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Effects of aging on the extractability of naphthalene and phenanthrene from Mediterranean soils

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Abstract

The effects of aging on the extractability of naphthalene and phenanthrene were investigated using laboratory batch assays. Experiments have been conducted with three soil matrices: a silty clay and two soils with different organic contents. Aging was conducted under abiotic conditions in water saturated and nonsaturated conditions, under a constant temperature (20 °C). The mobility of sorbed contaminants was evaluated through successive extractions in water, methanol, butanol and dichloromethane. Experimental results showed a reduction of the extractability of both naphthalene and phenanthrene with increasing aging times. The observed effects of aging might be related to slow diffusion of naphthalene and phenanthrene in sorbent microporosity and/or organic phases and possible evolutions of pollutant–sorbent interactions.

Keywords: Soil contamination; Naphthalene; Phenanthrene; Aging; Extractability

1. Introduction

Contamination of soil and underground water by organic compounds such as polycyclic aromatic hydrocarbons (PAHs) is a major environmental issue in France, as well as in most industrialized countries. PAHs, especially naphthalene and phenanthrene, are among the most frequently detected organic contaminants in contaminated groundwater [1]. Predicting the fate of such contaminants in soils and subsoils is a key issue for risk assessment or to evaluate the feasibility of remediation technologies [2,3].

In situ bioremediation has been proven as an appropriate technique for the decontamination of soils polluted by mono and polycyclic organic compounds at low to medium concentrations [4]. This approach can bear more economic profit than the other techniques as it makes it possible to degrade contaminants without using too destructive means [5]. The ability of bacteria to degrade xenobiotic hydrophobic compounds varies according to the state and location of contaminants in the soil [6,7]. It has been shown that adsorbed pollutants have a low bioavailability for degradation [8]. In the same way, a PAH present in the micro and nanopores of soil particles or in a liquid or solid phase is much less biodegradable than in aqueous solutions [3,9]. Transfer from the internal micro (nano) porosity or from the organic phase is indeed a kinetic limit to the mineralization of pollutants. The success of biological treatment of a contaminated site therefore depends on the mobility and bioavailability of pollutants in the soil [10].

It has often been observed that the mineralization of hydrophobic organic contaminants declined when contact time with soil increases [11]. Contaminants therefore become more resistant in time to extraction or biodegradation [12]. The overall phenomena observed in the evolution of contaminated soil characteristics in time are generally referred to as aging [13,14].

The general aim of this study is to generate scientific knowledge and data for the development of transport and evolution models of organic contaminants in soils taking into account slow kinetics-aging phenomena.

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2. Materials and methods

2.1. Chemicals

Experiments were carried out on two organic molecules selected as model contaminants, namely naphthalene and phenanthrene, which are the most common water-soluble PAHs. Both products used in the study were Aldrich products for analysis with a purity exceeding 98%. The main physicochemical properties are shown in Table 1. Aqueous stock solutions were prepared by mixing an excess of naphthalene or phenanthrene crystals in deionized water for 48 h in the dark at 20 °C, and filtering the solution on GF-C Whatman glass fibre filters of 1.2 μm pore-size. Naphthalene and phenanthrene concentrations in stock solutions (respectively 30.0 mg/L and 1.0 mg/L at 20 °C) were close to their solubility limits [15]. Before being used, naphthalene and phenanthrene concentrations in the solutions were determined by high-performance liquid chromatography (HPLC). In order to inhibit biodegradation phenomena, mercuric chloride $HgCl_2$ was added to the aqueous solution at a concentration of 400 mg/l.

2.2. Soils and soil fractions

Three matrices were selected in order to assess the effect of aging according to the characteristics of the sorbent. One of them was a silty clay (Clay Clarsol STF30) containing 0.7% of organic carbon and consisting mainly of montmorillonite. The silty clay was used to assess the role of mainly mineral microporosity in the evolution in time of the mobility of the tested organic contaminants. The other two materials used were natural soils, representative of a wide range of European and Mediterranean soils, which mainly differed in their organic matter content and nature (cultivated soil CSAC and meadow soil CSAP from the Côte Saint-André, Isère, France). Physical and chemical characteristics of the two soils are listed in Table 1. Soils were air dried overnight, then sieved at 2 mm.

2.3. Experimental procedure

Aging experiments were carried out in 25 mL sterile glass centrifuge tubes with Teflon® lined silicone caps in order to avoid adsorption of the contaminant as previously described [16,17]. All assays were conducted in triplicates and the average results are presented in this work. The mass ratio between the liquid and solid phases (L/S) was three, i.e. 6 g of sorbent (soil or soil fraction) were suspended in 18 mL of solution in order to limit the headspace ($\ll$1 mL) thus reducing losses through volatilization. The sorbents were suspended under sterile conditions in aqueous solutions of naphthalene or phenanthrene at initial concentrations of 15.0 and 0.50 mg L^{-1} respectively, well below the limits of solubility at 20 °C. The tubes were shaken vertically at room temperature for 24 h using a rotary shaker. They were then either stored vertically to be aged under water-saturated conditions or centrifuged in order to carry out successive desorptions (by replacing the supernatant with water) or to be aged under unsaturated conditions (by discarding the supernatant). Aging was conducted in the dark up to one year at a constant temperature of 20 °C.

Table 1
Main physical–chemical characteristics of naphthalene and phenanthrene

	Naphthalene	Phenanthrene
Molecular weight (g mol)	128.2	178
Volumic mass (g/cm^3)	0.96	0.98
Molecular volume (nm^3)	0.232	0.310
Fusion point under atmospheric pressure (°C)	80.5	101
Boiling point under atmospheric pressure (°C)	218.9	340
Solubility in water "S_w" (mg/L)	31.7	1.3
Octanol–water partition coefficient "log K_{ow}"	3.32	4.46
Organic carbon–water partition coefficient "log K_{oc}"	3.1	5.8

At given times (0, 1, 3, 6, or 12 months), the solid and liquid phases were separated by centrifugation at 4000 × g for 15 min (Polio SR 2002 centrifuge). The supernatant was then sampled with a glass syringe for analysis to determine the quantities adsorbed by the solid matrix according to contact time. After centrifugation and sampling, the pellets were weighed to determine the mass of residual solution remaining in the sorbet, and thereby deduce the amount of contaminant in the pore solution of the soil. The supernatant was then replaced by the same volume of water for the studies of desorption. Then, four successive desorptions with deionized water were carried out using the same protocol. Extraction was then conducted according to the same protocol as for desorption in water, except that the supernatant was replaced first by the same volume of methanol and then by butanol-1. Each tube was then placed in an Ultrasonic bath and was subjected to sonication for 10 min, using a Toshiba sonicator (wattage 50 W, operating frequency 33 kHz, capacity 1.5 L). After that, the tubes were shaken for 24 h, sonicated again for 10 min and centrifuged. The samples aged for 12 months were subjected to final extraction with the Soxhlet technique using dichloromethane as a solvent and during 3 h. Methanol, butanol and dichloromethane were used to extract naphthalene and phenanthrene because of their proven efficiency for PAH removal from soils [18,19].

2.4. Analytical methods

The soils were analyzed for total organic carbon (TOC) content using the Anne method [20] and cation exchange capacity (CEC) using the acetate ammonium method [21]. The moisture content was determined by weight loss after 24 h at 105 °C [16,17]. The chemical characteristics of the clay and the two selected soils were determined using X-ray diffraction analysis technique with an X-ray diffractometer (Philips PW 1729).

The porosity of the soils was determined by the mercuric technique and the microporosity by the nitrogen adsorption-desorption isotherms (at −196 °C) using the Brunauer Ennett Teller (BET) method, with Micromeritics Instruments (Institut de recherche sur la catalyse, CNRS, France).

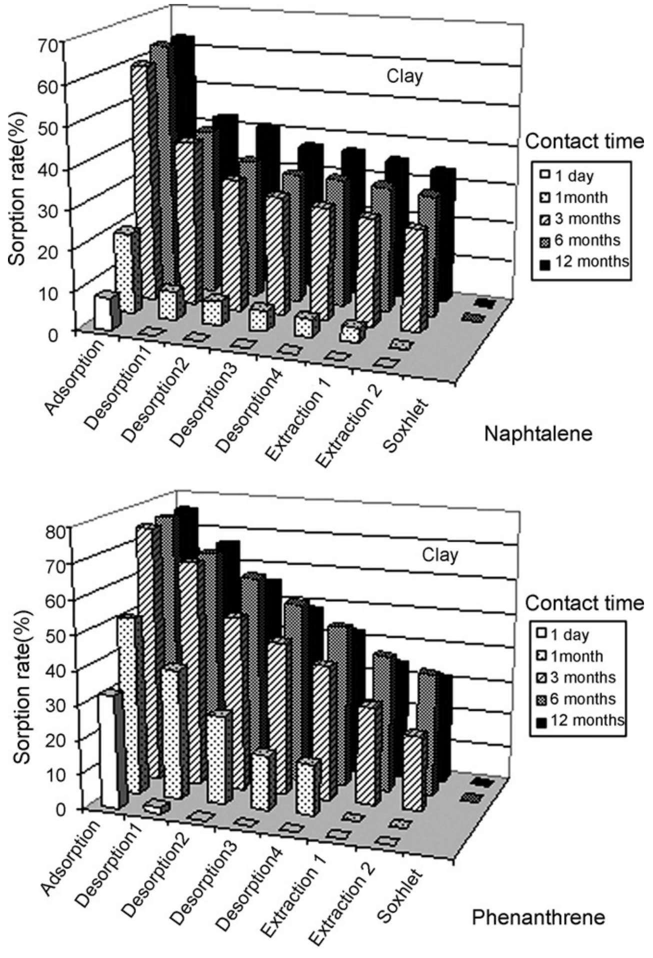

Fig. 1. Sorbed fractions of naphthalene and phenanthrene on silty clay before and after extraction procedures under saturated condition for different contact times ($T = 20\,^{\circ}\mathrm{C}$, liquid/solid ratio = 3).

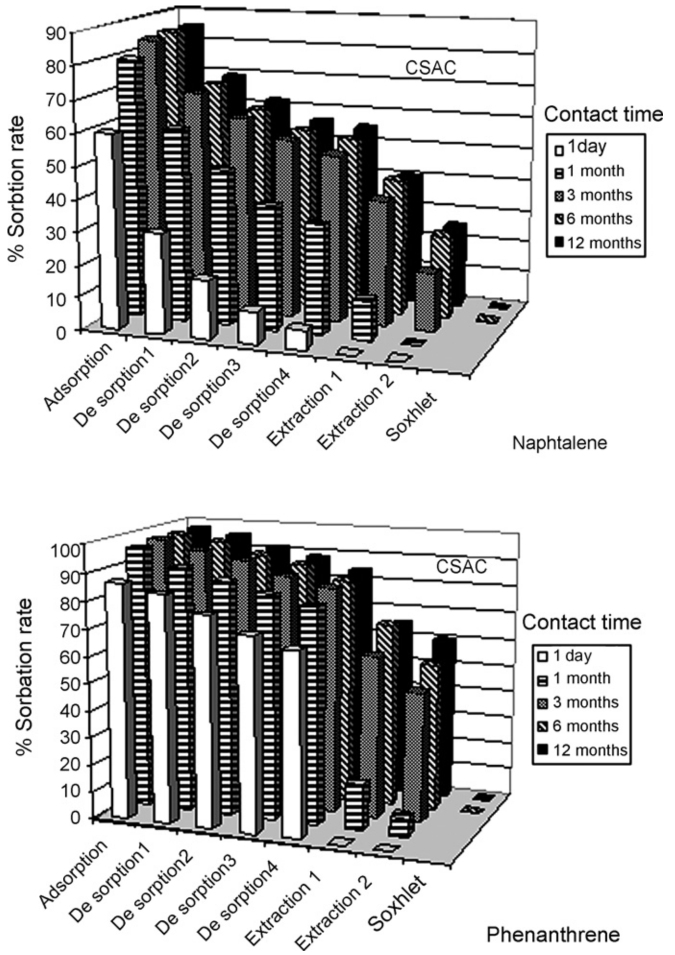

Fig. 2. Sorbed fractions of naphthalene and phenanthrene on culture soil CSAC before and after extraction procedures under saturated condition for different contact times ($T = 20\,^{\circ}\mathrm{C}$, liquid/solid ratio = 3).

Aqueous and organic extracts were analyzed for naphthalene and phenanthrene by HPLC using a Shimadzu LP-6A chromatograph equipped with an isocratic pump, a 20 μL Rheodyne 7010 injection valve, a 3 cm Kromasil C18 guard column, a 25 cm Kromasil C18 column, and a Shimadzu SPD-6A UV detector set at 254 nm to measure the absorbance of aromatic cycles [22]. The solvent used as a mobile phase was acetonitrile/water 80/20 (v/v) (HPLC solvent grade, Prolabo) at a constant flow rate of 1.0 mL/min. The sorbed amount (Qe) and percent removal (sorption rate) of naphthalene and phenanthrene were determined respectively according to the following equations:

$$Q_{\mathrm{e}}\,(\mathrm{mg/g}) = \frac{(C_{\mathrm{o}} - C_{\mathrm{e}}) \times V}{M} \tag{1}$$

$$\text{Sorption rate}\,(\%) = \frac{C_{\mathrm{o}} - C_{\mathrm{e}}}{C_{\mathrm{o}}} \times 100 \tag{2}$$

where C_{o} and C_{e} are the concentrations of the solution before and after adsorption expressed (mg/L), V is the solution volume (L), and M is the weighted portion of sorbent (g). Average and standard deviation values from experimental data were calculated according to standard procedure [23]. The maximal uncertainty was estimated at about 5%.

3. Results and discussions

3.1. Aging under water-saturated conditions

3.1.1. Silty clay

Results are shown in Fig. 1. Firstly, it can be noted that without aging (24 h contact) naphthalene and phenanthrene adsorption by clay was respectively about 8% and 33% of the contaminant masses added initially. During the first month of aging, sorption of both naphthalene and phenanthrene increased significantly as shown in Fig. 1. The contaminants sorbed during that time were less easily extracted since methanol or butanol was needed to fully extract them. Phenanthrene, which is a more hydrophobic molecule than naphthalene, showed a higher retention than naphthalene. The same trend was previously reported in other studies [24]. After this first month, up to three months of aging, it was observed that the retention of naphthalene and phenanthrene still increased significantly, and then stabilized between 3 and 12 months (Fig. 1). A significant fraction of contaminants sorbed at aging times above one month was not extracted by water or organic solvents. However, soxhlet extractions on samples aged for one year were almost quantitative,

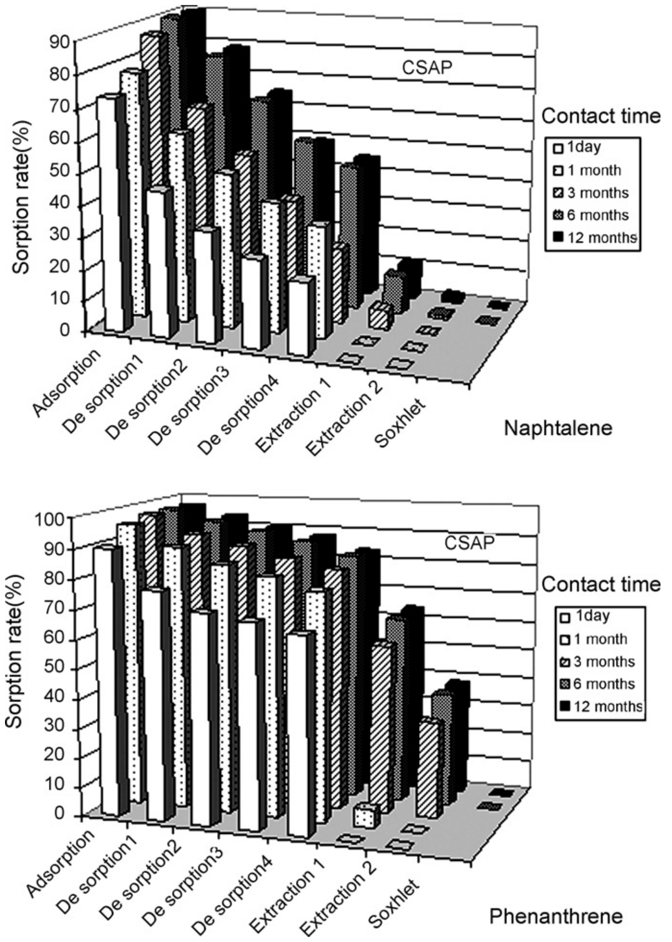

Fig. 3. Sorbed fractions of naphthalene and phenanthrene on meadow soil CSAP before and after extraction procedures under saturated condition for different contact times ($T = 20\,^{\circ}$C, liquid/solid ratio = 3).

indicating that losses by volatilization were quite small in the case of naphthalene (5%) and negligible for phenanthrene. It can therefore be concluded that the sorption equilibrium was only reached after a few months (indicating that the kinetics of the phenomena involved was rather slow) and that the extractability of the sorbed contaminants with water or organic solvents decreased drastically in time.

Hence, such observation is probably due to a mechanism of slow diffusion of naphthalene and phenanthrene into the microporosity of clay and its organic material. This mechanism appeared to be reversible since the sorbed contaminants were almost quantitatively extracted by soxhlet, indicating that the formation of bound residues or physical entrapments were not significant under the conditions of these tests [25,26].

3.1.2. CSAC and CSAP soils

Results for CSAC and CSAP soils are shown in Figs. 2 and 3, respectively. It globally reveals the same type of behaviour as observed with silty clay. The sorption of naphthalene and phenanthrene increased from 59% to 83% and 85% to 97% respectively over 12 months of contact. Sorption equilibrium was reached within one to three months of contact. Aging was also found to reduce very significantly the extractability of naphthalene and phenanthrene with water as well as organic solvents. While the contaminants were quantitatively extracted after one day of contact (Fig. 2), around 25% of naphthalene and 60% of phenanthrene was not extractable from CSAC soil with water or organic solvents after one year of contact. Losses of contaminants by volatilization were negligible since soxhlet extraction with CH_2Cl_2 after one year of aging allowed to recover almost quantitatively the contaminants (Fig. 2).

Table 2
Physical–chemical characteristics of the clay and the two selected soils (CSAC culture soil and SCAP meadow soil), from La Côte Saint-André (through 2 mm sieve)

Property	CSAC	CSAP	Clay
Sand (%)	39.8	35.7	5
Silt (%)	42.5	42.8	45
Clay (%)	17.7	21.5	50
TOC[a] (%)	1.49	3.14	0.7
CEC[b] (meq./100 g soil)	65	110	37.2
pH water	7.4	5.5	6.7
C/N	10.5	10.1	–
Moisture (%)	2.9	3.1	0.0
Porosity[c]			
Surface (m^2/g soil)			
Total (0.3–100 nm)	10.8	9.8	130.9
Micropores (0.3–1.7 nm)	9.3	4.4	28.4
Volume (cm^3/g soil)			
Total (0.3–100 nm)	0.016	0.020	0.143
Micropores (0.3–1.7 nm)	0.001	0.002	0.013

[a] Total organic carbon (TOC) content determined using Anne method.

[b] Cation exchange capacity (CEC) determined using the acetate ammonium method.

[c] Porosity determined by mercuric technique and microporosity by nitrogen adsorption-desorption technique. Micrometrics instruments (Institut de recherche sur la catalyse, CNRS, France).

Sorption of naphthalene and phenanthrene in meadow soil from the Côte Saint André (CSAP) after a 24 h contact was higher than with culture (CSAC) soil (Figs 2 and 3) This result is quite logical as CSAP soil has a higher organic carbon content than CSAC soil (Table 2). As with CSAC soil, naphthalene and phenanthrene retention by CSAP soil increased with contact time from 73% to 90% and from 90% to 97% in one year for naphthalene and for phenanthrene, respectively (Fig. 3). Furthermore, Fig. 3 shows that the extractability of the sorbed contaminants decreased with time. However, it can be noticed that the extractability of naphthalene and phenanthrene was generally better with CSAP soil than with CSAC soil. For instance, after 12 months of aging, only 3% of naphthalene and 38% of phenanthrene were not extracted from CSAP soil by the four water desorptions and the two solvent extractions against 25% and 60% respectively with CSAC soil (Figs. 2 and 3). This observation would oppose the direct proportionality reported in some studies between the organic carbon content of a soil and the extractability of the sorbed contaminants [27].

The observed phenomenon was mostly due to a higher microporosity of organic material in cultivated soil (CSAC) than in meadow soil (CSAP), as indicated by the analysis of the two soils (Table 2). The progressive diffusion of naphthalene and phenan-

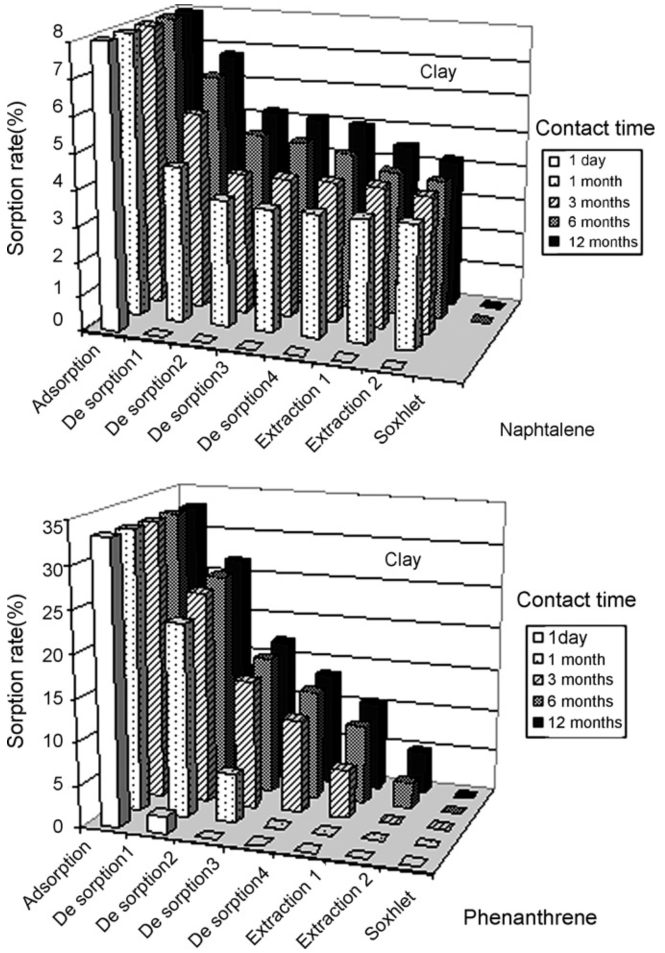

Fig. 4. Sorbed fractions of naphthalene and phenanthrene on silty clay before and after extraction procedures under unsaturated condition for different contact times ($T = 20\,^{\circ}$C, liquid/solid ratio = 3).

threne into the microporosity of the organic fraction reduces their extractability, more significantly for CSAC soil where microporosity is higher than in CSAP soil. Another hypothesis to explain the higher extractability of naphthalene and phenanthrene from meadow soil CSAP would be related to the fact that the solution extracted from CSAP soil has a higher dissolved organic material content than with CSAC soil (which has a lower organic carbon content). Indeed, it was noticed with CSAP soil that the supernatant had a brownish colour following centrifugation of samples. This colour was more accentuated in aged samples. The chromatographic analysis of the supernatant revealed the presence of non identified wide peaks attributed to dissolved organic matter which, therefore, would facilitate the dissolution of organic contaminants as already described by other authors [28].

3.2. Aging under unsaturated conditions

Under unsaturated conditions, the concentrations of sorbed contaminant cannot increase significantly during aging since the supernatant is discarded at time zero of aging and may therefore not gradually transfer the contaminants into the soil. The effect of aging was consequently evaluated only by considering the extractability of contaminants in water or organic solvents at increasing contact times.

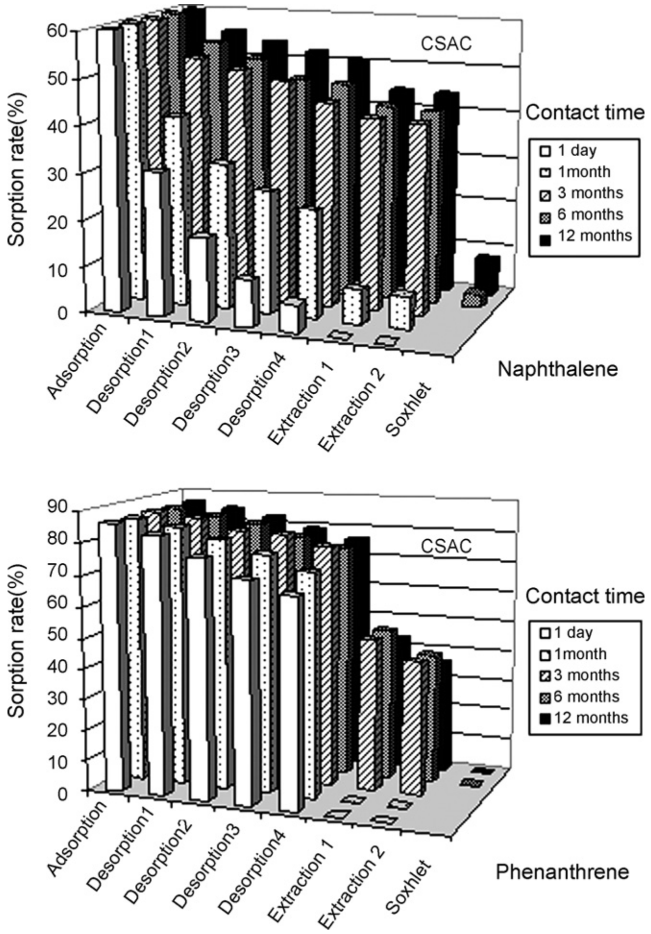

Fig. 5. Sorbed fractions of naphthalene and phenanthrene on culture soil CSAC before and after extraction procedures under unsaturated condition for different contact times ($T = 20\,^{\circ}$C, liquid/solid ratio = 3).

3.2.1. Silty clay

As already observed under saturated conditions (Fig. 1), results obtained under unsaturated conditions confirm that the extractability of naphthalene and phenanthrene decreased with time (Fig. 4). A mere extraction with water was enough to extract phenanthrene or naphthalene retained by silty clay for freshly contaminated samples while extraction with butanol and sonication or even soxhlet extraction was necessary for samples aged for 6 and 12 months. Losses of phenanthrene or naphthalene through volatilization were negligible since the contaminants initially added were quantitatively recovered. However, soxhlet extraction was necessary to extract the few percents of sorbed naphthalene while classical solvent extraction was sufficient for phenanthrene recovery, suggesting a stronger retention of naphthalene; which might be explained by a deeper diffusion of the smaller molecule (naphthalene) into the smallest pores [24].

3.2.2. CSAC and CSAP soils

Results are presented on Figs. 5 and 6, for CSAC soil and CSAP soil, respectively. The results obtained for phenanthrene

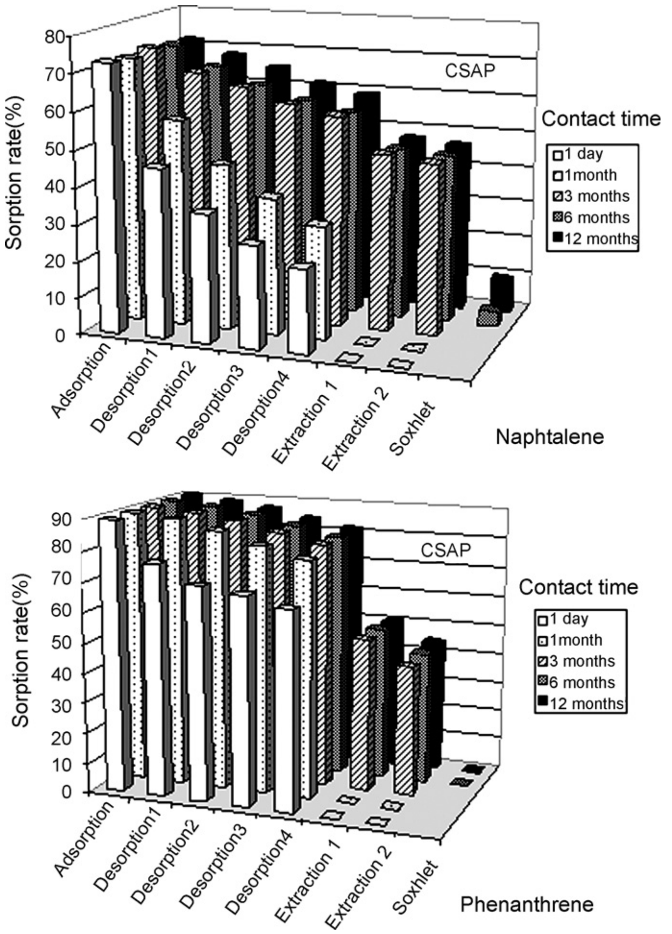

Fig. 6. Sorbed fractions of naphthalene and phenanthrene on meadow soil CSAP before and after extraction procedures under unsaturated condition for different contact times ($T = 20\,^{\circ}\mathrm{C}$, liquid/solid ratio = 3).

are similar to those obtained after aging under saturated conditions with the same soils. For naphthalene however, it was observed that, after one year under unsaturated conditions, more than 16% of the naphthalene initially added were apparently not extractable from both soils (Figs. 5 and 6), while only 2.8% of naphthalene were not extractable from CSAC soil and 0.5% from CSAP soil after one year under water saturated conditions (Figs. 2 and 3). This apparently increased sorption of naphthalene in soils aged under unsaturated vs. saturated conditions may in part be an artefact due to volatilization or biodegradation phenomena which are both favoured under unsaturated conditions. Indeed, the biocide effect of $HgCl_2$ may not be sufficient over one year incubation time under unsaturated conditions where supply of oxygen to micro organisms is increased and may stimulate the growths of aerobic naphthalene degraders. At the analysis of the soxhlet extracts, a new peak was detected just before the one of naphthalene, probably corresponding to some hydroxylated metabolite of naphthalene. Taken into account this peak of naphthalene would reduce the calculated fraction of nonextracted naphthalene to about 8% and 9% for CSAC and CSAP soils, respectively. Hydroxylated intermediate metabolites of naphthalene are known to be more strongly sorbed than the original nonpolar molecule [29]. These metabolites may be then strongly retained in the soils in the form of bound residues [30].

4. Conclusion

The results presented in this study show that PAHs aged under abiotic conditions in soils or silty clay are increasingly retained and less extractable than freshly added contaminants.

The clay used exhibited a significant capacity of retention which was related not only to its relatively high organic carbon content (0.7%) but probably also to the diffusion and physical trapping of naphthalene and phenanthrene molecules between the clay layers.

Aging of naphthalene and phenanthrene in soils was also found to reduce considerably their extractability in water or organic solvents within the first three months of contact. After three months and up to one year, the effect was found to be less drastic as the retention approached 90% to 100% of the amounts of contaminants initially added. These results may be explained by the slow molecular diffusion of the contaminants in the micropores or within the sorbent phases (organic matter), as already described by other authors [31].

Two twin soils were used in this study, which differed mainly in the nature and content of organic matter. Although the retention of naphthalene and phenanthrene on the meadow soil (CSAP) was initially higher than on the cultivated one (CSAC) due to its higher organic carbon content, it was observed that the effect of aging was more significant on the cultivated soil. This result can be related to the higher microporosity of the cultivated soil where the organic matter was probably more humified than in the meadow soil, suggesting that the diffusion of the contaminants in the micropores was the major mechanism of sorption under abiotic conditions. Aging, under water unsaturated conditions, was found to apparently enhance the sorption of naphthalene by the soils over one year of contact as compared to saturated conditions. This was probably due to a partial biodegradation of naphthalene (despite the presence of $HgCl_2$ used as a biocide agent) which resulted in the formation of hydroxylated metabolites more reactive with the soils.

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