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Development of solid-phase microextraction to study dissolved organic matter—Polycyclic aromatic hydrocarbon interactions in aquatic environment

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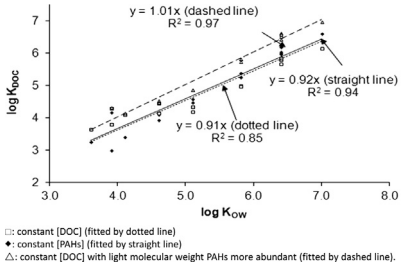
HIGHLIGHTS

- Deuterated naphthalene used as internal standard provides better quantification of freely dissolved PAHs than regular external calibration.
- K_{DOC} values of 18 PAHs were calculated thanks to SPME–GC–MS.
- Competition between PAHs, deuterated PAHs and DOM was demonstrated, pointing out the non-linearity of PAH–DOM interactions.
- Interactions of light molecular weight PAHs are stronger (higher K_{DOC} values) in absence of high molecular weight PAHs.

GRAPHICAL ABSTRACT



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ABSTRACT

Solid-phase microextraction coupled with gas chromatography and mass spectrometry (SPME–GC–MS) was developed for the study of interactions between polycyclic aromatic hydrocarbons (PAHs) and dissolved organic matter (DOM). After the determination of the best conditions of extraction, the tool was applied to spiked water to calculate the dissolved organic carbon water distribution coefficient (K_{DOC}) in presence of different mixtures of PAHs and Aldrich humic acid. The use of deuterated naphthalene as internal standard for freely dissolved PAH quantification was shown to provide more accuracy than regular external calibration. For the first time, K_{DOC} values of 18 PAHs were calculated using data from SPME–GC–MS and fluorescence quenching; they were in agreement with the results of previous studies. Competition between PAHs, deuterated PAHs and DOM was demonstrated, pointing out the non-linearity of PAH–DOM interactions and the stronger interactions of light molecular weight PAHs (higher K_{DOC} values) in absence of high molecular weight PAHs.

1. Introduction

Natural organic matter is a complex mixture of macromolecules originating from the biological and chemical degradation of plants or animals. In aquatic systems, dissolved organic matter (DOM)

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consists of organic macromolecules smaller than 0.45 μm. This fraction is well known for being able to modify the distribution [1,2], the bioavailability [3,4], the degradation [5,6] or the toxicity [1,7] of organic compounds, and particularly of Polycyclic Aromatic Hydrocarbons (PAHs). Because of these modifications, the presence of DOM in samples may also affect the analysis of PAHs [8]. PAHs are hydrophobic organic compounds coming mainly from petroleum and the incomplete combustion of organic matter. They are introduced into surface waters via atmospheric fallout, municipal effluents, leaching or oil spills, and they are environmentally problematic since some of them are mutagenic or carcinogenic [9].

To quantify the impact of DOM on the PAH fate, it is necessary to study the strength of interactions occurring between them. A few techniques can be used to study the interactions between DOM and PAHs, each of them with advantages and drawbacks. One of them, the fluorescence quenching, does not require the separation of free compounds from those associated with DOM. However, because DOM needs to be added to a DOM-free sample containing PAHs, this technique seems to be hardly applicable to samples collected in the natural environment containing PAHs and DOM [10]. Other techniques, particularly extraction or separation methods, can be used in association with analytical techniques, including dialysis, ultrafiltration, reverse phase chromatography or more recently Solid-phase microextraction (SPME). However, reverse phase chromatography was shown to disturb the equilibrium of the sample [11], and ultrafiltration and dialysis could raise sorption problems for hydrophobic compounds due to adsorption on the membrane that complicates free analyte analysis [12,13]. SPME seems to be the most promising technique since it appears to be faster, more sensitive and simpler than other techniques and since it is solvent free [13,14]. SPME, developed by Pawliszyn in the early 1990s [15], consists of a fiber coated with a phase that adsorbs (for sorbents) or absorbs (for polymers) analytes from a liquid, solid or gas sample. As a result of solvent or thermal desorption, analytes are then transferred into a liquid or gas chromatograph before being analyzed.

One aim of this study was to develop SPME coupled to GC–MS to achieve the best sensitivity that would allow for the accurate quantification of all PAHs and their interaction with DOM, at environmental trace concentrations. Particular attention was given to SPME parameters that are usually not greatly detailed in the literature, i.e. which liner is the most efficient, is the fiber gauge an important parameter, metal alloy vs. silica core fibers, etc. This detailed method development was intent to set up a basis for any interested teams that would want to use the same approach, and to give potential explanations of differences observed in papers using the same SPME fibers. A second goal of our study was to compare SPME–GC–MS with dialysis and fluorescence quenching methodologies to define the applicability domain of these three techniques and to characterize interactions between DOM and PAHs.

2. Materials and methods

2.1. Organic compounds

Four PAHs (phenanthrene, fluoranthene, chrysene and benzo[a]pyrene) were used as model compounds for the development of the analytical method, and their corresponding perdeuterated PAHs were used as internal standards for quantitative calibration in SPME (Table 1).

After development, interactions were studied for the 19 PAHs listed in Table 1. Solutions of PAHs were prepared in ethanol and then 50 μL of a solution of 25 $\mu g\,g^{-1}$ were added to 1L of ultrapure water (Milli-Q, Millipore, Molsheim, France) to obtain an aqueous solution of 1 $\mu g\,L^{-1}$ of each PAH. This aqueous solution was sonicated for 5 min to get a good homogenization, but, to avoid PAH adsorption on the stirring bar (which could reach 20% for benzo[a]pyrene, results not shown), no magnetic stirrer agitation was performed. These aqueous solutions were experimentally characterized using liquid–liquid extraction (LLE) with dichloromethane followed by GC–MS analysis. Deuterated PAHs were dissolved in ethanol at a concentration of 250 $ng\,g^{-1}$ and diluted in ethanol if necessary. The solvents used were ethanol absolute HPLC grade (ScharlauChemie S.A, Sentmenat, Spain) and dichloromethane for residue and pesticide analysis (Acros Organics, Geel, Belgium).

The DOM used for this study was Aldrich humic acid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany). This humic acid was added to 500 mL of pure water to obtain an aqueous solution of DOM and the latter was then filtered on a GF/F (Whatman, Maidstone, England) glass fiber filter (0.7 μm). The concentrations of Dissolved Organic Carbon (DOC) were measured using a Shimadzu TOC-V CSN (Shimadzu, Duisburg, Germany). Several aqueous solutions of Aldrich humic acid were prepared for the experiment; all were within $11.0 \pm 0.5\ mg\,L^{-1}$ and were characterized precisely.

2.2. Experimental precautions

All the glassware, after being carefully cleaned with detergent (TFD 7, Franklab, France) and rinsed with ultrapure water, was heated at 450 °C overnight before using it for PAH analyses and it was also rinsed with ultrapure water before DOC and spectrofluorometry analyses. For SPME and LLE experiments, blanks were made to check PAH ambient pollution and to be aware of any possible contamination of the samples. In SPME, blanks were performed by extracting an empty flask for 10 s to check the good desorption of the previous analysis. Generally, blanks represented less than 1% of the PAH areas of samples. For spectrofluorometry experiments, blanks of ultrapure water were made to test the cleanliness of cuvette and to correct spectra for the Rayleigh and Raman scattering bands.

2.3. Experimental protocols and analytical tools

2.3.1. SPME–GC–MS

SPME analyses of the 10 mL spiked water samples were performed with commercially available PDMS (polydimethylsiloxane) and PDMS-DVB (divinylbenzene) coated fibers from Supelco (Bellefonte, USA). Different sizes of the PDMS coating were compared (7 μm and 100 μm) and various parameters, (including extraction and desorption times, temperature, liner type), had to be optimized. After the immersion of the fiber in the sample, it was immediately desorbed into the GC–MS injection port. Analyses were performed in automated mode using a Combipal (CTC Analytics, Zwingen, Switzerland).

The GC was an Agilent 6890 model (Agilent Technologies, Massy, France) equipped with a 5972 mass selective detector, operated with an energy of ionization of 70 eV (electronic impact). The column used was an HP-5MS ((5%-phenyl)-methylpolysiloxane; 30 m × 0.25 mm i.d.; 0.25 μm film; Agilent Technologies, Chromoptic, Courtaboeuf, France). Both SPME and direct liquid injection (after LLE) were performed with the inlet temperature at 250 °C and in the pulsed splitless mode: A pulse pressure of 30 psi was maintained for 1 min, the purge flow to the split vent was 55 $mL\,min^{-1}$ after 2 min, and the gas saver was set at 20 $mL\,min^{-1}$ after 15 min. The carrier gas was helium (purity 5.6, Linde Gas, Toulouse, France) with a constant flow rate of 1.3 $mL\,min^{-1}$ and linear velocity of 42 $cm\,s^{-1}$. The column temperature was initially held at 60 °C for 2 min, and was then increased to 150 °C at 20 $°C\,min^{-1}$, to 250 °C at 15 $°C\,min^{-1}$ and to 310 °C at 10 $°C\,min^{-1}$, where it was held for 3 min. For the determination of PAHs, the mass spectrometer was