PAHs and hydrophobic soil components. Rather, sorption has been attributed to possible cation-π interactions between aromatic π-bonds in PAHs and the cations on soils' sorption sites (Zhu et al. 2004) as well as entrapment within soil materials pores.

Equilibrium and temperature studies

Study of sorption equilibria isotherms is an important method for investigating soil sorption and desorption processes because the relationship between the sorbed pyrene or fluorene and the equilibrium amounts in the soil–water solution can be ascertained using the isotherms. Hence, the effect of varying solution pyrene or fluorene concentration (20–100 µg/L) was studied at two temperatures (25 and 40 °C), ambient soil pH and at incubation times of 1440 and 4320 min for pyrene and fluorene, respectively.

The various equilibrium sorption trends are shown in Figs. 3, 4, while comparisons of the sorption and desorption studies are shown in Fig. 5. Figure 3a–f show the sorption trends of pyrene and fluorene as concentration
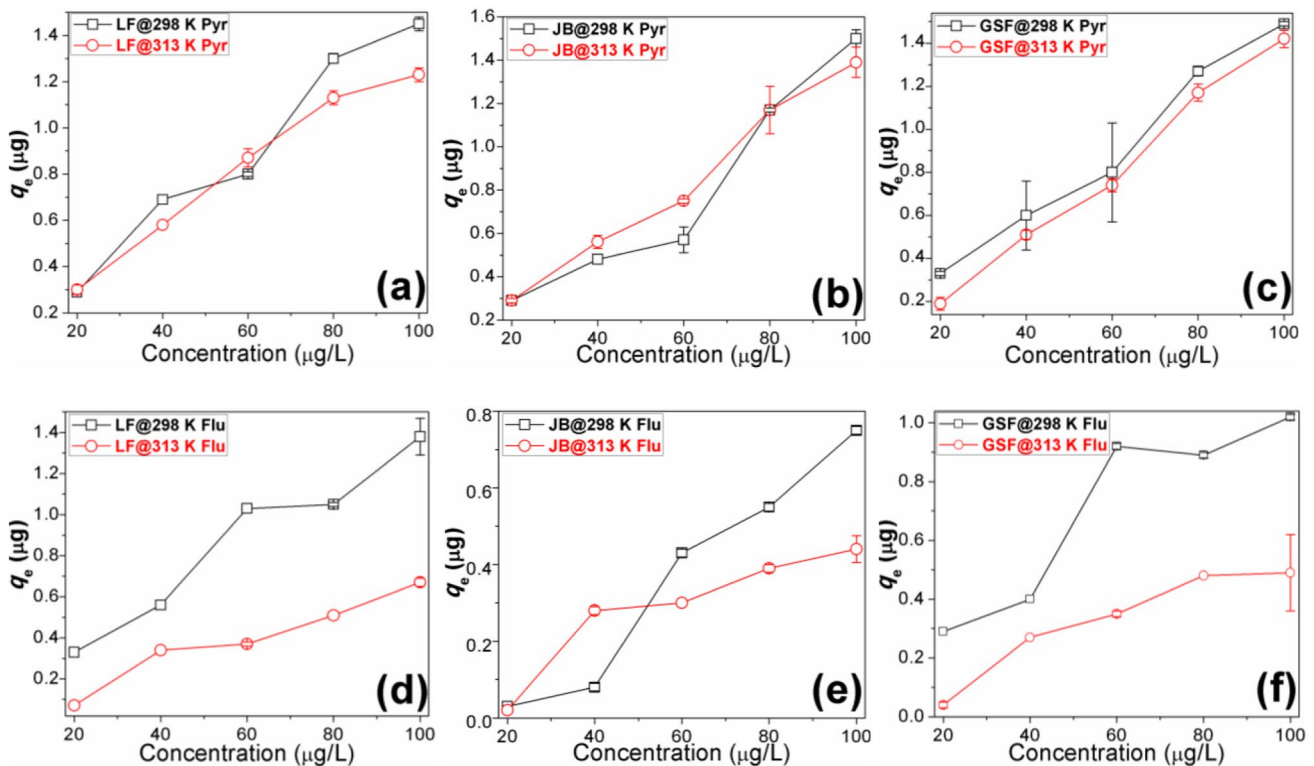

Fig. 3 Sorption trends at varying PAHs concentrations (20–100 µg/L) and temperatures (298 and 313 K) for (**a**) pyrene sorption on LF soil, **b** pyrene sorption on JB soil, **c** pyrene sorption on GSF soil, **d** flu-
orene sorption on LF soil, **e** fluorene sorption on JB soil, and (**f**) fluorene sorption on GSF soil (*Pyr* Pyrene, *Flu* Fluorene, *OMR* organic matter treated soils, *IOR* iron oxides treated soils)
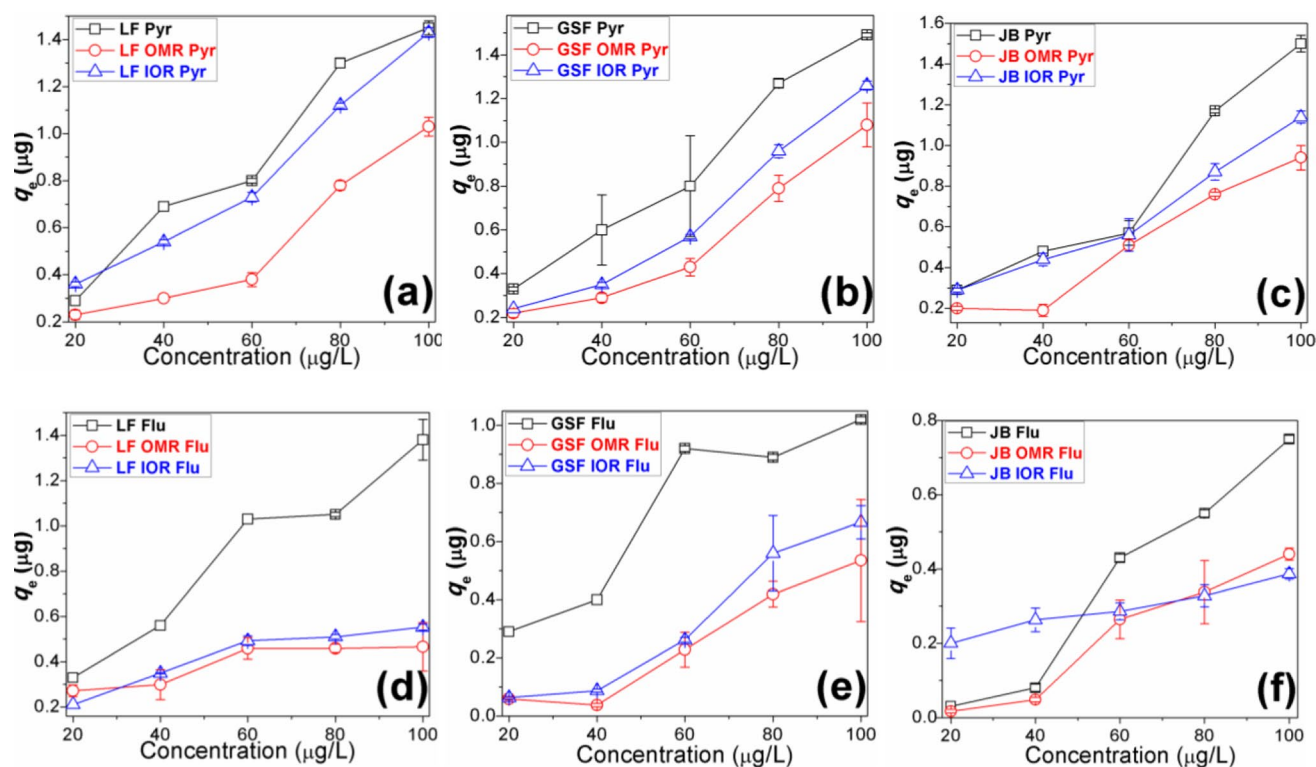
Fig. 4 Comparisons of the equilibrium sorption trends for both PAHs before and after soil treatments at 298 K (**a**) pyrene sorption on LF soil, **b** pyrene sorption on GSF soil, **c** pyrene sorption on JB soil, **d** fluorene sorption on LF soil, **e** fluorene sorption on GSF soil, and **f** fluorene sorption on JB soil (*Pyr* Pyrene, *Flu* Fluorene, *OMR* organic matter treated soils, *IOR* iron oxides treated soils)

and temperature increased from 20 to 100 µg/L and 298 to 313 K, respectively. It was observed that increasing the solution concentration of pyrene for these soils (Fig. 3a–c) resulted in higher sorption of pyrene from solution. Similar trend has been reported for pyrene sorption on soil (Teixeira et al. 2011). Similar trend was also observed for fluorene sorption on these soils (Fig. 3d–f).

Figure 3 also showed that raising the temperature of the soil solution from 298 to 313 K reduced the sorption of pyrene and fluorene (Ping et al. 2006). This suggested that these PAHs sorption is not enhanced by higher temperature. It may also be an indication that the sorption processes are via weak hydrophobic forces which require low energy for sorption, such as π–π interactions and van der Waal's forces. Koyuncu et al. (2011) and Shu et al. (2010) have reported similar reduction in organic pollutants sorption as temperature increased.

The reduced pyrene sorption which occurred as solution temperature increased was not significant throughout the studied concentration range for all soils (Fig. 3a–c). However, higher temperature had negative effect on fluorene sorption (significantly reduced). This negative effect of temperature on fluorene sorption became progressive and significantly higher with fewer soil sorption sites per molecule in solution; thus, the reduced fluorene sorption

was more obvious at higher concentration than at lower concentration. In comparing the differences in pyrene and fluorene sorption as temperature increased, the effect of temperature on these PAHs may be related to their solubility. Fluorene has a higher solubility (1.99 mg/L at 303 K) than pyrene (0.135 mg/L); thus when the solution temperature was raised, the potential for the fluorene molecules to go into solution was higher than that of the pyrene molecules, hence the significant reduction in fluorene when compared to pyrene sorption.

The JB soil exhibited a slight deviation at lower fluorene concentration; increased temperature resulted in higher sorption at low fluorene concentration (Fig. 3e). Though this soil recorded low organic matter content, this observation may be related to the presence of Illite and montmorillonite, 2:1 expansive clays (SM Table 1). Both soil constituents expanded in aqueous solution as temperature increased which resulted in the slightly higher sorption. However, at higher concentration, the pores of the expansive clays become saturated with no corresponding increase in sorption in comparison to sorption at 298 K. The consequent reduction in fluorene sorption at 313 K was ascribed to increased solubility and mobility of fluorene upon increase in temperature. For LF soil with high organic matter content and GSF with high iron oxides and aluminum oxides, this 'expansible
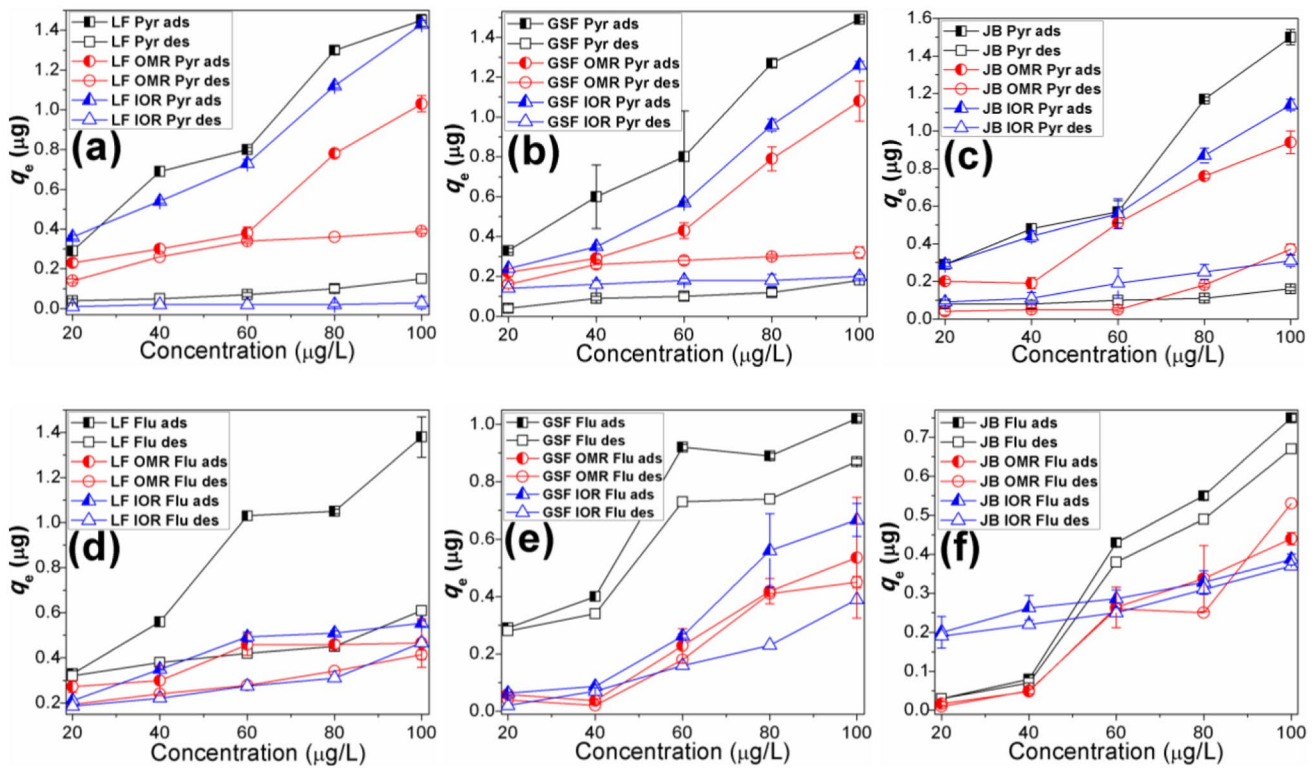
Fig. 5 Comparisons of the equilibrium sorption and desorption trends for both PAHs before and after soil treatments at 298 K (**a**) pyrene sorption and desorption on LF soil, **b** pyrene sorption and desorption on GSF soil, **c** pyrene sorption and desorption on JB soil, **d** fluorene sorption and desorption on LF soil, **e** fluorene sorption and desorption on GSF soil, and (**f**) fluorene sorption and desorption on JB soil (*ads* sorption, *des* desorption, *Pyr* Pyrene, *Flu* Fluorene, *OMR* organic matter treated soils, *IOR* iron oxides treated soils)

clays effect' is masked resulting in lower fluorene sorption at higher temperature.

Pyrene and fluorene sorption on the OMR and IOR treated soils showed similar concentration-dependent sorption trend as the whole soils (Fig. 4a–f). This pyrene and fluorene sorption trend was attributed to the tendency for multi-layer adsorption via π–π interactions to occur on the adsorbate as hydrophobic PAHs concentration increases (Diagboya et al. 2018; Mittal and Rockne, 2009; Olu-Owolabi et al. 2015). There was significant variation in the quantities of PAHs sorbed per soil. The whole soils had higher pyrene and fluorene sorption than the treated soils, while the OMR soils exhibited lower PAHs sorption when compared with the IOR and whole soils; pyrene and fluorene sorption trend is OMR > IOR > whole soils.

Lower pyrene and fluorene sorption on the OMR soils in comparison to the IOR soils is an indication of the contribution of organic matter in the sorption process. The hydrophobic PAHs sorbed on each soil was directly proportional to the quantity of non-polar and/or low-polarity humic substances and other organic matter present in the soil; the lower the polarity, the higher the affinity for pyrene and fluorene. Thus, removal of organic matter from these soils resulted in the lowest sorption of these non-polar/hydrophobic organic

pollutants. Other authors have reported similarly in literature (Guo et al. 2010; Huang et al. 2003).

The deviation observed for the JB OMR soil (Fig. 4f) which exhibited slightly higher fluorene sorption than the JB whole soil at low temperature was attributed to the presence of the 2:1 expansive clays (Illite and montmorillonite) as described above. Soil treatment by removal of organic matter and iron oxides from soils suggested the contributions of these soil constituents to both PAHs sorption: iron oxides contributed < 25% while organic matter contributed ≥ 50% to the sorption process.

Desorption and hysteresis

Desorption studies on both whole and treated soils were carried immediately after the equilibrium sorption experiments, and results are depicted in Fig. 5a–f. Desorption experiments can provide valuable information on the amount of pollutant released back into the environment after the sorption process, as well as the delay in sorption reversal (hysteresis). For soil pollution, hysteresis is desirable because high hysteresis implies lowered chemical reactivity of the pollutant(s) in the environment and consequently lower toxicity (Huang et al. 2003; Olu-Owolabi et al. 2014).

The results (Fig. 5a–f) show that the pyrene and fluorene amounts desorbed from the whole and treated soils were dependent on the quantities initially sorbed as well as proportional to soil constituents. All soils exhibited hysteresis which was attributed to their constituents, such as organic matter; soils with high organic matter content exhibited higher degree of hysteresis. This affirmed the observation that organic matter contributed more to sorption on these soils.

Higher hysteresis was observed for pyrene than fluorene, and this was more obvious in the presence of organic matter as seen in the whole and IOR soils (Fig. 5a–c). The pyrene sorption hysteresis trend is whole > IOR > OMR soils. Though fluorene desorption from these soils exhibited similar trend as pyrene, it had lower hysteresis or very high desorption with the exception of LF (Fig. 5d). For the GSF and JB soils with low organic matter contents, hysteresis was very low for both PAHs, but was more so for fluorene with desorption of almost 90% of the quantity sorbed in the JB soil.

Pyrene had higher sorption and lower desorption than fluorene in all soils. This trend was related to the number of cyclic aromatic rings in the chemical structures of these PAHs; the greater number of aromatic rings in pyrene resulted in a higher number of π–π interactions with other aromatic functionalities with the soils in comparison with fluorene (Diagboya 2015; Mittal and Rockne 2009). It is also believed here that the conjugated spatial arrangement of the fluorene aromatic rings reduces the strength of its π–π interactions with other aromatics, leading to lower sorption and higher desorption (Diagboya 2015; Mittal and Rockne 2009). The main mechanism proposed for these observed PAHs desorption hysteresis is the entrapment of both PAHs within with organic matter and inorganic (such as the expansive clays) matrices resulting in the slow rate of desorption compared with the sorption (Huang et al. 2003; Mittal and Rockne 2009; Site 2001).

The treatments showed the contributions of soil iron oxides and organic matter constituents to retention and desorption of both PAHs. Generally, removal of any of these soil constituents reduced sorption and enhanced sorbed PAHs desorption from these soils. Treated soils exhibited lower hysteresis than the whole soils for both PAHs, and comparatively, the organic matter removed-soils (OMR) had higher desorption or low hysteresis than the iron oxides removed-soils (IOR). The low hysteresis in the low organic matter soils implies easy availability of both PAHs in the soil–water solution and to biota, as well as possible aquifer contamination.

Thermodynamics studies

Thermodynamic parameters were determined to evaluate the energetics and feasibility of the sorption process using the fluorene data, and the calculated parameters are shown in Table 4. The standard free energy ($\Delta G°$) values were negative at both temperatures for both the whole and treated soils. These values implied that the process of sorption on these soils was spontaneous and feasible. The entropy change ($\Delta S°$) values were mainly negative in the whole as well as the treated soils; an indication of the decreases in entropy at the sorption site–solution interface as the sorption process progressed towards equilibrium.

An insight into the strength of interactions associated with the sorption process may be obtained from the enthalpy change ($\Delta H°$) values. From the calculated data, the $\Delta H°$ values ranged from -26.8 to 95.5 kJ mol^{-1} for the whole soils and -88.2 to 108.0 kJ mol^{-1} for the treated soils. The $\Delta H°$ values for several of the soils implied exothermic (negative) processes. These negative $\Delta H°$ values confirmed the exothermic nature of experimental results obtained which implied that increasing the sorption medium temperature would lead to lower amounts of PAHs sorption. However, two soils each from the whole and treated samples (LF, GSF, LF OMR and JB IOR) showed deviations from this exothermic system; these had positive $\Delta H°$ values, indicating endothermic processes requiring heat energy input in contrast to experimental data. Though the data implied that raising temperature would enhance sorption, higher temperature actually increased the fluorene solubility and consequently its mobility in solution. This reasoning is supported by the positive $\Delta S°$ values for these soils which implied increase in entropy of the PAHs molecules in solution. The magnitudes of the $\Delta H°$ values obtained for this study suggested that the interaction forces between fluorene and sorption sites involved weak hydrophobic forces, such as π–π interactions

Table 4 Thermodynamic parameters for the sorption of fluorene on the whole and treated soils

Soil	$\Delta G°$ (kJ mol^{-1})		$\Delta H°$	$\Delta S°$
	298 K	313 K	(kJ mol^{-1})	(kJ mol^{-1} K^{-1})
LF	-6.35	-11.5	95.5	0.34
GSF	-8.73	-13.6	88.9	0.33
JB	-15.5	-14.9	-26.8	-0.04
LF OMR	-5.97	-11.7	108	0.38
GSF OMR	-15.8	-12.2	-88.2	-0.24
JB OMR	-17.1	-17.1	-17.1	0.00
LF IOR	-9.07	-9.28	-5.01	0.01
GSF IOR	-14.7	-10.0	-107	-0.31
JB IOR	-7.37	-9.85	41.8	0.17

between hydrophobic fluorene, and no polar groups at the sorption sites.

Conclusion

Pyrene and fluorene sorption on OM-rich soil are high and nearly instantaneous, but lower with delayed equilibrium on the Fe oxides-rich soils. Relatively, lower amounts of fluorene were sorbed, at slower rates and equilibria. Iron oxides in these soils contributed < 25% to both PAHs sorption while OM contributed ≥ 50%; hence, without OM, soils exhibited slower and lower sorption than without Fe oxides. The presence of Fe oxides masked some sorption sites, thus its removal enhanced sorption. Desorption was dependent on the main contributory soil constituents during sorption; higher OM in soils enhanced the degree of hysteresis or lowered desorption, an affirmation of the contribution of OM to PAHs sorption on these soils. Hysteresis was higher for pyrene than fluorene.

Generally, removal of any of these soil constituents lowered sorption and enhanced PAHs desorption. In these agro-ecological zones, SOM is more influential in these hydrophobic PAHs sorption than iron oxides, while the exothermic nature of sorption implied higher chances of environmental pollution with global warming. Similarly, low hysteresis/ high desorption from low OM soils implied a risk of these PAHs being present in soil water solution, and subsequent contamination of the aquifer.

Higher pyrene sorption and its high hysteresis or low desorption implied its lower chemical reactivity in the environment, and consequently lower toxicity in comparison to fluorene. Ultimately, depletion of SOM and soil iron oxides may lead to increased risks of PAHs in the environment but generally, fluorene is much likely to reach the aquifer faster in warmer and low organic matter soils than in cooler and relatively high organic matter soils.

Declarations

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