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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.
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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.

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].

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

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).

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