Sorption and desorption of phenanthrene and fluorene in mangrove forest soils of the Morrocoy National Park, Venezuelan Caribbean

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The research proved the capacity of mangrove soils (of Boca del Zorro Spout) to sorb and desorb two low molecular weight PAHs, fluorene and phenanthrene. In order to evaluate this capacity, we determined the total organic carbon (TOC wt%) and the maturity of soil organic matter (SOM) by calculating the maximum vitrinite reflectance ($R_{o\ max}$). Additionally, batch-reactor experiments, water leaching and ultrasonication were conducted to study the sorption and desorption process. The mangrove soil presents a TOC content of 25% and a humification range of SOM that has reached the range of peat. Sorption isotherms were nonlinear following the Freundlich model. The values of the isotherm nonlinearity index (N) and organic carbon normalized sorption coefficients (log K_{oc}) are similar for fluorene and phenanthrene; therefore, they follow the same sorption mechanism in the mangrove soil. The log K_{oc} values obtained suggest that the soil is composed of a mixture of both recent organic matter and organic matter with an advanced degree of maturity. For this reason, for both polycyclic aromatic hydrocarbons (PAHs), the process responded to a non-linear model with limited sorption sites with variable potential energy. Both fluorene and phenanthrene presented a desorption percentage between 6–7% in mangrove soil sample. This allows us to infer that the bonds presented in the sorption process are associated with the insertion of fluorene and phenanthrene into the pores of the humified mangrove soil material. The research into mangrove soil displayed significant heterogeneity in composition and strong sorption of PAHs, as a result, mangrove soil presents natural filters in this area of the Venezuelan Caribbean.

Keywords: polycyclic aromatic hydrocarbons, organic soil, Freundlich isotherm, fluorene, phenanthrene

INTRODUCTION

Increased anthropogenic activities intensified the deterioration of several ecosystems, in response to these activities, increased efforts have been made in the last few decades to protect the environment throughout the globe. Mangrove forests represent one of these complex ecosystems. These forests develop in greater proportion in coastal regions of tropical and subtropical intertidal zones and have plant species that grow in extreme conditions, including highly saline, flooded soils with low oxygen environment (Bayen, 2012). Mangrove soils are composed of fine sediments like sand, silt, and clays (Jia et al., 2016), including smectite-type clays (Eswaran and Reich, 2005). These soils are rich in organic matter originated mainly from exudation of organic components and decomposition of plants that grow on their surface

(Barreto et al., 2016). Mangrove forest soils are affected by abiotic and biotic factors varying widely in time and location, and giving them very heterogeneous properties (Hossain and Nuruddin, 2016). Among the main types of soils associated with mangrove forests are Vertisols, which are rich in expansive clays (Eswaran and Reich, 2005), Histosols, which are rich in organic matter, and Gleysols, which are seasonally saturated (Tiner, 2009). Their enrichment in organic matter play an important role for in-situ chemical reactions and biogeochemical processes, including the sorption capacity of organic pollutants and metals (Martínez, 2012; Bayen, 2012; Jia et al., 2016).

The sorption capacity of soil is of high relevance for the remediation of contaminated soils (Lamichhane et al., 2016). In natural ecosystems, remediation processes proceed without an additional requirement of pre-treatment, especially in areas with accumulation of biosorbent or other natural sorbents (Xing, 2001; Olu-Owolabi et al., 2015; Jia et al., 2016), acting as filters for water contaminated both by organic and inorganic compounds

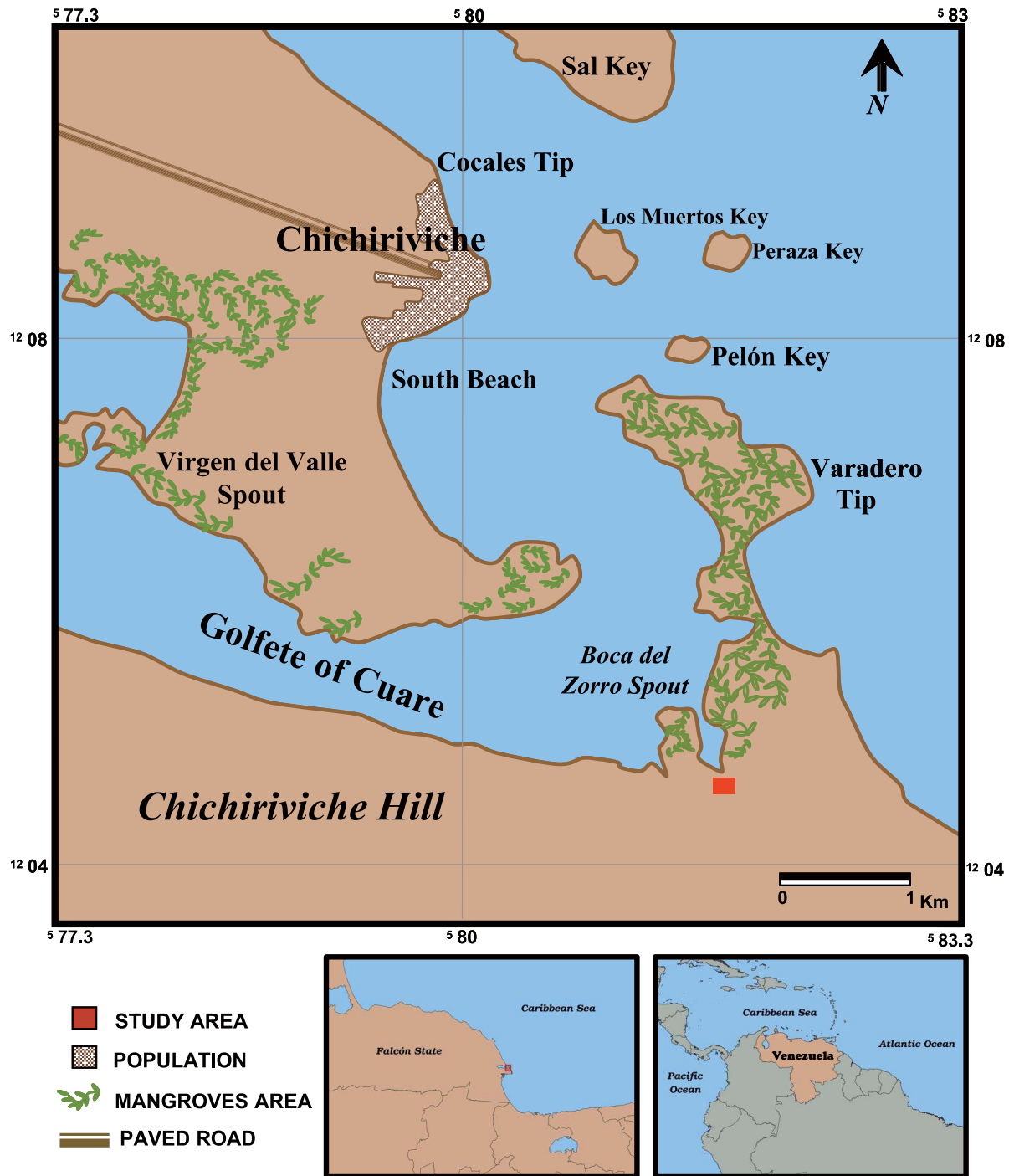*Corresponding author (e-mail: katyareategui@gmail.com)

Fig. 1. Study area, Boca del Zorro Spout in the Golfete of Cuare, Morrocoy National Park, Venezuelan Caribbean (Reategui, 2009).

(Bayen, 2012). The organic contaminants include Persistent Organic Pollutants (POPs). POPs found in the waters, such as PAHs, are partially transferred to soils in contact with them through equilibrium processes (Chiou *et al*., 1998; Kim and Lee, 2019). Several PAHs are known to be toxic, some being mutagenic and/or carcinogenic to biota; consequently, they have been classified as priority pollutants (ATSDR, 1995). Additionally, they belong to

a group of organic molecules that are not easily biodegradable, and tend to bioaccumulate due to their lipophilic behaviour (D'Adamo et al., 1997; Cortazar et al., 2008; Wang et al., 2016; Yu et al., 2019).

When evaluating the soil sorption capacity for contaminants, the studied substrate is typically characterized by sorption isotherm models to obtain interdependencies such as soil heterogeneity, the strength of the pollutant sorption, and an indication of the amounts of the contaminant that can be absorbed by these soils. However, little is known regarding PAHs sorption phenomena in natural substrates such as peat, mangrove, and soils rich in organic matter. The present research aims to evaluate the capacity of mangrove soils to sorb and desorb two low molecular weight PAHs, fluorene and phenanthrene, being within the most abundant PAHs in the aqueous phase in areas contaminated with hydrocarbons (Mojiri et al., 2019), assessing their effects on local ecosystem.

MATERIALS AND METHODS

Study area

Soil sampling was carried out in the Boca del Zorro Spout (E581827-N1204612), which is part of the mangrove forests surrounding the Golfete of Cuare which is located within the Wildlife Refuge of Cuare (Fig. 1), Morrocoy National Park, Falcón state, in the central-western region of Venezuela. The soils of this area have been classified as Vertisols and Gleysols, characterized by poor drainage conditions and fine textures (Barreto et al., 2016). The sampling site is located in a local depression with forests dominated by *Rhizophora mangle* L. (*Rhizophoraceae*), which generate a significant accumulation of organic matter. In some areas in the study site, Reategui (2009) observed a progressive change of soil color and odor at different depths, which may be originated by sea-level fluctuation around the mangrove. To achieve representative samples, the first 40 cm of the soil was sampled using a 10.2/20 cm diameter/length steel soil corer and the whole core (0–40 cm) was used for the experiment. The sampling was carried out at four sampling points within an area of 100 m². A composite sample was generated, which was air-dried at room temperature (Chen et al., 2011) for two days to remove the largest amount of water and then oven-dried (Xi and Chen, 2014) at 40°C for 24 hours to eliminate residual humidity. The temperature used in the drying process was lower than that used by Xi and Chen (2014), to avoid the volatilization of organic compounds associated with recent SOM. A subsample of soil was separated for the analysis of organic petrography. The remained dry soil was disintegrated and homogenized to a grain size of 0.149 mm using a 100-mesh screen (Zhang et al., 2009; Chen et al., 2011; Xi and Chen, 2014).

Sample characterization

Percent soil moisture was determined by gravimetric technique (ISO 11465:1993). Total carbon (TC) content was determined by a dry combustion carbon analyzer (LECO C-144), calibration curves were constructed to determine sample concentration. Certified LECO patterns were used to calibrate and determine TC. To determine total organic carbon (TOC) content of soil, the carbonate fraction was eliminated by mixing 1 g of soil with 10 mL of 10% HCl and stirring at 50°C for a 3 hours period (Breuning-Madsen and Awadzi, 2005) without altering the SOM content. The residual solid was filtered and washed with hot deionized water until chloride test resulted negative. Finally, the carbon content was determined again in a LECO analyzer and interpreted as the TOC content (Wilke, 2005).

The SOM maturity was determined by calculating the maximum vitrinite reflectance ($R_{o\ max}$) from the mean random vitrinite reflectance measurement ($\overline{R}_{o\ ran}$) with oil immersion (ISO 7404-5:1984), which was later adjusted to the maximum vitrinite reflectance ($R_{o\ max}$) by Eq. (1):

$$R_{o\ max} = 1,066\overline{R}_{o\ ran}. \tag{1}$$

For organic petrography, the samples were first crushed to less than 20 mesh, embedded in epoxy resin, and then polished. The reflectance value is obtained by measuring 250 sample points with a Leitz Microscope MPV-SP. The low and the high reflectivity in the vitrinite population were measured in random mode ($\overline{R}_{o\ ran}$) with non-polarized light. The calculated 250 points average value represent the mean random reflectance of vitrinite ($\overline{R}_{o\ ran}$) of the carbonaceous material.

Sorption experiment

Batch-reactor experiments were conducted to evaluate phenanthrene and fluorene sorption in a soil-water system, as described in other studies (Ling et al., 2009; Zhang et al., 2010; Xi and Chen, 2014; Jia et al., 2016). 100-mL glass volumetric flasks with Teflon-lined caps were used as batch reactors. Aluminum foil was used to wrap the volumetric flasks to minimize possible losses of PAHs due to photochemical decomposition. Batch isotherm experiments were conducted in triplicate.

In aquatic environment, dissolved organic matter (DOM) can be strongly linked to hydrophobic organic pollutants, affecting their mobility, bioavailability, toxicity, and their last fate (Shi et al., 2007; Hur et al., 2011; Moeckel et al., 2014). On the other hand, the presence of DOM enhances non-linear phenanthrene sorption in some sorbents, such as carbon, but also has some effects on sorption capacity and reversibility (Zang and He, 2013).

Based on the reasons above, acetonitrile was added as a solvent, which acts as an organic modifier (Fernández *et al.*, 2008), since it simulates the presence of DOM, and favors the solubility of phenanthrene and fluorene in an aqueous solution (Moeckel *et al.*, 2014). Each PAHs solution was prepared by dissolution of the solid standard in a 1:40 ratio of an acetonitrile-water mix, for a final solvent concentration of 2.5%, which is within the optimal range of percentage (<10%) to avoid the co-solvent effect that acetonitrile could exert on the sorption process of organic pollutants (Fernández *et al.*, 2008). This mixture promotes the stability of PAHs solution for the duration of the test, and at the same time prevents their biological degradation. Under these conditions, the stability of the solutions was maintained for up to three days.

According to time dependence and preliminary equilibrium studies, it was determined that 24 hours was enough time to reach the sorption equilibrium in the solute-sorbent systems analyzed. Preliminary experiments were conducted to obtain a solid-to-water ratio and ensure that the final PAHs solution concentration remained in the range of 20–80% (Chiou *et al.*, 1998; Zhang *et al.*, 2009; Chen *et al.*, 2011); these are optimal percentages so that the concentration of the final aqueous solution is above the detection limit of the equipment and can be easily quantified.

For the sorption experiments, 0.1 g of soil was mixed with 80 mL of PAHs solution. The initial concentration was 0.26 to 1.20 mg L^{-1} for phenanthrene and 1.2 to 5.0 mg L^{-1} for fluorene. Each assay was continuously shaken for 24 hours on a Burrel Model 75 shaker.

In this study, the separation of the supernatant solution by centrifugation (Chiou *et al.*, 1998; Karapanagioti *et al.*, 2001; Chen *et al.*, 2011) or microfiltration (Martínez *et al.*, 2012; La *et al.*, 2017) was found to result in significant analyte losses and non-reproducible values in the PAHs quantification. The losses in centrifugation separation were associated with the non-homogeneity of the PAHs in the supernatant liquid column. Losses of up to 43% on the phenanthrene and fluorene solution were observed when taking an aliquot of the liquid after centrifugation. Most probably, centrifugal forces cause the analytes to remain at the bottom of the residual liquid column, just above the solid surface, reducing the concentration of PAHs in the remaining liquid. This behavior was also observed in other studies (Amaro *et al.*, 2009; Zhang *et al.*, 2016). Amaro *et al.* (2009) recommended for this type of samples the following procedure: decantation of the residual liquid, rinsing of the residue, and joining the leachates into a final known volume. On the other hand, filtering through a vacuum micro-filtration system changed the concentration of the residual liquid due to the evaporation of the organic solvent existing in the PAHs aqueous solution, modifying its solubility,

and producing its precipitation on the filter. Therefore, after 24 hours shaking, the samples were set apart for sedimentation for 1 hour and then decanted. The decanted liquid phase was filtered manually with a polytetrafluoroethylene (PTFE) syringe filter of 0.45 μm. For later analysis, an aliquot of this solution was stored in a 2 mL vial.

All experiments were done at soil pH (5.2 ± 0.1). Blank samples without soil were analyzed to review possible losses due to volatilization and sorption over the volumetric flask walls. The blank samples did not show any significant phenanthrene and fluorene volatilization or sorptive losses on the glassware during the experiment. Also, blank samples, without phenanthrene or fluorene, verified that the sorbent did not generate peaks at the same wavelength as the PAHs studied.

Time dependence of the sortion process

Sorption kinetic tests (Teixeira *et al.*, 2011; Olu-Owolabi *et al.*, 2014, 2015; Diagboya *et al.*, 2018) were performed to assess the equilibrium time of both PAHs. 0.1 g of soil was mixed with 80 mL of the solution with the highest concentration of PAHs (1.2 mg L^{-1} phenanthrene, 5.0 mg L^{-1} fluorene) and constantly agitated with a Burrel Model 75 shaker. Sorption tests were carried out at different time intervals up to 33 hours. After each sorption time, the sample was allowed to sediment for 1 hour, decanted and filtered for its subsequent analysis.

PAHs analysis

The final solute concentrations in the aqueous phase (*Ce*) were measured by High Performance Liquid Chromatography (HPLC) using an Agilent Technologies 1200 series with a Diode Array Detector (Agilent DAD), and a Zorbax C18 reverse phase column (5 μm, 4.6 mm × 150 mm). Gradient elution was used as the mobile phase, starting from v:v 50/50 acetonitrile/water at time 0, increasing linearly to v:v 80/20 in 15 min, then it is brought back to v:v 50/50 in 5 min. The additional five minutes of solvent injection was used to avoid drastic variation in the background signal that occurs in the next injection. As result, the system was brought to the initial condition and the quality of the chromatogram was improved. The mobile phase flow rate was 1.5 mL min^{-1}, using a detection wavelength for phenanthrene and fluorene of 254 nm.

The sample injection volume was 10 μL for fluorene and 50 μL for phenanthrene. For the quantification process, calibration curves were made for each PAH, with phenanthrene and fluorene standards under the same conditions and concentrations used in the sorption experiment previously described.

Data analysis

To describe the sorption process mathematically, the

Table 1. Properties of the studied substrate

	Moisture (wt%)	TC (wt%)	TOC (wt%)	$R_{o\ max}$	pH
Soil	10.6 ± 0.1	27.7 ± 0.5	25.1 ± 0.5	0.23 ± 0.02	5.2 ± 0.1

TC: Total carbón.
TOC: Total carbón organic.
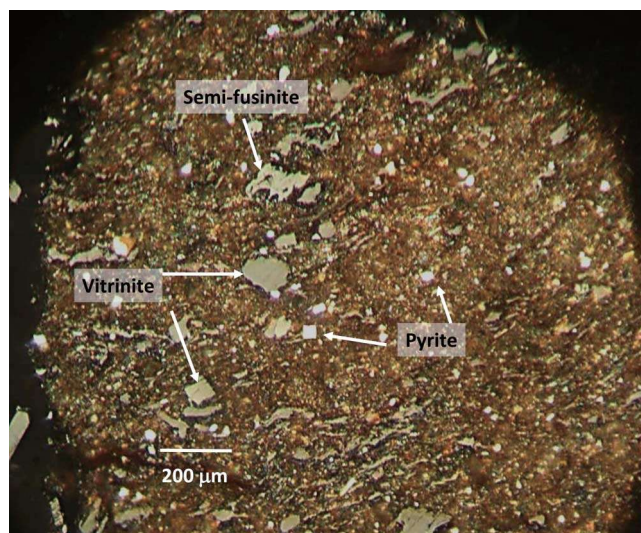$R_{o\ max}$: maximum vitrinite reflectance.

Fig. 2. Micrography under transmitted light microscope.

simplest way is a linear model (Delle Site, 2001; Karapanagioti *et al.*, 2001; Zhang *et al.*, 2009), which describes the accumulation of solute by the sorbent as directly proportional to the solution phase concentration (Weber *et al.*, 1991) (Eq. (2)):

$$qe = K_d Ce. \qquad (2)$$

Where qe (mg kg^{-1}) is the solute concentration in the solid phase at equilibrium, Ce (mg L^{-1}) the solute concentration in the aqueous phase at equilibrium, and K_d is the partition coefficient equal to the ratio of the solute-sorbate. K_d incorporates both, sorption at the mineral surface and partitioning into any natural organic matter (Farrel and Reinhard, 1994). Its value is equal to the slope of the qe vs. Ce graph (Delle Site, 2001; Zhang *et al.*, 2009). Typical units for K_d are L kg^{-1}. qe can be calculated by Eq. (3):

$$qe = \frac{\left(C_0 - Ce\right) \times V}{m}. \qquad (3)$$

Where V is the volume of solution, m is the mass of

sorbent used, C_0 and Ce are the initial and in the equilibrium concentration of PAHs, respectively.

Several authors have shown that the sorption mechanism in soils is far from a linear behaviour due to the presence of heterogeneities in the sorbent (Weber *et al.*, 1991; Delle Site, 2001; Zhang *et al.*, 2009). These heterogeneities result from the presence of different mineral and organic phases in the soil. Minerals such as clays, quartz, and micas have different sorption strength over non-ionic organic compounds (Delle Site, 2001). SOM can also be composed of a great variety of polar, aliphatic, aromatic compounds of different sizes and structures (Weber *et al.*, 2001). For these systems, the Freundlich isotherm is the most widely used in a non-linear equilibrium sorption model (Weber *et al.*, 1991; Mc Ginley *et al.*, 1996; Foo and Hameed, 2010). This model has the general form of Eq. (4):

$$qe = K_f \times Ce^N. \qquad (4)$$

Where, K_f is the Freundlich constant related to the sorption capacity and N (dimensionless value) is the isotherm nonlinearity index (Zhang *et al.*, 2009) that describes the curve of the isotherm and relates to the sorption intensity. The value of N represents a joint measure of both the relative magnitude and diversity of energies associated with a particular sorption process. When N values are lower than 1, it indicates a nonlinear isotherm, where the marginal sorption energy decreases with increasing surface concentration (Farrel and Reinhard, 1994; Delle Site, 2001). The value of K_f depends on the units with which qe and Ce are expressed; in this study, K_f is expressed in mg^{1-N} L^N kg^{-1} (Delle Site, 2001). For the determination of these empirically derived coefficients, Eq. (5) was adjusted to its logarithmic form:

$$\log qe = \log K_f + N \log Ce. \qquad (5)$$

The qe vs. Ce log graph has a slope equal to N and an intercept equal to the log K_f. Many of the sorbents with organic matter exhibit non-linear behavior. This is because the SOM contribution (humic acids, fulvic acids, and humins) to the sorption capacity of the soil (Weber *et al.*, 2001) is bigger than the contribution from other components (Means *et al.*, 1980; Olu-Owolabi *et al.*, 2015), es-
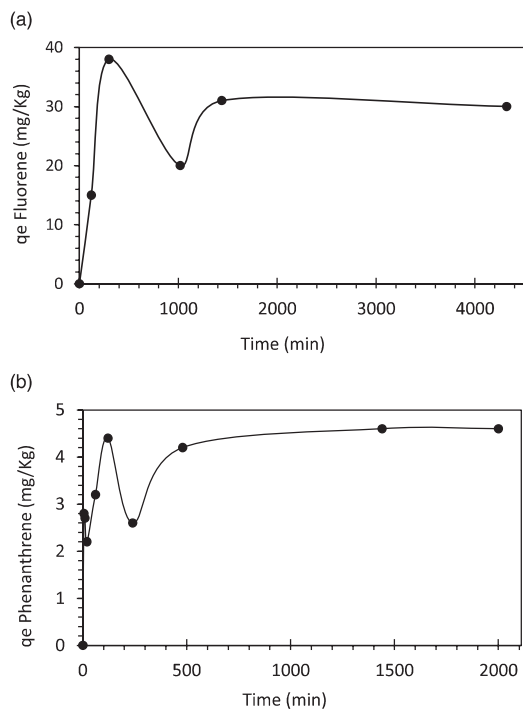
(a)

(b)

Fig. 3. Sorption trend with time (a) Fluorene; (b) Phenanthrene.

pecially if found in higher proportion than the mineral component (Cm) (Cm/SOM < 30) (Delle Site, 2001). Since sorption occurs predominantly by partition into the SOM, it is more useful to normalize the K_f to the organic carbon content of soil and express the distribution coefficient in K_{oc} or K_{foc}. K_{oc} is defined as the measurement of the distribution coefficient of an individual PAHs between the SOM and water, and represents the coefficient of hypothetical distribution of a sorbent composed entirely of organic carbon. This coefficient is dependent on the concentration and is determined at a fixed concentration of analyte at equilibrium, for example, in this study: (Ce) of 1 mg L^{-1}, following Eq. (6):

$$K_{oc} = K_{foc} \times Ce^{N-1}. \qquad (6)$$

Where K_{foc} is the organic-carbon normalized Freundlich distribution coefficient, calculated by the Freundlich model (Zhang et al., 2009), according to Eq. (7):

$$K_{foc} = \frac{K_f}{foc}. \qquad (7)$$

Where foc is the TOC content for each gram of the studied soil, expressed as a percentage. The units of K_{oc} are L kg^{-1}.

Desorption experiment

For the desorption experiments, 80 mL of the solutions with the highest PAHs concentration (5 mg L^{-1} for fluorene and 1.2 mg L^{-1} for phenanthrene) were stirred for 24 hours with 0.1 g of soil. After 1-hour sedimentation time, the solid was separated from the liquid supernatant by centrifugation for 20 minutes. A centrifuge Thermo Electron Corporation, model IECHN SII, at a speed of 2000 rpm, was used. The solid was washed with deionized water and centrifugated again for 20 minutes; this procedure was repeated 2 more times until the washing solutions did not register detectable PAHs values (Huang et al., 1998). Finally, the washed solid was mixed with 80 mL of deionized water for 20 minutes in a Transonic TP 690 brand ultrasound at a temperature of 33°C, followed by 20 minutes of sedimentation time before decant the solution. The liquid phase was filtered with 0.45 μm PTFE syringe filter, and analyzed by HPLC to evaluate the concentration of PAHs. Tests were conducted in triplicate. Desorption percentages were calculated with Eq. (8) (Gupta et al., 2009):

$$\%Desorption = \frac{Amount\ of\ PAHs\ desorbed}{Amount\ of\ PAHs\ sorbed} \times 100. \qquad (8)$$

RESULTS AND DISCUSSION

Characterization of soil substrate

Soil samples were of dark gray to blackish color, with presence of small fragments of leaves and stems mixed with blackish matter, and were characterized by a strong odor due to the presence of hydrogen sulfide (H_2S). This gas is the sub-product of anaerobic sulfate-reducing bacteria activity (Hossain and Nuruddin, 2016). High moisture content (Table 1) resulted from extensive periods of

Table 3. Sorption isotherm parameters for phenanthrene and fluorene according to the linear model and the Freundlich model

PAHs	Freundlich equation							Linear equation	
	N	$\log K_f$	R^2	K_f	n	$K_{foc} = K_{oc}$ (1 mg/L)	$\log K_{oc}$	R^2	K_d
Flu	0.75 ± 0.06	3.31 ± 0.02	0.9879	2041 ± 103	1.341	8164	3.91	0.9425	1963
Phen	0.77 ± 0.09	3.30 ± 0.07	0.9503	1995 ± 92	1.308	7980	3.90	0.8763	2560

N: intensity of sorption.
n: $1/N$.
K_f: Freundlich constant.
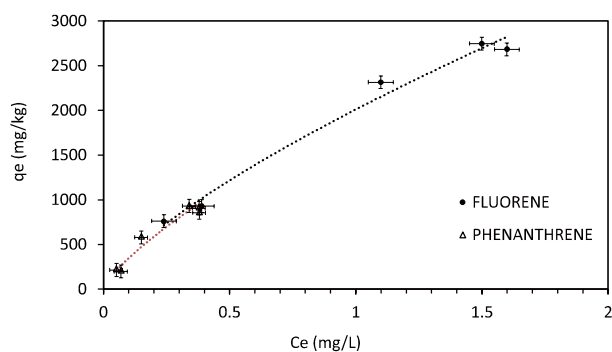$K_{foc} = K_{oc}$: coefficient of hypothetical distribution of a sorbent composed entirely of organic carbon.

Fig. 4. Sorption isotherms for phenanthrene and fluorene in the studied soil (error bars indicate standard deviation values of three replicates).
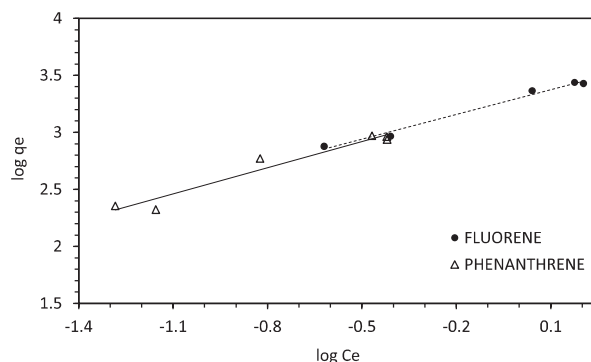

Fig. 5. Linearized isotherm of the Freundlich model.

flooding. Additionally, they contain a high quantity of silts and clays with a high-water retention capacity, such as montmorillonite (Barreto *et al.*, 2016). The TOC content obtained (25 ± 1 wt%; Table 1) is within the range reported by Barreto *et al.* (2016) for the mangrove forests in this area (between 0.5 and 26 wt%). This high value results from the anoxic conditions in flooded soils, which SOM needs for staying preserved.

Organic petrography researches provide information about the SOM maturity range ($R_{o\,max}$), the maceral composition, and the mineral matter distribution (ISO 7404-5:1984). The measured $R_{o\,max}$ values (0.23 ± 0.02) indicated that the studied soil had reached a degree of humification in the range of peat (0.20–0.27), being rich in lignin, polysaccharides, humic substances, and cellulose (Killops and Killops, 2005).

Organic petrography analysis also showed the presence of small pyrite fragments and certain macerals (Fig. 2). The presence of pyrite confirms the development of anoxic conditions and activity of sulfate-reducing bacteria. On the other hand, maceral fragments of the inertinite group were observed, such as fusinite and semi-fusinite. Vitrinite is found in small fragments, some of which kept

the replica of plant tissue. The high production rate of the plant biomass in combination with the high sedimentation rates in mangrove soils (Middleton and McKee, 2001) and continuous condition in flooded soils, favor the mixture of recent SOM, SOM in different stages of degradation, and at the beginning of diagenetic processes.

Sorption time

The results of the incubation time on sorption showed that equilibrium fluorene (Fig. 3a) and phenanthrene (Fig. 3b) sorption on the mangrove soil were attained within 1440 min. When reaching equilibrium, the concentration of fluorene and phenanthrene remained constant. The experiment lasted 33 hours, with no apparent change in the equilibrium condition. Figures 3a and 3b show that both PAHs displayed the same sorption behavior. The sorption process occurs in two stages: a fast stage followed by a slow one, regardless of the initial concentration. In the initial stage, rapid PAHs sorption at high rates was observed, during which the highest values of qe were reached, followed by a cycle of desorption-sorption of PAHs, where qe decreases around 50% of the maximum value reached, and then qe increased again until the second stage begins. The second state is interpreted as a steady state with a tendency close to horizontal, which

represents the point close to equilibrium; this occurs at 240 min for phenanthrene and 1000 min for fluorene. This behavior has been reported by several authors for fluorene and pyrene sorption, in soils with organic matter content (Teixeira et al., 2011; Olu-Owolabi et al., 2014, 2015; Diagboya et al., 2018). At higher soil/sorbate ratios, sorption occurs rapidly due to the relative abundance of sorption sites (Voice et al., 1983; Delle Site, 2001; Teixeira et al., 2011). Both PAHs presented similar sorption kinetics for the mangrove soil, this emphasizes that the sorption time depends mainly on the type of soil, its homogeneity, and the content and type of SOM.

Phenanthrene and fluorene sorption

The average sorption percentage of each PAHs was determined from the qe values (Table 2) and the initial concentrations in solution. For fluorene, this was 75-80% and for phenanthrene, it was 72–80%. The high sorption values of the PAHs confirm that there was no solvent effect that could have interfered with the interaction in the soil sample. Sorption isotherms of phenanthrene and fluorene at 25°C were calculated, using the linear model (Fig. 4) and the Freundlich model (Fig. 5). Table 3 shows the parameters derived from the regression applied to each sorption model. The isotherms of both PAHs do not fit the linear model, with the regression coefficients (R^2) less than 0.95 (Table 3). The linear representation of the Freundlich model (Fig. 5) presents an R^2 value greater than 0.95, indicating that the Freundlich model is the one that best describes the sorption behavior of phenanthrene and fluorene for the mangrove soil used in this research. Freundlich's model considers a heterogeneous sorption surface and limited sorption sites with variable potential energy (Yuan et al., 2010). Initially, sorption occurs mainly in the higher energy sites, and as the covered area increases, the lower energy sites are successively occupied (Farrel and Reinhard 1994).

The N values (Table 3) for both PAHs are less than one; the value of fluorene is lower than the phenanthrene, although the differences were not statistically significant (0.75 ± 0.06 and 0.77 ± 0.09, respectively). N values much lower than one, it reflects an isotherm that is farther from linearity, and more heterogeneous sorption sites (Xing, 2001; Foo and Hameed, 2010). This corroborates that for the soil used in this study, the partition mechanism is not the only one presented in the sorption process. Additionally, for soils with high organic matter content, the low N values reflect sorption in SOM with a high degree of maturity (Oren and Chefetz, 2005; Zhang et al., 2009).

Comparing the values of K_f (Table 3), fluorene and phenanthrene present statistically similar values of sorption capacity in the mangrove soil (2041 ± 103 and 1995 ± 92, respectively). According to these results, both PAHs have a similar sorption mechanism because they belong to the same group (PAHs) and have very little difference in molecular structure and size. However, for many organic compounds and particularly the neutral hydrophobic ones, the sorption capacity is directly proportional to the amount of SOM associated with the sorbent (Karickhoff et al., 1979; Means et al., 1980) and to the type of SOM. Many authors have shown that the sorption coefficient (K_{oc}) is estimated from the octanol-water partition coefficient (K_{ow}) using the appropriate correlation equations, according to the type of organic compound and the characteristics of the sorbent (Karickhoff et al., 1979; Means et al., 1980; Doucette, 2003; Guigue et al., 2017). One way to evaluate whether the sorption model is adjusted to the behavior of the contaminant in the sorbent and its relationship with the organic matter characteristics is to compare the experimental log K_{oc} value with the estimated log K_{oc}, from the correlation equations (Karapanagioti et al., 2000; Chen et al., 2011). In this study, the log K_{ow} values used for phenanthrene and fluorene were 4.51 and 4.19, respectively (Guigue et al., 2017). The estimated values of log K_{oc} for phenanthrene and fluorene are between 4.3–4.2 and 3.98–3.87, according to the correlations proposed by Karickhoff et al. (1979) and Means et al. (1980), respectively. The log K_{oc} values for phenanthrene (3.90) and fluorene (3.91) in the mangrove soil studied, are similar and close to the log K_{oc} values estimated for both. The experimental log K_{oc} value greater than the estimated log K_{oc} value is related to sorption in highly humified or mature SOM, which has undergone a high degree of condensation. Lower values but close to the estimated value of log K_{oc}, are associated with the presence of recent SOM (Karapanagioti et al., 2000). Researches carried out on isolated humic acids show that with the increase of humification degree of the SOM, the value of log K_{oc} also increases (Simpson et al., 2003). The higher the log K_{oc} values, the more significant is the influence of SOM type and concentration on the sorption process (Karapanagioti et al., 2000). On the other hand, recent studies have concluded that the polarity of the SOM is the predominant regulator of the sorption magnitude of hydrophobic organic compounds, and high log K_{oc} values are associated with low SOM polarity values (Kang and Xing, 2005).

The SOM contained in mangrove soils comes not only from sources such as leaf litter and roots, but also from allochthonous ones, such as organic matter transported and sedimented from rivers and seawater (Kristensen et al., 2008). Barreto et al. (2016) reported a variety of functional groups determined by Fourier Transform Infrared Spectroscopy (FTIR) in the soils from the study area; among these are: amides, amines, carbonyl-containing compounds, and alcohols, which suggest that the SOM extracted from the soils is aliphatic in nature and has polar groups. Moreover, Barreto et al. (2016) detected aro-

Table 4. Sorption coefficient normalized to the carbon content for previous studies and this work

Origin	TOC (wt%)	PAHs	$K_{oc}(Ce = 1 \text{ mg L}^{-1})$	Reference
Mangrove soil	25	Phenanthrene	3.90	Presented study
Mangrove soil	25	Fluorene	3.91	Presented study
Florida peat	49	Phenanthrene	3.7	Karapanagioti *et al.* (2001)
Soils with coal fragments	5.9	Phenanthrene	4.4–4.5	Karapanagioti *et al.* (2000)
Soils with fragments of carbonization (Charcoal)	0.76	Phenanthrene	4.2–4.3	Karapanagioti *et al.* (2000)
Bamboo leaves	44	Phenanthrene	3.93	Chen *et al.* (2011)
Bamboo leaves	44	Fluorene	3.51	Chen *et al.* (2011)
Compost humic acid	55.9	Phenanthrene	4.18	Simpson *et al.* (2003)
Peat humic acid	55.2	Phenanthrene	4.15	Simpson *et al.* (2003)
Soil humic acid	49.1	Phenanthrene	4.43	Simpson et al. (2003)

K_{oc}: *coefficient of hypothetical distribution of a sorbent composed entirely of organic carbon.*
TOC: *Total carbón organic.*

Table 5. Values of the desorption process for the studied PAHs

PAHs	mg sorbed ± 0.01	mg desorbed ± 0.0005	$\%E_{desorption} \pm 1$
Phenanthrene	0.06	0.0043	7
Fluorene	0.28	0.0168	6

$\%E_{desorption}$: *desorption percentage.*

matic functional and -OH groups from phenolic groups. On the other hand, biochemical studies on soils of *Rhizophora mangle* L, similar to those of this study, have reported a total soil sugar content in the order of 0.2% (Lacerda *et al.*, 1995; Balakrishnan *et al.*, 2016).

According to these compositional characteristics, it can be validated that several sorption mechanisms are present in the mangrove soil, which justifies the low N values associated with non-linear sorption processes. At the same time, the experimental log K_{oc} values, close to the estimated log K_{oc}, confirm the influence of the hydrophobicity of the SOM, a high compositional heterogeneity, and an advanced degree of humification.

The experimental log K_{oc} values lower than the estimated log K_{oc} ones were caused by the polarity of the organic compounds in the mangrove soil. The presence of functional groups such as alcohols and carbonyl groups in the studied soil are associated with carbohydrates such as polysaccharides derived from the degradation of plant matter. Several researches have shown that the presence of polar compounds in the SOM structure decreases the K_{oc} value, resulting in a negative correlation of this value concerning the polarity expressed as the (N+O)/C ratio (Kang and Xing, 2005; Chen *et al.*, 2011; Xu *et al.*, 2020). As a result of this, once entering into the soil micropores, these compounds reduce the hydrophobic properties of the soil, inhibiting the sorption of non-polar molecules such as PAHs (Xu *et al.*, 2020).

The SOM of the studied mangrove has polar functional groups associated with organic matter of recent accumu-lation and other groups of humic composition, which have undergone a process of degradation and early diagenesis; the latter are those that promote the strong sorption of non-polar compounds in the soil. The high TOC content of the studied mangrove soil does not ensure a high sorption capacity for non-polar pollutants. Moreover, the composition and type of SOM affect the sorption capacity to a greater degree.

On the other hand, the fact that both PAHs have the same N value may be related to the composition of the SOM, which plays a determining role in the sorption mechanism of these compounds. Oren and Chefetz (2005) found similar N values for phenanthrene and naphthalene in river sediment samples, although these PAHs have different physicochemical properties. The results reflect that the sorption mechanism is controlled by the composition of the sorbent. When Oren and Chefetz (2005) analyzed the sediment as a whole, the N values did not distinguish sorption preference towards either of the two PAHs, which suggests the same sorption mechanism for both of them. However, when separating the humic acidic and humin fractions, sorption preference of each PAHs in each sorbent is observed. Other studies suggest the possibility of close association of SOM with the soil's inorganic matrix, which strongly modifies the particle surfaces and/or the nature and properties of SOM, thus influencing its binding capacity (Garbarini and Lion, 1986). This is associated to the high non-linearity of the sorption process in this study, and the presence of different sorption forces towards the PAHs.

Comparison of phenanthrene and fluorene sorption in several sorbents

The equilibrium concentration values, 1 μg L^{-1} and 1 mg L^{-1} were used as standard values to compare the values obtained with other studies. The concentration of 1 mg L^{-1} was used to compare the log K_{oc} values of fluorene and phenanthrene with those reported by Chen *et al.* (2011). Table 4 compares log K_{oc} values for phenanthrene and fluorene sorption, in sorbents that have three characteristics: high TOC content, polar compounds, such as sugars, and humified or carbonized organic matter (coalificated). According to the results obtained in the research, the TOC content, the type of SOM, and the presence of polar groups affect the phenanthrene and fluorene sorption mechanism. As shown in Table 4, among these sorbents are: the peat (Karapanagioti *et al.*, 2001), alluvial soils with coal fragments, and the ones with fragments of carbonized material (Karapanagioti *et al.*, 2000), Bamboo leaves with high content of sugar (polar compounds) (Chen *et al.*, 2011), and humic acid extracts from substrates with different degrees of humification (Simpson *et al.*, 2003). In this study, the log K_{oc} values are close to those reported by Karapanagioti *et al.* (2001) and Chen *et al.* (2011) for natural organic substrates, which corroborate a similar sorption mechanism. The common characteristic between these substrates and the soil sample used in this study were the presence of aromatic groups, which are in humic substances and lignin and have a high sorption capacity towards non-polar pollutants such as phenanthrene. Moreover, the values reported by Simpson *et al.* (2003) for humic acid extracts confirm that natural sorbents derived from plant residues or soils rich in recent organic matter contain polar compounds which inhibit non-polar and aromatic compounds sorption such as PAHs sorption.

On the other hand, the soil sample with carbon fragments and carbonized material had higher log K_{oc} values than those of the mangrove soil (Table 4). Though, these samples had lower TOC content, their higher log K_{oc} values reflect the high degree of maturity of the organic matter. The carbon or carbonized material (charcoal) had undergone a thermal process that led to the formation of condensate arrays and structures of greater aromaticity, which favor the PAHs sorption and resulted in an optimum phenanthrene sorption capacity. The similarity in planarity with the carbon structure is an additional effect on the sorption capacity on this sorbent (Xu *et al.*, 2020). Nevertheless, there are very few studies in the literature that present K_{oc} values for fluorene, therefore a greater number of tests should be performed with this PAH.

Desorption process

The desorption percentages obtained for the mangrove soil sample (6–7%) were similar for both PAHs (Table 5). These values reflect the high sorption degree for these compounds in the mangrove soil and are comparable to those obtained by Bezza and Nkhalambayausi-Chirwa (2015) in soils with 2.2 %wt TOC. They reported a desorption value of 10% for phenanthrene in 192 hours. However, Yang *et al.* (2013) found in silty-clay soils with 0.378% SOM, desorption value less than 0.1% for phenanthrene. Richardson and Aitken (2011) studied the soils close to a gas manufacturing factory with an SOM of 8.3%, finding desorption values lower than 37% for fluorene and phenanthrene. All these studies indicate a biphasic behavior in the desorption velocity, with rapid desorption at the beginning and a velocity decrease until reaching equilibrium. Also, other studies on polar and hydrophobic organic compounds sorption (Huang *et al.*, 2003; Oren and Chefetz, 2005; Yang *et al.*, 2013) suggested that, the sorption processes for most organic compounds are reversible but are affected by an effect of "hysteresis" (slow reversibility of the process). The reversibility of this process is related to the intermolecular forces that are dominating the system. This phenomenon has been more evident in soils with a high content of organic matter and related to the chemical bond between PAHs and humic acids in the soil (Huang *et al.*, 2003; Olu-Owolabi *et al.*, 2015). In this study, the used mangrove soil sample had a high TOC content with an advanced state of maturity, becoming peat, containing an appreciable amount of humic substances in its structure. Various researchers have proposed phenanthrene sorption within the micropores of humic acids present in SOM, which can cause their deformation and subsequent difficulty in the desorption process (Oren and Chefetz, 2005; Xu *et al.*, 2020). Likewise, Weber *et al.* (2001) indicates that not only the deformation of the small pores of the SOM matrix is produced due to non-polar compound sorption, but also ocurrs the penetration of PAHs in non-porous areas and forces the sorption in the internal structure of the SOM. Although, no tests were performed to determine the equilibrium time of desorption, sonication of the sample is comparable to a prolonged process of extraction of the contaminant compounds absorbed in the soil. We can assure that the phenomenon of hysteresis in this soil is very large, showing an appearance of irreversibility, and indicates a slow stage of desorption over long periods.

In studies on soils contaminated with PAHs, it has been verified that the desorption of these compounds continues to occur in the natural environment, influenced by other factors such as the natural production of surfactants due to bacterial activity, but at a very low rate (Bezza and Nkhalambayausi-Chirwa, 2015; Helmy *et al.*, 2015). The sorption process and the hysteresis phenomenon observed in the studied mangrove soil favor the removal of the pollutant from water in contact with the soil, in addi-

tion to this, the reduced reactivity of adsorbed pollutants, since the chemical bonds that are present, it is stable. However, additional studies may be necessary to assess how these bond breaks or destabilize with time and with changes in external conditions, such as physicochemical conditions of the medium, change in pH, salinity, temperature, among others.

For example, Lamichhane *et al.* (2016) determined that the sorption of this type of contaminants is favored with the increase of the water salinity. Also, Chen *et al.* (2011) determined increases in the K_f and N variables of the Freundlich model by increasing the salinity of the aqueous phase. In the study area, the water level is fluctuating every day with the tides, so that mangroves must adapt to sudden changes in salinity. According to these results, in the coastal environment of the mangrove forest, this desorption process will be much less favored. These results reaffirm the idea that mangrove forests are natural filters that immobilize organic pollutants.

CONCLUSIONS

In this study, it was demonstrated that the mangrove soil of the Boca del Zorro Spout presents a degree of humification in the peat range with a high TOC content. The presence of pyrite indicated anoxic conditions in the soil. Phenanthrene and fluorene exhibit non-linear and strong sorption in the mangrove soil described best by the Freundlich model. The two PAHs sorption capacities were significantly influenced by the presence of aliphatic and aromatic functional groups. These groups originate from the mixture of recent SOM with SOM at the beginning of the humification process, which resulted in a considerably lower N value due to a more heterogeneous energy distribution at the sorption sites. However, the presence of polar groups in the mangrove soil decreases its sorption potential and originates an experimental log K_{oc} value lower than estimated. The log K_{oc} values for phenanthrene and fluorene in the studied mangrove soil were similar to those presented by other natural sorbents, in which the aromaticity/aliphaticity, maturity, and polarity of organic matter affected its sorption capacity.

The values of N and K_{oc} for both studied PAHs did not present a statistically significant difference, due to their similar molecular structure, indicating a similar sorption mechanism. The high TOC content, the high maturity, and the high heterogeneity of the mangrove soil appear to be the controlling factors for the sorption mechanism of these compounds. A very high sorption hysteresis was observed for phenanthrene and fluorene. We conclude that the organic components of the mangrove soil present a high sorption degree for both PAHs. Possibly, they are entering micropores of the humic substances, hence their desorption process in the natural environment is very slow, inhibiting their bioavailability.

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