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A comparative study of the sorption of O-PAHs and PAHs onto soils to understand their transport in soils and groundwater

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) and their oxygenated derivatives (O-PAHs) are identified in soils and groundwater of industrialized sites and contribute to the risk for Humans and the Environment. Nevertheless, data are scarce in literature concerning their retention and transfer in soils and no soil - water partition coefficients are available for these compounds. Sorption of two PAHs, fluorene and acenaphthene and two O-PAHs, 9H-fluorenone and dibenzofuran onto two soils with different organic carbon contents was evaluated and compared by determining their sorption isotherms. Effect of ionic strength and liquid to solid ratio, on fluorene and fluorenone sorption was also evaluated. Sorption equilibrium is achieved within less than 24 hr of mixing and linear sorption models best fit the isotherm data. Acenaphthene and dibenzofuran are similarly sorbed onto the soil. K_D of fluorene is higher than the one of fluorenone, showing a smaller affinity of fluorenone towards the solid phase. This means that O-PAH could form larger contamination plumes in groundwater than PAHs. Decreasing the L/S ratio from 100 to 50 and 30, increases the sorption of fluorenone onto the soil by 56% and 67% respectively, while the sorption of fluorene is slightly increased. Increasing the ionic strength of the aqueous phase also modifies the sorption of fluorenone, contrary to the sorption of fluorene which is slightly affected.

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) and their hydrogen substituted derivatives such as: O-PAHs, N-PAHs and S-PAHs

are present in the Environment (Achten and Andersson, 2015; Bandowe et al., 2018a, 2018b). Incomplete combustion of fossil fuel, biomass and biofuel is mainly responsible for the formation and release of PAHs/derivatives PAHs into the environment (Achten and Andersson, 2015; Alves et al., 2017; Bandowe et al., 2018a; Lundstedt et al., 2007). PAHs, which are frequently encountered in the environment, represent the most commonly known category among these compounds,

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due to their documented persistence, toxicity and bioaccumulation (Abdel-Shafy and Mansour, 2016; Beesley et al., 2010; Lundstedt et al., 2007; Wilcke, 2000). Since 1976, the US EPA listed 16 PAHs as priority pollutants, based on available analytical techniques, their occurrence in the environment and their hazardous properties (Keith, 2015). These PAHs are used, by scientists, as a representative of all non-polar molecules (Andersson and Achten, 2015); this list served as a crucial support over the past decades towards assessing the risk for Humans and the Environment imposed by PAHs contaminated sites. Nevertheless, this list emphasizes only non-polar compounds, ignoring the more hydrophilic and mobile polar fraction (Andersson and Achten, 2015). Many studies highlighted the presence of polar derivative PAHs at significant concentrations in soils contaminated with PAHs (Alves et al., 2017; Lundstedt et al., 2014; Musa Bandowe et al., 2011; Sun et al., 2017; Wei et al., 2015). Among this polar fraction, O-PAHs are of emerging concern in the Environment (Bandowe et al., 2018a; Idowu et al., 2019; Lundstedt et al., 2007; Wilcke et al., 2014). Indeed, these O-PAHs are found in the same pollution sources than PAHs, such as coal tar and creosote (Lemieux et al., 2009; Lundstedt et al., 2007, 2003), or in urban soils (Dreij et al., 2020; Yadav and Devi, 2021; Zdráhal et al., 2000). They are as well found in groundwater of sites contaminated by coal tar or creosote (Johansen et al., 1997; Pereira et al., 1987; Schlanges et al., 2008). Moreover, O-PAHs can be produced through photochemical (Vione et al., 2006), thermochemical and biological oxidation reactions of PAHs (Bandowe et al., 2018a; Idowu et al., 2019; Lemieux et al., 2008; Lundstedt et al., 2007). Some O-PAHs were measured at concentrations higher than the ones of their parent PAHs in some soils. Consequently, O-PAHs are sometimes regarded as strong persistent dead-end transformation products of their parent PAHs (Idowu et al., 2019; Layshock et al., 2010; Lundstedt et al., 2007). For instance, the half-lives of dibenzofuran under natural attenuation were shown to be close to the ones of naphthalene in two contaminated sites (Blum et al., 2011).

Over the past two decades, global concerns began to raise regarding underestimated toxicological effects of O-PAHs in the environment (Andersson and Achten, 2015; Idowu et al., 2019; Witter and Nguyen, 2016), especially because most remediation methods by oxidation processes applied in PAH-contaminated sites promote their formation (Abdel-Shafy and Mansour, 2016; Achten and Andersson, 2015; Lundstedt, 2003; Lundstedt et al., 2006, 2003). However, despite the different analysis techniques available at laboratory scale for these compounds to identify and quantify them in water, soils or Particulate Matter in the atmosphere (PM) (Walgraeve et al., 2010), O-PAHs are not yet included in monitoring programs or risk assessment studies of PAHs contaminated sites. In France, this could be due to the unavailability of standardized methods for their analysis in groundwater and soils by private laboratories, with prices and time frame compatible with polluted site and soil studies done by consulting companies and consistent with the polluted site and soil methodology where an extraction on the total water sample is mandatory. Pulleyblank et al. (2019) already pointed out the lack of standardized methods and compared five different

extraction techniques from contaminated soils and waters. The development of such a method to get the total amount of pollutants (dissolved, colloids and particles) have been done recently for French risk assessment (Trouvé et al., 2021). Besides, there is a lack of knowledge on the behavior of O-PAHs in soils. Nevertheless, analyses of O-PAHs and PAHs in soils at different depths were conducted at the field scale. Results showed a preferential transfer of O-PAHs over PAHs in these soils (Bandowe et al., 2018a; Musa Bandowe et al., 2011; Wilcke et al., 2014). At this scale, non-polar compounds were found close to the pollution sources in groundwater whereas the more polar compounds were detected downstream these sources, showing a preferential transfer of O-PAHs in groundwater compared to PAHs (Schlangles et al., 2008). Therefore, O-PAHs can form large groundwater contamination plumes (Johansen et al., 1997; Pereira et al., 1987; Zamfirescu and Grathwohl, 2001).

Among the processes influencing the fate and transport of organic pollutants in soil, sorption is known to be crucial (Lemière et al., 2001). Therefore, given all these concerning properties of O-PAHs coupled to their potential toxicity (IARC, 1984; Idowu et al., 2019; Lundstedt et al., 2007), it becomes necessary to understand their retention and release in soils, along with the physical and chemical parameters and the underlying mechanisms responsible for their fate and transport in soil and groundwater. Given that PAHs sorption onto soil is affected by parameters such as: organic matter content, particle size and surface area, compound solubility, ionic strength, temperature, pH, contact time and pollution age (Lamichhane et al., 2016; Lemière et al., 2001), an evaluation of the effect of such parameters on the sorption of O-PAHs would be an adequate starting point in order to meet these desired objectives. Nevertheless, research is scarce in literature on this subject; many papers only presumed that they can be preferentially released and transferred in soils compared to PAHs, regarding their physical and chemical properties, and particularly their polarity (Achten and Andersson, 2015; Idowu et al., 2019; Meyer et al., 1999; Yu, 2002). Experiments conducted at the laboratory scale in order to confirm this hypothesis are uncommon in literature (Lundstedt et al., 2007; Weigand et al., 2002, 1999). Some studies deal with O-PAHs release from contaminated soils (Arp et al., 2014). But to date, no soil/water partitioning coefficients are available for O-PAHs and parameters responsible for their sorption in soils containing very low concentration of pollutants (<1 mg/kg of PAH) have not been investigated; nevertheless, this knowledge is a first step in the characterization process of their sorption in soils and their transfer in groundwater. Thus, in this article, sorption onto two non-polluted soils with different organic matter contents of two PAH/O-PAH couples (fluorene / 9H fluorenone and acenaphthene / dibenzofuran) was evaluated and compared using batch equilibrium method. Effect of two experimental parameters on sorption of one PAH/O-PAH couple (fluorene / 9H fluorenone) onto one soil was further investigated: liquid to solid ratio and ionic strength. The originality of this work mainly focuses on O-PAHs since data regarding these organic micro-pollutants, particularly kinetic and isotherm models of their sorption onto non contaminated soils, are not yet abundant in literature.

1. Materials and methods

1.1. Reagents and chemicals

Dibenzofuran was chosen because it is one of the most abundant O-PAHs in groundwater of sites contaminated with PAHs (Ren et al., 2021; Trouvé et al., 2021). The corresponding PAH in terms of molecular composition is acenaphthene. Other authors showed that fluorenone is abundant in soils (Idowu et al., 2019; Musa Bandowe et al., 2011; Obrist et al., 2015). Given its contrasted solubility comparing to dibenzofuran, this O-PAH was also chosen, as well as its parent PAH (fluorene).

Acenaphthene (ACE) and dibenzofuran (DBFUR) were both purchased from Alfa Aesar (Germany) with purity of 97% and 98%, respectively. Fluorene (FLU) and 9H-fluorenone (FLUone) were purchased from Acros Organics (South Africa) with both purity of 98% and 99+%. Individual standard solutions (1 g PAH/O-PAH/L) were prepared by dissolving an appropriate amount of the purchased solids in methanol (Acros Organics, South Africa, 99.9%). All solutions were kept in amber bottles at 4°C to avoid exposure to light prior to use. Acetone (Acros Organics, South Africa, 99.9+%) was used for cleaning purposes. The physico-chemical properties of these compounds were given in **Appendix A Table S1**.

Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99+%) and sodium azide (NaN_3 , 99+%) were obtained from Fisher Scientific, United Kingdom. Background solutions were prepared by dissolving appropriate amounts of the latter two salts in MilliQ-UV ultrapure water (PURELAB Option, ELGA, United Kingdom). NaN_3 was used as an inhibitor of microbial growth and activity during the experiments. CaCl_2 was used to adjust the ionic strength of the background solutions. The working solutions were prepared by diluting an appropriate volume of the earlier prepared PAH/O-PAH standard solutions, in the background solution.

1.2. Soil collection and characterization

Two soils were studied (Soils A and B). Soil A was sampled from the upper horizon (0–30 cm) of a close protection perimeter of a drinking water well in France. Soil B was sampled from the upper horizon of a non-contaminated zone near a former gasworks site in Switzerland. Both soils were dried at room temperature, then sieved through a 2 mm stainless steel mesh prior to use. The sampling sites were chosen to reflect the variability in soil properties, particularly the organic matter content and the carbon to nitrogen ratio (from analyses performed by INRA, Arras-France) according to National and European standards (AFNOR a to g). Data are detailed in **Table 1**.

The analysis of the 16 PAHs and 11 O-PAHs was previously performed by GC/MS after extraction in ASE (Accelerated Solvent Extraction). The total amount measured of PAHs and O-PAHs were equal to 1 and 6 mg/kg earth, respectively for soils A and B. These values verify the absence of contamination of the soil by these compounds in comparison with sites polluted by PAHs where the concentration can reach more than 10,000 mg/kg earth (Lundstedt et al., 2003). This soil can therefore be used in this research to address the objective of understand-

Table 1 – Soil composition.

Composition(g/kg)	Soil A	Soil B	Method
Clay (< 2 µm)	277	136	NF X 31-107
Fine silt (2/20 µm)	291	133	NF X 31-107
Coarse silt (20/50 µm)	331	100	NF X 31-107
Fine sand (50/200 µm)	67	266	NF X 31-107
Coarse sand (200/2000 µm)	34	365	NF X 31-107
Organic carbon	64.2	23.4	NF ISO 10693
Total nitrogen	4.4	3.32	NF ISO 13878
Total limestone	9	99	NF ISO 10693
Organic matter	111	40.4	NF ISO 14235
Carbon to Nitrogen ratio (C/N)	14.7	7.04	NF ISO 10694/ NF ISO 13878
pH	7.6	7.8	NF ISO 10390
Cation exchange capacityw (cmol+/kg)	25	16.5	NF ISO 23470

ing the transfer of O-PAHs into uncontaminated soil after release from a pollution source.

Both soils have neutral pH and low clay content. Soil A is mainly composed of silts (62 wt.%) with a low limestone content. On the other hand, sand makes up the majority of soil B texture (63 wt.%) having about ten times more limestone content than soil A. However, the organic carbon content is relatively low for both soils, accounting for 6.42 wt.% and 2.34 wt.% for soil A and B, respectively. Furthermore, the dissimilarity in carbon to nitrogen ratio between the two soils (14.7 and 7.04 for soil A and B, respectively) indicates a varying degree of organic matter decomposition and, hence, highlights the difference in organic matter content and its composition (Tan, 2014).

1.3. Analysis

Quantitative analysis of PAH/O-PAH concentration in solutions was performed after filtration in triplicates. The liquid supernatant was analyzed in a high precision quartz cell (Hellma Analytics, Germany) using a fluorescence spectrophotometer (F-2700, Hitachi, Japan) equipped with a 150 W Xenon lamp and a monochromatic light monitoring ratio calculation photometric principle. Considering the various fluorescence properties of each individual PAH/O-PAH, the wavelength program of the fluorescence detector ($\lambda_{\text{ex}}/\lambda_{\text{em}}$) and the corresponding linearity ranges were set as follows: 262/302 nm for FLU (0.5–500 µg/L), 262/306 nm for FLUone (100–3000 µg/L), 280/320 nm for ACE (1–1000 µg/L) and 278/314 nm for DBDUR (5–600 µg/L). Solutions having higher PAH/O-PAH concentration that the one of the upper limit of the calibration range, were diluted accordingly.

1.4. Sorption experiments

Individual PAH/O-PAH sorption from aqueous solution onto soils was performed using the batch equilibrium technique (Kalbe et al., 2008; Organisation for Economic Co-operation and Development, 2000). All experiments were conducted in triplicate in 125 mL glass vials sealed with screw caps equipped with Teflon-lined septa at a temperature of $(21 \pm 2)^\circ\text{C}$. The amount of soil added to each vial (3, 1.8 and 0.9 g)

Table 2 – Experimental conditions of the sorption experiments.

	Soil	L/S	C _{Ca} (mmol/L)	NaN ₃ concentration (g/L)
Influence of L/S ratio	A ^a	50	2 ^b	0.2
		30	2 ^b	0.2
Influence of ionic	A ^c	100 ^b	20	0.2
		100 ^b	100	0.2

^a Studies carried out on FLU, FLUone, ACE and DBFUR;
^b Bold characters correspond to experiments performed in reference conditions;
^c Studies carried out only on FLU and FLUone.

was adapted in order to obtain the appropriate liquid to solid ratio (L/S of 30, 50 and 100 L/kg respectively) while keeping 90 mL as the total volume of the aqueous phase. Experiments were also performed with different background solutions (2, 20 and 100 mmol/L of CaCl₂ with 0.2 g/L of NaN₃). Experimental conditions are summarized in Table 2. The following combination of experimental parameters was chosen as reference conditions: L/S ratio of 100, 0.2 g/L of NaN₃ and 2 mmol/L of (CaCl₂) abridged to C_{Ca}, for the background solution. Experiments were performed three times and results are given as means in Tables and Figures with the standard deviations.

Prior to experiments, a conditioning step of the soil was performed: 10 mL of the background solution were added to the soil and shaken during 1 hr at 10 r/min in an overhead shaker (Heidolph, Reax 20, Germany), in order to moisten the dry soil and prevent experimental artifacts (Vessigaud, 2007). Then 80 mL of the appropriate solution were added to the vial and mixed in order to reach the equilibrium time using the same apparatus. When the percentage of sorption is achieved being constant, equilibrium was reached. For all experiments, the suspension was then filtered through glass fiber filters with pore size of 0.7 μm (Fisherbrand, Fisher Scientific, United Kingdom). Simultaneously, blank vials containing PAH/O-PAHs solution in the absence of soil and control vials containing background solution and soil in the absence of the studied PAH/O-PAHs, underwent the same procedure to account for potential losses due to photolysis or wall adsorption, and to evaluate the leaching of organic matter initially present in the dry soil, into the aqueous phase. PAHs/O-PAHs concentrations in the supernatant were then determined with a fluorescence spectrophotometer and the amounts of sorbed PAH/O-PAHs were calculated according to Eq. (1):

$$q_t = \frac{V}{M} (C_0 - C_t) \quad (1)$$

where, q_t (μg/kg) is the mass concentration of sorbed solute at time t (hr), V (L) the volume of solution, M (kg) the mass of soil, C_0 (μg/L) the initial solute concentration of PAH/O-PAH and C_t (μg/L) the solute concentration at time t . t (hr) is the equilibrium time.

1.4.1. Sorption kinetic experiments

Preliminary experiments were performed to determine the equilibrium time for each experimental condition. The study

consisted of monitoring the PAH/O-PAH aqueous phase concentration along all the experiment (up to 72 hr). After the conditioning step presented previously, glass vials were filled with the appropriate amount of soil and 80 mL of the background solution containing each PAH/O-PAH at the following concentrations: 500 μg/L for fluorene (FLU) and dibenzofuran (DBFUR); 1000 μg/L for acenaphthene (ACE) and 10,000 μg/L for fluorenone (FLUone). These different initial concentrations were chosen according to the solubility of the compound and the expected remaining amount in solution after the sorption process. When initial PAH/O-PAH concentrations and PAH/O-PAH concentrations in solution after sorption were higher than the upper limit of the fluorescence spectrophotometer linearity range, the solutions were diluted in order to be in the linearity range. These vials were shaken at 10 r/min in an overhead shaker (Reax 20, Heidolph, Germany) at room temperature (21±2°C). For FLUone, a high concentration was used to ensure high signals during measurements of its concentrations by fluorimetry given the fact that FLUone fluorescence emission is weaker. The concentration of PAH/O-PAH was measured along the sorption experiment at seven different times: 1, 4, 16, 20, 24, 48 and 72 hr. The results of the kinetic studies are presented as the percentage of sorbed PAH/O-PAH with respect to mixing time.

1.4.2. Sorption isotherm experiments

Sorption isotherm experiments were carried out in order to evaluate the interactions of the studied PAH/O-PAH with the soil and the aqueous phase. Sorption isotherms were determined using the experimental protocol detailed in Section 2.4. Initial aqueous concentrations of PAH/O-PAHs were within the following ranges: FLU = 15–1500 μg/L; ACE = 50–3500 μg/L; DBFUR = 50–2800 μg/L; FLUone = 3000–23,000 μg/L.

2. Results and discussion

2.1. Sorption of PAHs/O-PAHs in reference conditions

2.1.1. Sorption kinetics

Fig. 1 illustrates the sorption percentage evolution of the four PAHs/O-PAHs versus time during the sorption kinetic experiments carried out in reference conditions onto soils A and B.

As depicted in this figure, the four PAHs/O-PAHs exhibit a two-stage sorption process onto both soils, that can be explained as follows: a first stage occurring within the first hour of contact and corresponding to a fast sorption of PAHs/O-PAHs onto the more accessible sites within the soil matrix followed by a second much slower stage during which sorption steadily increases before reaching equilibrium steady state condition within less than 24 hr of mixing. At equilibrium, PAH/O-PAH sorption is constant, and no significant desorption nor degradation are recorded. In the light of these results, the equilibrium time was fixed at 24 hr of mixing. These observations can be explained as follows: initially, sorption sites are abundant which favors the interaction with the PAHs/O-PAHs and makes their sorption easier. This sorption is favored by the high concentration difference between the bulk solution and the solid liquid interface. This leads to higher sorption rates observed within the first hour of contact. Afterwards,

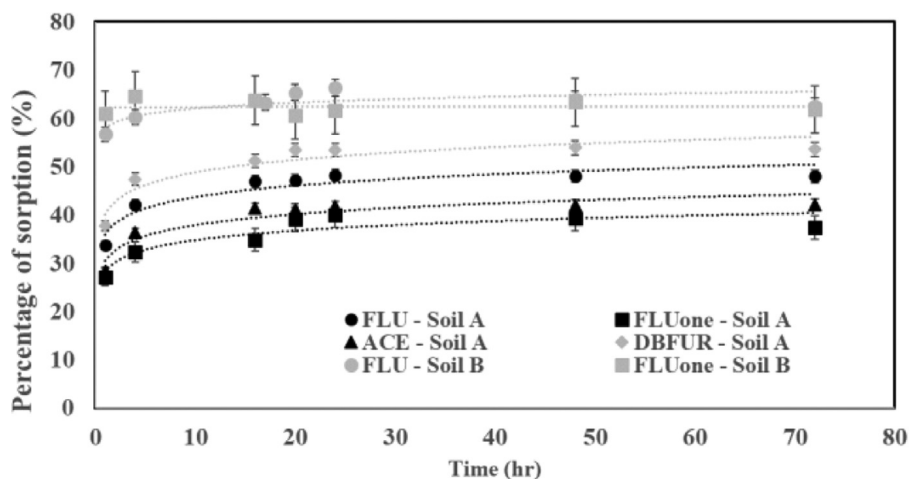


Fig. 1 – Sorption kinetics of PAHs/O-PAHs onto soils A and B in reference conditions: $C_{ACE(0)} = 1000 \mu\text{g/L}$, $C_{DBFUR(0)} = 500 \mu\text{g/L}$, $C_{FLU(0)} = 500 \mu\text{g/L}$, $C_{FLUone(0)} = 10,000 \mu\text{g/L}$.

Table 3 – Coefficients of sorption kinetics in reference conditions for FLU, FLUone, ACE and DBFUR onto soil A and for FLU and FLUone onto soil B (L/S 100; C_{Ca} 2 mmol/L).

PAH/O-PAH	Soil	1 st order				2 nd order			
		Exp. $q_e (\times 10^{-3} \mu\text{g/kg})$	Cal. $q_e (\times 10^{-3} \mu\text{g/kg})$	$k_1 (\text{hr}^{-1})$	R^2	Cal. $q_e (\times 10^{-3} \mu\text{g/kg})$	$k_2 (\times 10^5 \mu\text{g}/(\text{kg}\cdot\text{hr}))$	R^2	
FLU	A	23	7	0.14	0.969	23	10	0.999	
	B	27	4	0.10	0.876	26	-11	0.999	
FLUone	A	360	130	0.08	0.328	350	0.14	0.974	
	B	560	27	0.02	0.071	540	-4.4	0.999	
ACE	A	35	11	0.18	0.911	35	51	0.999	
DBFUR	A	24	13	0.32	0.711	25	9	0.999	

Exp. q_e : experimental value of q_e ; Cal. q_e : model’s calculated value of q_e .

sorption is slowed down due to the occupation of the surface sites and probably by the presence of diffusional limitations within the particles of soil. Nevertheless, at this stage, the relative importance of these mechanisms for PAHs and O-PAHs cannot be determined.

In order to study the mechanism of the sorption process, kinetic experimental data are fitted to pseudo-first order and pseudo-second order kinetic models following the equations below:

$$\text{First order} \quad q_t = q_e (1 - e^{-k_1 t}) \quad (2)$$

$$\text{Second order} \quad q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (3)$$

where, q_t ($\mu\text{g/kg}$) and q_e ($\mu\text{g/kg}$) are the amount of sorbed solute per mass of soil at any time and at equilibrium, respectively; k_1 (hr^{-1}) and k_2 (hr^{-1}) are the rate constants of the first-order and second-order sorption models. q_e , k_1 and k_2 , for first and second order models, are evaluated from the slope and the intercept of the straight-line plot of $\ln(q_e - q_t)$ against t , and the plot of t/q_t against t , respectively (Kowanga et al., 2016; Lagergren, 1898). Results are summarized in Table 3.

The second order model best fits with experimental data for all PAHs/O-PAHs and for both soils with correlation coef-

ficients (R^2) ranging from 0.974 to 0.999, compared with the first order model with R^2 values ranging from 0.071 to 0.969. In addition, experimental q_e values estimated using the second-order kinetic model are similar to those experimentally obtained. The small deviations observed in q_e values have been attributed to the uncertainties inherent in obtaining the calculated q_e values.

Similar two-stage sorption phenomenon and 24 hr equilibrium time were found in literature regarding FLU sorption onto soils having Soil Organic Matter (SOM) values ranging from 4.68% to 5.29%, neutral pH values and sandy soil texture. Experiments were conducted at a L/S value of 20 and initial FLU aqueous concentration of 100 $\mu\text{g/L}$ (Olu-Owolabi et al., 2015). In addition, Javier Rivas et al. (2008) performed kinetic sorption experiments of ACE onto a soil having an organic matter fraction of 3.2% with L/S values ranging from 250 to 2000; kinetic studies showed a two-stage sorption phenomenon that 56% to 85% of ACE was sorbed onto soil within 60 minutes of contact and with an initial aqueous concentration ranging from 0.89 to 2.8 mg/L. In addition, these authors showed that sorption onto soil at different L/S values followed a two-stage process similar to our results; however, equilibrium was achieved faster (Javier Rivas et al., 2008). This could be attributed to the differences in L/S values between the two studies.

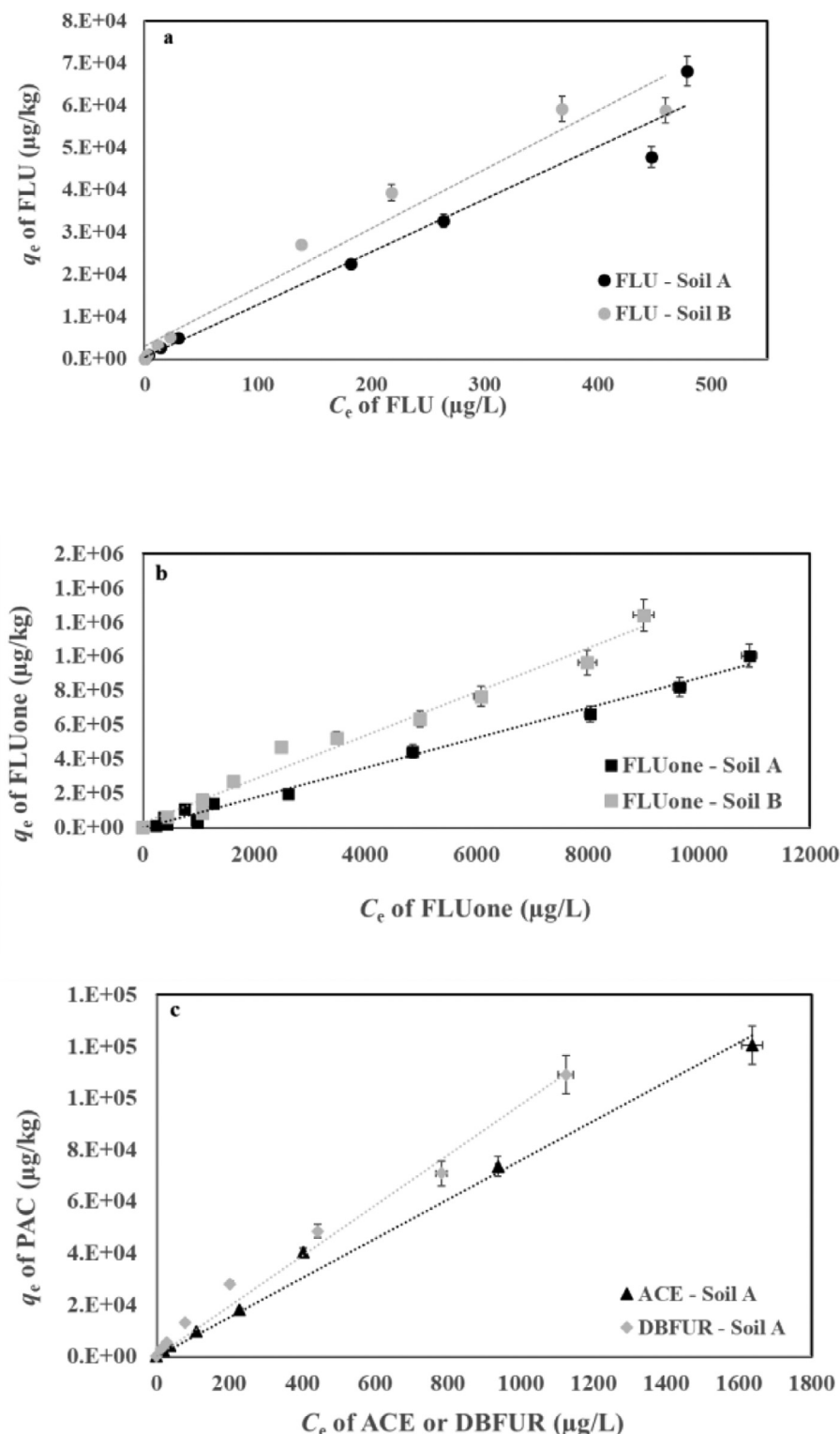


Fig. 2 – Sorption isotherms at equilibrium in reference conditions onto soils A and B for FLU (a), FLUone (b) and ACE/DBFUR (c).

2.1.2. Sorption isotherms

Isotherms of individual compounds in the same conditions for both soils were determined. They are presented in Fig. 2.

As illustrated, PAH/O-PAH sorption is concentration dependent and increases with the increase of concentration. Isotherm experimental data were fitted to three mathematical

models using the equations below Eqs. (4)-(6). Furthermore, PAH sorption onto soils is generally considered as a linear partitioning between soil water (dissolved organic matter) and soil organic matter (Karickhoff et al., 1979). Therefore, correlations relating the partitioning of PAHs in soil-water systems to soil organic carbon content (f_{oc}) have been pre-

Table 4 – Summary of Linear and Freundlich sorption parameters for sorption of PAHs/O-PAHs onto both soils A and B in reference condition (L/S 100; C_{cal} 2 mmol/L).

Model		Soil	FLU	FLUone	ACE	DBFUR
Linear	K _D (L/kg)	A	130 ± 7	90 ± 7	80 ± 6	90 ± 8
		B	150 ± 8	130 ± 12	-	-
	R ²	A	0.969	0.989	0.989	0.984
		B	0.955	0.973	-	-
Freundlich	K _{OC} (L/kg)	A	2000 ± 100	1400 ± 100	1200 ± 90	1500 ± 200
		B	600 ± 300	500 ± 500	-	-
	K _F	A	300	36	130	370
		B	480	124	-	-
n	A	1.18	0.91	1.08	1.25	
	B	1.25	0.99	-	-	
R ²	A	0.996	0.886	0.996	0.997	
	B	0.996	0.951	-	-	

–: Experiments with ACE and DBFUR were not performed onto soil B

viously reported (Adeola and Forbes, 2021; Ahangar, 2010; He et al., 1995; Javier Rivas et al., 2008; Olu-Owolabi et al., 2015; Walter et al., 2000). In order to evaluate this relation, the soil - water organic carbon partition coefficients (K_{OC}) were calculated as well using Eq. (7) (Karickhoff et al., 1979) and are presented in Table 4.

$$\text{Linear} \quad q_e = K_D C_e \quad (4)$$

$$\text{Freundlich} \quad q_e = K_F C_e^{1/n} \quad (5)$$

$$\text{Langmuir} \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$K_{OC} = \frac{K_D}{f_{OC}} \quad (7)$$

where, q_e (µg/kg) is the amount of sorbed PAH/O-PAH per mass of soil, C_e (µg/L) is the equilibrium aqueous concentration of the PAH/O-PAH; K_D (L/kg) is the sorption distribution coefficient for linear model calculated from the slope of the isotherm plot (Limousin et al., 2007); K_F is Freundlich distribution coefficient and n is an empirical constant used as an indicator of site energy heterogeneity. Linear model represents a special case of the Freundlich model when n is equal to unity. The values of isotherm constants are evaluated from the intercept and the slope of the linear plot of log(q_e) versus log(C_e) (Freundlich, 1907); q_m (µg/kg) is the Langmuir maximum sorption capacity and K_L (L/µg) is a constant corresponding to solute-sorbent surface interaction. The values of q_m and K_L can be determined from the linear plot of C_e/q_e versus C_e (Langmuir, 1918). The results obtained from the Langmuir model are given in Appendix A Table S2.

As shown in Appendix A Table S2, the low correlation coefficients (R²) ranging from 0.1 to 0.8 indicate that the Langmuir model cannot describe the sorption of the four PAHs/O-PAHs onto any soil. This result was expected considering that the soils are very heterogeneous and PAHs/O-PAHs sorption onto the sites cannot be described by a monolayer formation as this model suggests. On the other hand, linear sorption

model shows the best fit to the experimental data obtained for both PAHs and O-PAHs regarding the sorption onto both soils over the studied PAH/O-PAH concentration ranges with R² values ranging from 0.955 to 0.989. This linearity is further confirmed by the constant n of the Freundlich model, showing values close to unity (1.08 – 1.25). These results are comparable with the linear sorption mechanism of PAHs found in the literature (Karickhoff et al., 1979; Lamichhane et al., 2016; Limousin et al., 2007). K_{OC} values for the four PAHs/O-PAHs were estimated using Eq. (7). Besides, experimental K_{OC} values were compared with the values estimated by the correlation shown in Eq. (8) and using the parameters relative to PAHs proposed by Karickhoff (a = 0.9 and b = -0.346).

$$\log K_{OC} = a \log K_{OW} + b \quad (8)$$

where, K_{ow} represents the octanol-water partition coefficient.

For instance, calculated K_{oc} of FLU in this study (2000 L/kg for soil A) is of the same order of magnitude as the one predicted using Eq. (8): 2600 L/kg with a logK_{OW} of 4.18 (Lundstedt et al., 2007). For soil B, K_{oc} is higher (6400 L/kg) which still stays in the same order of magnitude. This result confirms that soil organic matter is mainly responsible for PAH sorption onto soils. Nevertheless, FLU sorption onto soil B (f_{OC} = 2.34%; C/N = 14.7) is stronger compared to the one onto soil A (f_{OC} = 6.42%; C/N = 7.07). This result could be attributed to the degree of non-polar character (polarity) and composition of SOM affecting their hydrophobic interactions with FLU, which control its sorption onto soils. The higher the polarity, the lower the affinity for hydrophobic PAHs (Delle Site, 2001; Guo et al., 2010; Hwang et al., 2003; Ukalska-Jaruga et al., 2019). In addition, it is suggested that clay minerals also contribute to the sorption of hydrophobic PAHs onto soil having low organic matter content (Cao et al., 2008). K_{oc} calculation relies on the fact that organic matter structures and compositions have no influence on its reactivity (Means, 1998). Nevertheless, these different soil samples are characterized by different compositions, structures and origins of soil organic matter. In this way, some authors consider that soil organic matter is an heterogeneous medium composed of two amorphous domains: expanded and condensed domains (Gunasekara et al., 2003;

Gunasekara and Xing, 2003; Huang and Weber, 1997; Kohl and Rice, 1999; Ukalska-Jaruga et al., 2019; Xing et al., 1996). In expanded domain of organic matter, sorption is linear, fast, reversible and due to partitioning, whereas in condensed domain of organic matter, sorption is not linear, slowed and not reversible, with a sorption due to partitioning and adsorption (Luthy et al., 1997; Weber et al., 2001).

Abdul and Gibson studied FLU sorption at 22°C onto two sandy soils having f_{OC} values of 0.2% ($L/S = 3$) and 1.87% ($L/S = 30$) (Abdul and Gibson, 1986). The sorption isotherms fitted to the linear model with K_{OC} values of 2400 and 3260 L/kg, respectively. The soil - water organic carbon partition coefficient K_{OC} of FLU in this study (Table 4) is slightly lower than the value obtained by Abdul and Gibson but is still of the same order of magnitude, meaning that soil organic matter content is the main parameter explaining PAH sorption onto soils.

In these experimental conditions, FLUone exhibits a distinct behavior in the soil-water system compared to FLU. The partition coefficients of FLUone are 30% and 13% lower than the ones calculated for FLU for soil A and B, respectively. Hence, FLUone expressed a lower affinity for the soil matrix than FLU. Compared to FLU, the amount of FLUone in the aqueous phase of the soil is higher in such a system, thus this O-PAH could have the ability to be more easily transferred than FLU within the soil system. This result is consistent with the different solubility in water between FLU and FLUone, 1.69 and 25.30 mg/L, respectively. Furthermore, FLUone sorption onto soil B ($K_D = 130$ L/kg) is found to be stronger by 44% than the one onto soil A ($K_D = 90$ L/kg). This behavior has to be compared to the increase of 15% in FLU sorption between the two soils (130 and 150 L/kg for soil A and B, respectively). A distinct behavior between the O-PAH and its parent PAH, highlights that different mechanisms are taking place during sorption of the two compounds. Furthermore, these results highlight the minor impact of the SOM on the sorption of FLUone compared to the sorption of FLU, which is known to be controlled by a partitioning between SOM and DOM. This mechanism is probably not the main one controlling FLUone sorption onto soils.

On the other hand, taking into consideration the analytical uncertainties (Table 4) estimated in the values of K_D for ACE and DBFUR and regarding their isotherms for soil A presented in Fig. 2c, it can be highlighted that these compounds display analogous sorption behaviors onto the soil in the studied experimental conditions. This result is compatible with the relatively close values of water solubility of these two compounds, 3.90 and 3.10 mg/L for ACE and DBFUR, respectively. These first results on O-PAHs sorption onto soils, indicate that the solubility of O-PAHs could be an important parameter (among others) influencing their behavior in soils. Besides, the predicted K_{OC} value for ACE ($\log K_{OW} = 3.92$) using Eq. (8) is 1500 L/kg, which is very close to the one obtained experimentally in this study (1200 L/kg). Furthermore, non-linear sorption model was found to be a representative fit for the experimental data observed by Rivas et al. (2008) for ACE. These authors carried out sorption experiments at ambient temperature on the smallest fraction of soil particles (soil samples with a particle size distribution below 1.25 mm) with initial aqueous concentrations within the range of 0.89 to 2.8 mg/L and values of L/S ranging from 250 to 2000. The isotherm was linear for C_e values

lower than 0.7 mg/L, followed by a concave evolution during which ACE sorption was favored onto soil for C_e values within the range of 0.7 – 1 mg/L. This behavior was attributed to the trapping of ACE by the limited fraction of SOM released into the aqueous phase when contacted with the soil at low concentration of ACE in solution. In contrast, our study employs a higher concentration of soil (i.e., lower L/S ratios); thus, soil sorption sites are abundant and SOM trapping of ACE in the aqueous phase is limited.

2.2. Effect of the L/S ratio on the FLU/FLUone sorption kinetics and isotherms

An isotherm behavior is strongly dependent on the operational conditions and methods used during the experimental study (Limousin et al., 2007). Indeed, any change in experimental conditions may affect the processes controlling PAHs/O-PAHs sorption in a soil - water system, such as the ratio of the two phases, L/S (Schweich and Sardin, 1981). For this study, the L/S ratio was set to 30, 50 and 100 and only soil A was used. Kinetic constants are given in Appendix A Table S3.

Kinetic experiments were carried out in order to determine the minimum amount of time required to reach the steady state conditions. The results for FLUone are presented in Fig. 3. For FLU, the influence of the L/S ratio on kinetics is given in Appendix A Fig. S1. Despite the different initial concentration for the two molecules, the influence of the L/S ratio gives similar kinetic curves for the two compounds.

Sorption onto soil A of both FLU and FLUone and for all values of L/S , follows a two-stage sorption phenomenon like the one observed in the reference conditions. Moreover, experimental data derived from experiments carried out at L/S ratios of 30 and 50, are similar for both PAH/O-PAHs. The decrease by a factor 2 of the L/S ratio (from 100 to 50) leads to a significant increase of the sorption percentage for both molecules. From $L/S = 50$ to $L/S = 30$, the sorption is increased again but as regard to standard deviation, this phenomenon is very low. Equilibrium conditions are reached within less than 24 hr. Results (Appendix A Table S3) show that the pseudo-second order kinetic model fits better than the pseudo-first order model for FLU and FLUone sorption. It is observed that the estimated model sorption capacity (q_e) values and coefficients (R^2) are better correlated (0.999) to the experimental values for the pseudo-second order kinetics. Hence, similar kinetic sorption mechanisms are obtained as in the reference conditions.

According to the latter result, sorption isotherms were determined. Results are presented in Fig. 4 for FLUone. The three isotherms are superimposed in the graph. The influence of the L/S ratio for FLU is given in Appendix A Fig. S2. There is no significant influence of the ratio L/S on FLU sorption.

Table 5 summarizes the parameters relative to the sorption models fitted to the experimental data for FLU and FLUone sorption at different L/S ratios. As in reference conditions, linear model best describes the experimental results for all L/S ratios and for both PAHs/O-PAHs. K_D and K_{OC} values derived from sorption isotherms and their respective variation with respect to the ones obtained in the reference conditions are presented in Table 5. Results from the Langmuir modelisation were given in Appendix A Table S4.

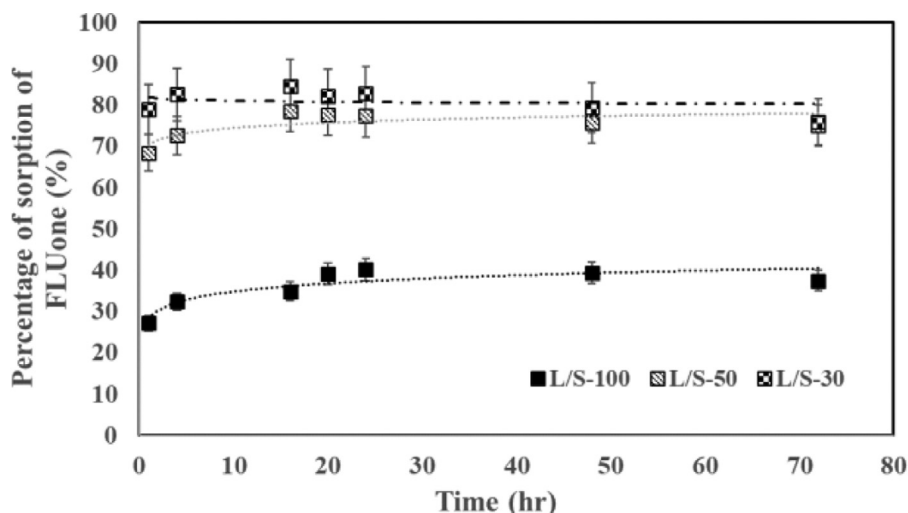


Fig. 3 – Sorption kinetics FLUone onto soil A at different L/S ratio. For all L/S values: $C_{FLUone(0)} = 10,000 \mu\text{g/L}$.

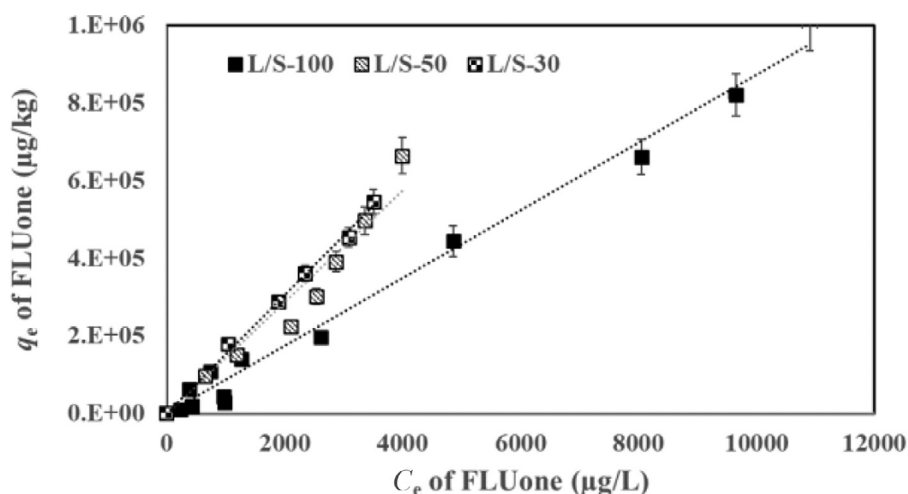


Fig. 4 – FLUone sorption isotherms onto soil A at different L/S ratios.

Table 5 – Summary of Linear and Freundlich sorption parameters for sorption onto soil A of FLU and FLUone at different L/S values (L/S 50 and 30; C_{Ca} 2 mmol/L; reference: L/S 100).

Model		L/S	FLU	FLUone
Linear	K_D (L/kg)	50	140 ± 7	140 ± 10
		30	160 ± 7	150 ± 10
	R^2	50	0.993	0.942
		30	0.998	0.995
Variation of K_D (%)	K_{OC} (L/kg)	50	2200 ± 100	2200 ± 200
		30	2500 ± 100	2400 ± 200
		50	+8	+56
Freundlich	K_F	50	390	100
		30	240	330
	n	50	1.23	0.9
		30	1.08	1.1
R^2	50	0.998	0.953	
	30	0.999	0.993	

As illustrated in Fig. 4, Appendix A Fig. S2 and in Table 5, varying the L/S ratio has a minor effect on FLU sorption onto the soil compared to FLUone sorption. The incremental decrease of L/S from 100 (reference conditions) to 50 and 30 slightly favors FLU sorption by 8% and 15%, respectively. Furthermore, obtained K_{OC} values for FLU in all conditions are within the range of 2000 – 2500 L/kg; hence, values are of the same order of magnitude as the Karickhoff K_{OC} value yielded by Eq. (8) (2000 L/kg). Moreover, taking into consideration the slight variation in FLU sorption (Fig. 4 and Table 5), the obtained K_{OC} values and the relative uncertainties, it could be supposed that FLU sorption is nearly unaffected by the variation of L/S. This result was expected given the mechanism responsible for PAH sorption in soils, which is governed by the partition at equilibrium between SOM and dissolved organic matter (DOM), which is linear for FLU in these experimental conditions.

On the other hand, FLUone sorption increases by 56% and 67%, respectively, when the same variation of L/S is applied.

Hence, the influence of increasing the soil concentration on the sorption of FLUone shows a significant and non-linear dependence to FLUone sorption. The higher sensitivity of FLUone to a variation in L/S ratio can suggest that the main mechanisms responsible for its retention in soils are not only based on a contaminant partitioning at equilibrium between the solid and the liquid phases as already known for the SOM/DOM partitioning for PAHs.

A dependency on the soil concentration was already observed regarding the sorption of hydrophobic compounds in some previous studies (Voice et al., 1983). In their study, the sorption of hydrophobic compounds including naphthalene decreased when the soil concentration increased (i.e., L/S decreased). This was explained by a possible formation of microparticles that were transferred to the solution and not removed from the suspension during the separation procedure. Compared to Voice et al. (1983) the opposite behavior is observed in our study regarding the small and the great increase in FLU and FLUone sorption respectively, but this is not necessarily directly comparable, given that different experimental procedures were applied. In addition, the materials used in the study of Voice et al. (1983) were sediments with a size below 60 μm and had an organic carbon content of 2.9% and 3.8%. At these low organic carbon contents, it is likely that other soil constituents like clay minerals could play a role in PAH sorption and that the mechanism is different than the one responsible for PAH sorption onto soil organic matter. Our results concerning a small increase in FLU sorption when increasing the solid phase concentration are therefore consistent with the laws of thermodynamic equilibria because under thermodynamically ideal conditions, the ratios of concentrations between two immiscible phases should be constant and independent of the mass or volume of each phase. Nevertheless, the great increase in FLUone sorption with an increase in soil concentration could mean that linear partitioning at equilibrium between the solid and liquid phases is not the main mechanism responsible for FLUone retention in soils. FLUone sorption could be greatly influenced by the transfer of soil materials (not only organic matter) between the two phases (solid and liquid) during the course of the experiment. The amount of transferred materials is governed by mass transfer and controlled by the concentration gradient between the two phases; hence, it is directly proportional to the soil concentration in the system (Voice et al., 1983). The increase in FLUone sorption onto soil could be attributed to a sorption competition which takes place between FLUone and the transferred materials.

These results show a different behavior between FLU (PAH) and FLUone (O-PAH) that could be attributed to different retention mechanisms and sorption sites in soils between PAHs and O-PAHs.

2.3. Effect of ionic strength on FLU/FLUone sorption kinetics and isotherms

Variations of Ionic Strength (IS) were realized by increasing by factors of 10 and 50 the concentration of C_{Ca} in the background solutions with respect to the one in the reference conditions.

Kinetic experiments given in Fig. 5, show the same behavior seen in previous conditions for both compounds; sorption

Table 6 – Summary of Linear and Freundlich sorption parameters for sorption onto soil A of FLU and FLUone at different IS (C_{Ca}) values (L/S 100; C_{Ca} 20 and 100 mmol/L; reference: C_{Ca} 2 mmol/L).

Model		C_{Ca} (mmol/L)	FLU	FLUone
Linear	K_D	20	110 \pm 9	140 \pm 10
		100	120 \pm 6	90 \pm 8
	R^2	20	0.998	0.950
		100	0.984	0.967
	K_{OC}	20	1700 \pm 100	2200 \pm 200
		100	1900 \pm 100	1400 \pm 100
Variation of K_D (%)		20	-15	+33
		100	-7	+0
Freundlich	K_F	20	340	1 400
		100	820	330
	n	20	1.24	1.37
		100	1.51	1.18
	R^2	20	0.997	0.933
		100	0.973	0.922

equilibrium is assumed to be reached within 24 hr and sorption isotherm experiments were carried out accordingly. Kinetic coefficients of FLU and FLUone sorption in these conditions are presented in Appendix A Table S5.

Sorption of both PAH and O-PAH fits better to the pseudo-second order kinetic model, that can estimate the experimental q_e values with R^2 values ranging from 0.995 to 0.999. Thus, the underlying phenomena potentially responsible for this apparent sorption of FLU and FLUone in these conditions are similar to the ones identified in the reference conditions.

Isotherm sorption experiments were carried out and the effects of Ionic Strength of the background electrolyte on FLU and FLUone sorption isotherms were evaluated. Experimental data are shown in Fig. 6 while Table 6 summarizes the effect of varying the IS on FLU and FLUone sorption with respect to the sorption models. Langmuir model does not represent the experimental data and results are given in Appendix A Table S6. In contrast, experimental data is found to fit better the linear sorption model (R^2 : 0.950 – 0.998 for all conditions). The respective variation in sorption (K_D) in comparison to the ones obtained in the reference conditions are depicted in Table 6.

The effect of varying the IS is relatively distinct between FLU and FLUone. Increasing C_{Ca} by factors 10 and 50 leads to a decrease of only 15% and 7% in FLU sorption, respectively. Considering the close data repartition (Fig. 6a) and the relative uncertainties related to K_D and K_{OC} values for FLU (Table 6), it could be concluded that FLU sorption is not affected by an IS variation. In addition, experimentally derived K_{OC} are always in line with the value calculated with Eq. (8). This result is somehow conflicting in comparison with PAH sorption dependence on IS found in literature. Indeed, PAH sorption capacity was found to increase when the solution salinity increased; increasing the IS (i.e., concentration of ions in the liquid phase) may have a salt-out effect on the sorption of hydrophobic PAHs. This could decrease the solubility of PAHs in solution and favor their sorption onto the solid phase (Weston et al., 2010); more ions in solution could tightly bind water molecules into hydration shells, hence depleting

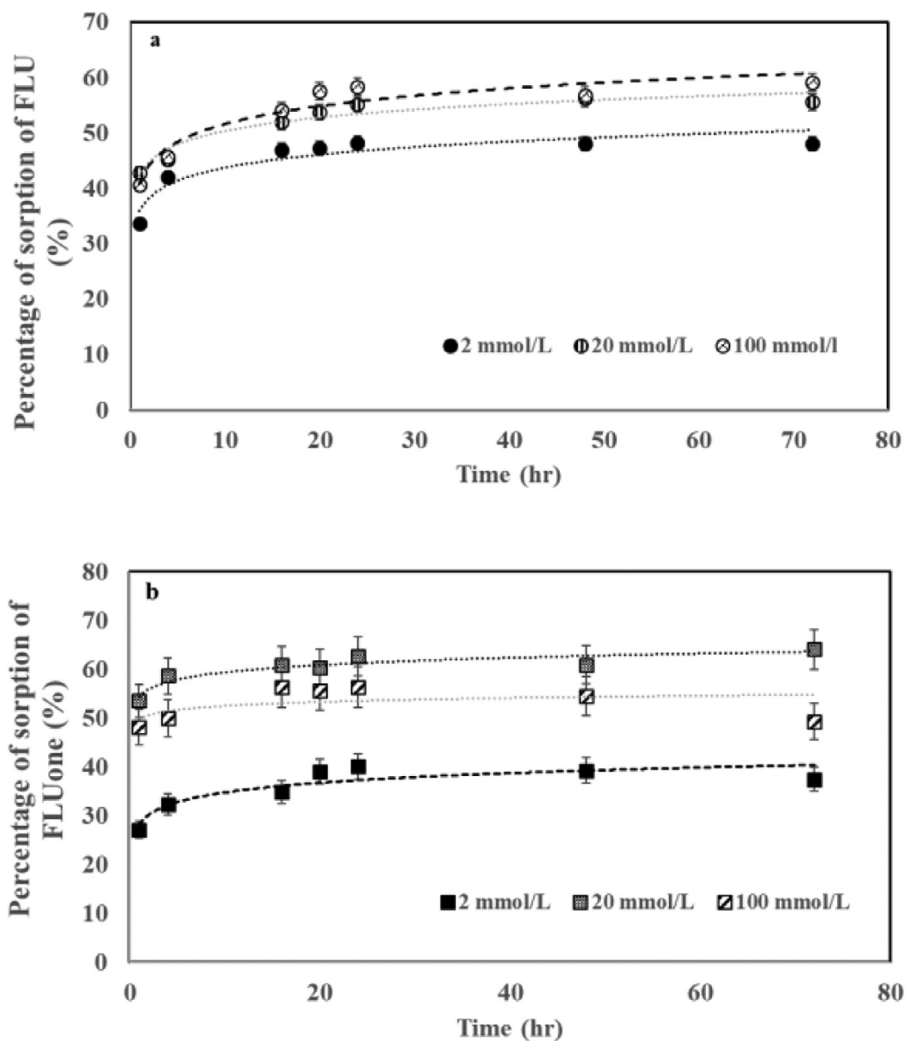


Fig. 5 – Sorption kinetics of FLU (a) and FLUone (b) onto soil A at different IS values (C_{Ca}); for all C_{Ca} values: $C_{FLU(0)} = 500$ L/kg, $C_{FLUone(0)} = 10,000$ L/kg.

the tightly bound water molecules available for binding (Karickhoff et al., 1979; Lamichhane et al., 2016; Sun et al., 2009). However, considering the high value of L/S used in this study (i.e., low soil concentration) compared to the one used in previous cited studies (L/S ranging from 20 – 50), it could be presumed that the amount of transferred (released) materials from the soil was limited in our case (L/S: 100). Thus, the amount of salt in solution was insufficient in order to occupy all vacant sites and the bound water molecules were abundant for FLU occupancy and its solubility was not affected by the addition of salt. Furthermore, the partition of the transferred material in the aqueous phase, especially the organic part known for its binding to the hydrophobic PAHs, is not affected as well (Limousin et al., 2007). Hence, the partition of FLU between SOM and DOM is not affected.

On the other hand, FLUone exhibits a contrasting behavior when IS is increased. The first increment in C_{Ca} by a factor of 10 significantly increases FLUone sorption by 33%. However, an increase in C_{Ca} by a factor of 50 has no effect on FLUone sorption compared to the reference condi-

tions. This could be explained as follows: the first quantity of ions added to the solution occupied the sites earlier available for FLUone binding. This leads to the decrease in FLUone's high solubility in the aqueous phase and favors its sorption onto the soil. Then, the greater increase in ion concentration in solution leads to a competition of sorption onto soil, taking place between the polar FLUone and the ions present in solution. This could mean that O-PAHs sorption is affected by competing ion exchange phenomena and that a fraction of the sorbed FLUone could be replaced by the major background electrolyte ions (Bourg and Sposito, 2011; Sposito, 2008). Therefore, this phenomenon is dependent of the ions concentration in solution affecting the degree of the competition (Limousin et al., 2007). This indicates that O-PAH sorption could be controlled by mechanisms at the surface of soil particles. These results raise research needs regarding the nature and the extent of the mechanisms involved in O-PAH sorption and their interactions with the ions present in solution, which are obviously distinct than the one of PAHs.

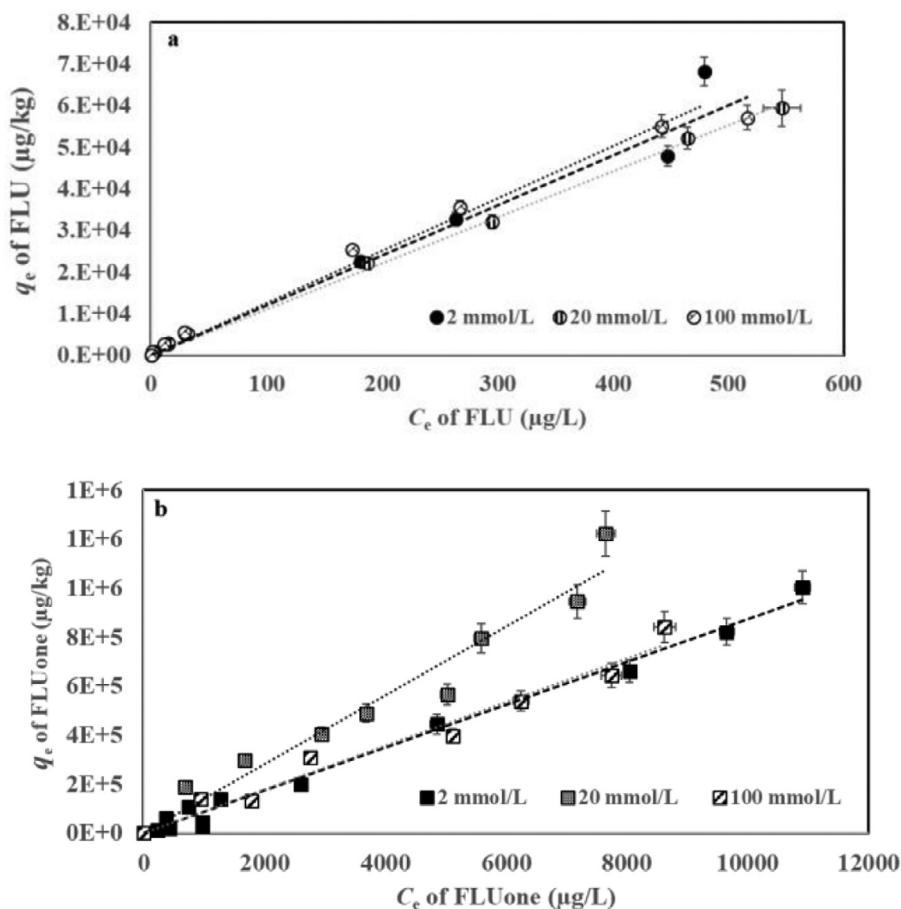


Fig. 6 – FLU (a) and FLUone (b) sorption isotherms onto soil A at different values of IS (C_{Ca}).

3. Conclusions

These results represent a first experimental data evaluating O-PAHs sorption on non-contaminated soils and gives a preliminary insight regarding their retention and transfer in groundwater. This study provided meaningful first information regarding O-PAHs behavior in soils and the following conclusions can be pointed out regarding PAHs and O-PAHs sorption onto soils:

- (1) Kinetic experiments of the studied PAHs/O-PAHs show that the sorption process is composed of two stages: a first fast sorption during the first hour of mixing followed by a second slower process before reaching equilibrium within 24 hr. Experimental data fit to a pseudo-second order kinetic model.
- (2) The solubility of a given O-PAH could be an important parameter (among others) influencing its retention and release in soil. FLUone is less sorbed than FLU in all studied experimental conditions. This behavior reflects the greater potential capacity of O-PAHs to migrate further from the pollution sources than PAHs and to form larger pollution plumes in groundwater.
- (3) Varying the L/S ratio significantly influences FLUone sorption in contrast to FLU.
- (4) Varying the ionic strength of the aqueous phase has a strong effect on FLUone sorption, where a slight effect is observed on FLU sorption.
- (5) Mechanisms and sorption sites responsible for FLUone sorption onto soil are different than those responsible for PAH sorption and do not mainly rely on a partition at equilibrium between soil organic matter and dissolved organic matter. They could be due to surface retention mechanisms.

Further studies are necessary and in progress at different scales (lab and field scales) in order to better understand the migration potential of O-PAHs and investigate the underlying mechanisms. Further experiments on columns are already going on in order to better identify and understand O-PAH mechanisms of sorption.

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Appendix A Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jes.2021.11.001.

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