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Characteristics of a solid coal tar sampled from a contaminated soil and of the organics transferred into water

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ABSTRACT

Most often, only TOC and the concentrations of the 16 PAHs of the US EPA list are monitored in contaminated soils of former coking plants or MGPs. The objective of the present study was to provide a detailed characterization of the organic extracts of (i) coal tar particles sampled from a contaminated soil and (ii) of water at equilibrium with these particles. Chromatographic techniques were used (HPLC, GC–MS) as well as Fourier Transform Infrared Microscopy. An accurate description was obtained, showing the predominance of aromatic compounds in the coal tar and the preferential transfer of polar compounds and aliphatic hydrocarbons into water.

1. Introduction

Coal tar-contaminated soils have accumulated over decades in the vicinity of former manufactured gas plants (MGPs) and coking plants [1]. Coal tars are Non-Aqueous Phase Liquids (NAPLs) that may have evolved to the solid state [2]. They contain hundreds of organic compounds: aromatic compounds, namely polycyclic aromatic hydrocarbons (PAHs), heterocyclic PAHs, phenol, BTEX, etc. as well as aliphatic and polar hydrocarbons [3]. Most of these chemicals are toxic, some of them being carcinogenic or mutagenic [4]. Coal tars are poorly soluble in water and refractory to biodegradation, they are persistent in contaminated soils and behave as long-term contamination sources. Transfer of organic compounds and of PAHs from coal tars into water has been widely studied [5–8]. Transfer at equilibrium has been generally interpreted by Raoult's law, despite this law may not apply for real coal tars. Mass transfer limitation is mainly due to the transfer through a film at the NAPL/water interface [9–14].

In a previous contribution, we investigated the transfer of organic matter and of the 16 PAHs of the US EPA list from solid coal tar into water [2]. Solid coal tar had been sampled in the soil of a former coking plant. We carried out column experiments with re-circulating water, at three particle sizes and temperatures. The results were interpreted with (i) a linear partitioning model of total organic carbon (TOC) and PAHs between coal tar particles and water and (ii) a diffusion model. In this previous study, the concentration of the 16 PAHs and TOC were considered as global entities. The present contribution aims at providing a fine characterization of the coal tar and of the organic compounds transferred into water at equilibrium. In most papers, only the 16 PAHs of the US EPA list are taken into account but many other organic compounds are transferred into water. More information about these compounds is required, for a better understanding of PAH transfer and better risk assessment.

Characterization was based on the use of complementary analytical techniques: chromatographic analyses were run for the molecular characterization of the extractable organic fractions (gas chromatography coupled to mass spectrometry and high performance liquid chromatography); they were combined to Infra-Red microscopy with Fourier Transform (μIRTF) [14–17]. GC–MS provides accurate information on low molecular mass compounds ($\sim$ 500 Daltons). Infrared spectroscopy is a good complementary analytical method that gives structural indication on the global extractable organic matter.

2. Materials and methods

2.1. Coal tar samples

Coal tar pieces (2 kg) were sampled in the soil of a former coking plant of the North East of France. They were split into cubes (side: 5 cm), solidified in liquid nitrogen, crushed and sieved. Three granulometric classes of spherical beads were obtained, that were stored at 4 °C [2]. In the present study, we worked with the

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particles sieved between 1.9 and 2.0 mm. The elemental composition was determined with a CHNSO analyzer Carlo Erba 1106. The molar fractions were: 55.42% C, 40.92% H, 0.73% N, 0.84% S, 2.09% O exhibiting very low H/C (0.74) and O/C (0.04) atomic ratios. Such values revealed that the aromatization and polycondensation had occurred and correspond to a highly condensed organic matter [17,18].

Coal tar beads were submitted to solvent extraction and the organic extract was analyzed by HPLC, GC–MS and μ-FTIR.

2.2. Transfer of organic compounds into water

Water extraction experiments were performed to measure the transfer of organic compounds into water. A jacketed column containing a fixed bed of coal tar beads (10 g) was flushed by ultra pure water at 20 °C. Water was re-circulated until a steady-state was reached (see details in [2]). The global concentration of dissolved organic matter in the water reservoir (100 mL) was monitored by OD measurement at 254 nm (U-2000 spectrophotometer, Hitachi). The experiment was stopped when a constant OD was reached. The aqueous solution at equilibrium with coal tar particles was analyzed: pH and TOC were monitored (PHM210 MeterLab Tacussel, TOCmeter Appollo 9000), the organic compounds were extracted by liquid/liquid extraction and analyzed by HPLC, GC–MS and μFTIR.

2.3. Extraction and fractionation

2.3.1. Solid extraction

Coal tar particles were extracted in dichloromethane by accelerated solvent extraction system (ASE® 200, Dionex) with cells of 11 mL [19]. The empty cell, with a glass fiber filter inserted on one side and silica glass beads to improve the sample dispersion, was washed at 120 °C for 1 min to remove traces of organic contaminant. Then, an aliquot of solid samples (1 g) was loaded into the cell. Extraction conditions were as follows: 5 min heat up time, 5 min static time, 150% flush, 200 s purge with nitrogen, pressure: 100 bars, temperature: 80 °C. A mass balance provided the extraction yield. The extract was then ready for further fractionation.

2.3.2. Liquid–liquid extraction

The organic compounds of the water were extracted with a mixture 50/50 (v/v) of dichloromethane/hexane: 2 mL of the organic phase were added to 25 mL of the aqueous phase and mixed during 10 min before decantation.

2.3.3. Organic extract fractionation

Aromatic and aliphatic hydrocarbons were separated from polar compounds by liquid chromatography on a silica column eluted by a 65/35 (v/v) pentane/dichloromethane mixture. Polar compounds were recovered with a 50/50 (v/v) methanol/dichloromethane solution. The recovered fractions were weighed.

Further fractionation of hydrocarbons was carried out using a silica column. Successive elutions by pentane and by a 65/35 (v/v) pentane/dichloromethane mixture enabled us to separate aliphatic from aromatic hydrocarbons. The fraction of recovered aliphatic hydrocarbons was very low (less than 1%) but despite this low amount GC–MS analyses could be run.

2.4. Analyses

2.4.1. HPLC

The 16 PAHs of the US EPA list were analyzed by HPLC [2] using a Prosphere column (250 × 4.6 mm, packing diameter 5 μm) and a diode array detector (Bio-Teak instruments) (wavelength: 254 nm). The mobile phase was acetonitrile/water, the flow rate 1.2 mL min^{-1} and the elution gradient: 10 min isocratic mode 50/50 (v/v); 30 min gradient mode from 50/50 to 90/10; 15 min isocratic mode 90/10 and 7 min of isocratic stabilization 50/50 (v/v).

2.4.2. Gas chromatography–mass spectrometry (GC-MS)

Aliphatic and aromatic hydrocarbons and polar compounds were analyzed by gas chromatography–mass spectrometry (HP 5890 Serie II GC coupled to a HP 5972 mass spectrometer) equipped with a split–splitless injector and a 60 m DB-5 J&W, 0.25 mm i.d, 0.1 μm film fused silica column. The temperature program was 60–300 °C at 3 °C.min^{-1} followed by an isothermal stage at 300 °C for 15 min (constant helium flow of 1 mL min^{-1}).

Because of the presence of carboxylic acids in the polar fractions, silylation using BSTFA + TMCS 99/1 (v/v) was carried out to improve chromatographic resolution [20]. A small aliquot of sample was dissolved with the derivative solution at 4 mg mL^{-1} and treated during 15 min at 50 °C. Then, 1 μL solution was directly injected into the gas chromatograph.

The compounds were identified according to their mass spectra and retention time with reference to the Wiley and US National Bureau of Standards computerized mass spectral libraries.

2.4.3. Fourier transform infrared microspectroscopy (*μFTIR*)

Aromatic hydrocarbons and polar compounds were analyzed using the diamond-windows of a compression cell [16]. The μFTIR analysis was performed on a Brücker IFS-88 Equinox spectrometer coupled with a Brücker multipurpose infrared microscope which was fitted with a 250 μm narrow band MCT detector cooled to 77 K. The standard analytical conditions were 15× infrared objective, 40–60 μm diameter infrared spot, 60 scans (30 s) and spectral resolution of 4 cm^{-1}. Spectra were ratioed to the background collected on a clean diamond-window in the same analytical conditions. The assignments of the main IR bands were determined by reference to previous works [15,21,22].

3. Results and discussion

3.1. Extraction–fractionation

The organic extract represented only 33.9 wt% of coal tar particles (Fig. 1a). This low value was consistent with the elemental

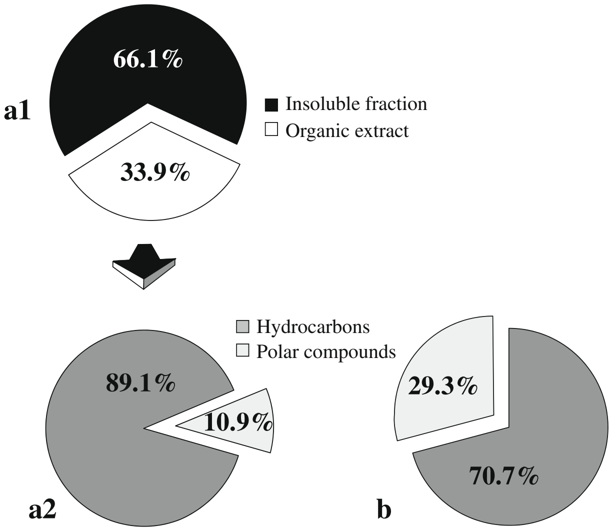

Fig. 1. Weight composition of: (a1) the coal tar particles, (a2) the organic extracts from the coal tar particles and (b) the water at equilibrium with coal tar.