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Aging as the main factor controlling PAH and polar-PAC (polycyclic aromatic compound) release mechanisms in historically coal-tar-contaminated soils

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Abstract

In industrial sites, historically contaminated by coal tar (abandoned coking and manufactured gas plants), other families of organic pollutants than the 16 PAHs (polycyclic aromatic hydrocarbons) classified by the US-EPA can occur and induce potential risk for groundwater resources. Polar PACs (polycyclic aromatic compounds), especially oxygenated and nitrogenated PACs (O-PACs and N-PACs), are present in the initial pollution and can also be generated over time (i.e., O-PACs). Their aqueous solubilities are much greater than those of the PAHs. For these reasons, we need to increase our knowledge on polar PACs in order to better predict their behavior and the potential on-site risk. Batch leaching tests were carried out under various conditions of temperature, ionic strength, and availability of pollutants to determine the mechanisms and key parameters controlling their release. The results show a release of low-molecular weight PAHs and polar PACs mainly by dissolution, while higher molecular weight PAHs are mainly released in association with colloids. Aging mainly controls the former mechanism, and ionic strength mainly controls the latter. Temperature increased both dissolution and colloidal mobilization. The Raoult law predicts the PAC equilibrium concentration for soils presenting high pollutant availability, but this law overestimates PAC concentration in aged soils (low pollutant availability). This is mainly due to limitation of PAC diffusion within coal-tar particles with aging. The most soluble PACs (especially polar PACs) are the most sensitive to aging. For better prediction of the PAC behavior in soils and water resources management, aging needs to be taken into account.

Keywords: Availability; Ionic strength; Oxygenated PACs; Nitrogenated PACs; Groundwater; Colloidal mobilization

Introduction

In Europe, between the eighteenth and twentieth centuries, coal was a major source of energy (Van Krevelen 1993). In order to meet the increase in energy needs, thousands of coking and manufactured gas plants were built for coke and gas production respectively. During the twentieth century, the progressive transition from coal to petroleum and natural gas induced the dismantling or the abandonment of these industrial sites (Mannion 2006). Nowadays, due to these coal-related activities, about 200,000 sites have been diagnosed as polluted by polycyclic aromatic hydrocarbons (PAHs). Due to their toxicity, their mutagenic and carcinogenic potential, 16 PAHs have been listed as priority pollutants by the US Environmental Protection Agency (US-EPA). These 16 PAHs are organic pollutants derived from coal transformation which are under regulation and by consequence measured for site diagnosis or monitored during remediation treatment. However, others families of organic pollutants, especially polar PACs such as oxygenated and nitrogenated polycyclic aromatic compounds (O-PACs and N-PACs), occur on these industrial sites and could induce a risk for superficial and groundwater resources. O-PACs and N-PACs occur in the initial pollution (coal tar) associated with PAHs (Lundstedt et al. 2006a, 2007), but can also be produced (especially O-PACs) during remediation treatments (Lundstedt et al. 2006b, 2007) or during natural attenuation (through biotic or abiotic processes) (Biache et al. 2011; Lundstedt et al. 2007; Wilcke et al. 2014). Recent studies revealed that some O-PACs and N-PACs can be equally or even more toxic than their corresponding PAHs (Lübckevon et al. 2011; Wincent et al. 2015). Moreover, due to their higher solubility and lower lipophilicity compared to PAHs (Lundstedt et al. 2007), polar PACs are leached in higher proportion (Schlanges et al. 2008) and mainly as dissolved form (Lundstedt et al. 2007). As a matter of fact, these polar PACs can be found downstream in the aquifer, while PAHs are only detected near the source, on the tar-contaminated site (Schlanges et al. 2008).

Based on the sole knowledge of PAHs, two main mechanisms are involved in the release of contaminants from coal tar polluted soil into water: (i) PAC dissolution from coal tar and (ii) PAC desorption from the contaminated soil matrixes (mineral or organic constituents). These two mechanisms can be influenced by environmental factors, such as temperature, ionic strength, pH, concentration, and nature of dissolved organic matter (DOM) as well as time. Temperature affects PAH mobilization by increasing (i) their water solubility (Feitkenhauer and Märkl 2003) and (ii) the diffusion of the contaminants into coal-tar particles (Benhabib et al. 2006) or in the pores of soil particles (Feitkenhauer and Märkl 2003). The increase in temperature can lead to a higher PAH mass transfer to water and generally to an enhanced desorption (Enell et al. 2005) and dissolution processes (Benhabib et al. 2006). On the contrary, increase in ionic strength tends to decrease PAH solubility (Schwarzenbach 1993), PAH dissolution (Mahjoub et al. 2000), and desorption processes (Lamichhane et al. 2016). In addition, ionic strength and pH as well as DOM (dissolved organic matter) amount and structure control colloid mobilization in water (Marschner 1998). Colloids are known to be carrier and facilitator phases for PAH mobilization and transportation in water (Marschner 1998). If DOM concentration can increase with pH (Curtin et al. 2016), pH modification has only an indirect effect on PAH release as it has no or limited effect on neutral organic compounds, especially on their dissolution and sorption (Lamichhane et al. 2016). Another major parameter, scarcely discussed in the literature, controlling PAH mobilization into water is time. With time, the contaminant availability is gradually reduced, decreasing the PAH release from coal tar to water (Luthy et al. 1993). This phenomenon, known as "aging" is an important parameter to take into account, especially in historically industrial contaminated site.

In literature, many studies discuss these different parameters in order to describe and predict PAH behavior in contaminated soils. However, industrial soils (from coking plant to manufactured gas plant) are characterized by the predominance of anthropogenic organic matter in which natural recent carbon is absent or limited (Pernot et al. 2013). Thus, they strongly differ from natural (agricultural, forest...) soils. Most of the studies are performed on natural laboratory spiked soils or sediments (Bi et al. 2006; Abu and Smith 2006; Kleineidam et al. 2004) or on fresh pollution (coal tar) (Endo et al. 2008), and may not be representative of historically contaminated soils subjected to aging processes (Luthy

et al. 1993). Furthermore, to our knowledge, only few studies have been published on the parameters affecting O-PAC and N-PAC water release.

The purpose of the present study is to improve our knowledge (i) on the parameters influencing O-PAC and N-PAC release from soil to water and (ii) on the involved mechanisms. Two industrial soils, sampled on coking plant sites were used to perform 24-h batch leaching tests according to a design of experiments (DOE) with three parameters (i) temperature, (ii) ionic strength, and (iii) aging (or availability level). The pH was not considered in the DOE as the two coking plant soils presented a strong buffering capacity (pH could not be set without affecting the ionic strength). After carrying out the batch leaching tests, the soil-water mixture was separated and the leachates were analyzed to determine the aqueous concentration at equilibrium of the 16 US-EPA PAHs, but also 11 O-PACs and 5N-PACs. The differences of behavior between the two families were studied, and the water release mechanisms were investigated.

Materials and methods

Soils samples

The PAC-polluted soils were sampled from two former coking plants in Lorraine (France): COK1 (Homécourt) and COK2 (confidential site). COK1 was in operation from 1922 to 1981 and COK2 from 1912 to 1970, the pollution having thus aged over periods from 30 to 100 years. After sampling, the soils were air-dried, sieved at 2mm, and freeze-dried. The chemical (pH, carbonate, and total organic carbon contents) and physical characteristics (Laboratoire d'Analyse des Sols, INRA, Arras, France), the mineral and maceral compositions (Weatherford Laboratories, Shenandoah, TX, USA) were determined for both soils (Table 1).

Thermal treatment

A thermal treatment was applied on both soils to increase the pollution availability without modification of the other main compartments (mineral fraction and insoluble organic matter) (Biache et al. 2015; Usman et al. 2016). The soils were preheated at 100 °C for 5 days in 2-L Schott bottles hermetically sealed under inert atmosphere (Ar) to prevent air oxidation. Analyses were performed on the initial and preheated soils to determine the thermal treatment impact on PAC content and distribution.

Batch leaching test

Water solution (500 mL), prepared using deionized water (ELGA PURELAB Option-Q) plus a biocide azide (NaN_3 , 200 mg/L) to prevent PAC biodegradation, was added to 50 g of soil (liquid/solid ratio of 10) in a 1-L Schott bottle. The soil-water mixture was shaken under dark conditions with a rotary-shaker (Heidolph, Reax 20) at 10 rpm during 24 h (NF ISO 18772). The soil-water mixture was then pre-separated by centrifugation (5 min, 2500 G). The supernatant was filtered by vacuum filtration on a 0.70- μm pore-sized glass microfiber filter (Grade GF/F, Whatman). The leachates (20 mL) were kept for dissolved organic carbon (DOC) measurement, and the remaining volume (400 mL) was extracted by solid-phase extraction (SPE) for PAC quantification.

Experimental design

A DOE with three parameters and two levels was set up to study the influence of each parameter and their interactions on PAC release from soil to water. The parameters investigated were temperature (3 °C (t), 28 °C (T)), ionic strength evaluated by electrical conductivity (EC) (500 $\mu\text{S}/\text{cm}$ (s), 5600 $\mu\text{S}/\text{cm}$ (S) for COK1 and 2000 $\mu\text{S}/\text{cm}$ (s), 5600 $\mu\text{S}/\text{cm}$ (S) for COK2), and PAC availability (limited initial availability (a) or thermally increased availability (A)). High levels of ionic strength were chosen to

match those found on field samples, mainly due to high sulfate content. The batch leaching tests were performed in temperature-controlled chamber, by adding a CaCl₂ water solution to the initial solution to modify the ionic strength and with either the initial soil (low availability) or the preheated soil (high availability). The different conditions of the DOE are summarized in Table S1. To evaluate the repeatability of the experiments and measurements during the DOE, triplicates were carried out under intermediate conditions (central points of the DOE: 16 °C, EC of 3050, and 3800 µS/cm for COK1 and COK2 respectively, initial and preheated soils mixed with a 1:1 m:m ratio— Table S2).

Table 1: Grain texture, agronomic parameters, maceral, and mineral composition of the two coking plant soils (COK1 and COK2)

	COK1 soil	COK2 soil
Grain texture (without decarbonation)		
Clay (< 2 µm) (g/kg)	96	55
Fine silt (2-20 µm) (g/kg)	138	114
Coarse silt (20-50 µm) (g/kg)	83	94
Fine sand (50-200 µm) (g/kg)	134	190
Coarse sand (200-2000 µm) (g/kg)	549	547
Agronomic parameters		
pH (water)	8.77	7.77
Total carbon (g/kg)	150	95
Organic carbon (g/kg)	110	85
Total CaCO ₃ (g/kg)	329	80
Phosphorus P ₂ O ₅ (g/kg)	-	0.049
Total nitrogen (g/kg)	1.82	1.55
Maceral and mineral composition		
- <u>Organic matter (% vol)</u>	<u>26.6</u>	<u>21.1</u>
Anthropogenic (% vol)	26.0	20.8
- Coal (% vol)	9.3	6.9
- Coke and char (% vol)	12.1	12.1
- Tar and pitch (% vol)	4.6	1.7
Natural (% vol)	0.6	0.3
- <u>Mineral matter (% vol)</u>	<u>73.4</u>	<u>78.9</u>
Anthropogenic (fly ash/bottom ash) (% vol)	15.8	19.9
Sediments (% vol)	57.6	58.9

Analytical methods

pH and electrical conductivity

Before soil/leachate centrifugation, pH and EC were measured using a multi-probes pH-EC-meter (HANNA HI 255).

Dissolved organic carbon measurements

The leachate DOC was determined, within 24 h at the most after the experiment, with a TOC-V CSH analyzer (Shimadzu) according to a catalytic combustion oxidation method carried out at 680 °C. The DOC results were normalized to the mass of the leached soil.

Organic matter extraction for PAC quantification in soils

The organic matter was extracted from the soil (2 g) with dichloromethane using an accelerated solvent extractor (ASE 350, Dionex; 2 cycles of 5 min at 130 °C, 100 bars). Sodium sulfate and copper powder were added to each sample prior to extraction to eliminate residual water and

molecular sulfur, respectively. After adjusting the volume at 20 mL with dichloromethane, aliquots of the solvent extracts (3 mL) were placed in preweighed vials. The extractable organic matter (EOM) content was determined by weighing the vials after solvent evaporation under a gentle N₂ flow.

PAC extraction from the leachates

In order to quantify the PACs leached from the soils during the leaching tests, the filtered leachates were extracted by SPE using Oasis HLB cartridges (200 mg, 6 mL, Waters). Before extraction, the SPE cartridges were conditioned with the following solvents: dichloromethane: ethyl acetate (v:v; 8:2), methanol, and deionized water. Deuterated surrogates ([²H₈]dibenzofuran, [²H₁₀]fluorene, [²H₁₀]anthracene, [²H₈]anthraquinone, [²H₁₀]fluoranthene, and [²H₁₂]benzo[ghi]perylene, supplied by CIL Cluzeau; 100 µL at 24 µg/mL) were added to the leachates which were then eluted through the SPE cartridges at a flow rate of 10 mL/min. The SPE cartridges were air-dried, and the PACs were eluted three times with 4 mL of dichloromethane: ethyl acetate (v:v; 8:2). Eluted compounds were concentrated to 1 mL of dichloromethane after evaporation with a gentle N₂ stream for GC-MS (gas chromatograph-mass spectrometer) analysis. Recoveries of the surrogates were determined after each SPE extraction and each analytical result was corrected accordingly.

PAC quantification

PAC quantification (in soils and leachates) is carried out using internal calibration. An internal deuterated PAC standard mixture ([²H₈]naphthalene, [²H₇]quinoline, [²H₁₀]acenaphthene, [²H₈]fluorenone, [²H₁₀]phenanthrene, [²H₁₀]pyrene, [²H₁₂] chrysene, and [²H₁₂]perylene, supplied by CIL Cluzeau; 20 µL at 12 mg/mL) was added to the organic extract (80 µL) before GC-MS analyses. The instrument was calibrated using internal calibration method for 16 PAHs, 11 O-PACs, and 5N-PACs at 12 different concentrations (low calibration range: 0.024, 0.048, 0.06, 0.12, 0.18, and 0.3 µg/mL; high calibration range: 0.3, 0.6, 1.5, 3, 6, and 9.6 µg/mL; deuterated internal standard: 2.4 µg/mL). The two calibration ranges were verified with control standard analyses (at 0.06 and 3 µg/ mL) every ten samples and a deviation lower than 20% was accepted. Experimental and analytical blanks were also monitored regularly to assess external contamination. Analyses were performed on an Agilent Technologies 7820A GC equipped with a silica DB5-MS column (60 m× 0.25mm id × 0.25 µm film thickness) coupled to an Agilent Technologies 5975 inert MS operating in single-ion monitoring (SIM) mode (Table S3). The oven temperature was programmed as follows: 70 °C (held 2 min) to 130 °C at 15 °C/min, then 130 to 315 °C at 4 °C/min, and then 315 °C (held 25 min). The carrier gas was helium at 1.5 mL/min constant flow. The injection was set in splitless mode at 300 °C.

Soil specific area

The specific area of the soil was determined before and after the thermal treatment (Belsorp-mini II, BELJAPAN Inc). Prior adsorption, the samples were degassed at 30 °C under vacuum. The conventional B.E.T method was performed to complete step-by-step volumetric adsorption desorption cycles of nitrogen gas at 77 K. The soil specific area was calculated according to the NF X 11-621 method (AFNOR 1975).

Results

Initial soil characteristics

The soil textures (Table 1) were characterized by high sand (> 68%) and low clay (< 9.6%) contents and belonged to the sandy loam and loamy sand classes for COK1 and COK2, respectively, according to the FAO guideline for soil description (Food and Agriculture Organization of the United Nations 2006). The pH values were high (8.8 and 7.8 in COK1 and COK2 respectively) due to high carbonate content (especially in COK1) (Table 1). They also exhibited a high TOC content (11.0 and 8.5% in COK1 and COK2 respectively). In addition, the mineral and maceral compositions, determined by particle counts, revealed the predominance of anthropogenic organic matter (coal, coke, and coal

tar), whereas the natural organic matter (NOM) was almost absent (< 1%). These characteristics are typical of coking plant soils (Pernot et al. 2013), making them clearly different from natural soils (forest, agricultural...).

The EOM content was higher in COK1 than in COK2 (21.4 and 14.3 g/kg respectively) and represented nearly 20% of the TOC for both soils (Table S4). The COK1 and COK2 soils also differed in their PAC content, with concentrations of 16 PAHs (2424 and 936 mg/kg respectively), 11 O-PACs (333 and 148 mg/kg respectively), and 5 N-PACs (31 and 18 mg/kg respectively), being 2.6, 2.3, and 1.7 times higher in COK1 than in COK2, respectively. However, the proportion of polar PACs compared to total dosed PACs was equivalent in both soils (12–13% of O-PACs and 1–2% of N-PACs) (Table S4). In addition, the PAC molecular distribution was characterized by the predominance of (i) 3–4 ring PAHs (from fluoranthene to chrysene in COK1 and from phenanthrene to chrysene in COK2); (ii) 3 O-PACs (benzo(a)fluorenone, benzanthrone, and benzo(cd)pyrenone in COK1 and dibenzofuran, 9H-fluorenone, and benzo(a) fluorenone in COK2) among the 11 analyzed O-PACs; and (iii) 2 N-PACs (carbazole and benzo(c)acridine) among the five analyzed N-PACs.

Preheated soil characteristics

The thermal pretreatment performed to increase the availability of the pollutants neither affected the EOM concentration nor the 16 PAH and N-PAC contents and their respective distribution in both soils (Table S4). An increase (~30%) in O-PAC content was observed (from 333 to 442 mg/kg and 148 to 196 mg/kg for COK1 and COK2, respectively). The most affected O-PACs were 9H-fluorenone, benzo(a)fluorenone, and benzoanthracenedione, but their distributions were not modified. This higher O-PAC content could be an evidence of an air oxidation of the PAHs into O-PACs (Biache et al. 2011; Faure 2003; Hanser et al. 2015) in spite of the use of an inert atmosphere during the preheating treatment. Nevertheless, the O-PAC proportion of the analyzed PACs remained similar between the preheated soils (15 and 17% in COK1 and COK2, respectively) and the initial soils (12 and 13% in COK1 and COK2, respectively) (Table S4). After preheating, the soil specific areas varied from 12.8 to 5.9 m²/g (54% decrease) in COK1 and from 15.1 to 11.4 m²/g (25% decrease) in COK2 (Table S4). As both soils did not present any microporosity, we assumed that when heated, the coal tar at the surface of the soil particles melted due to lower viscosity and either covered larger area (decreasing the surface roughness) or agglomerated the particles into larger-sized pieces (decreasing the free area for N₂ adsorption). Simultaneously, no change of the mineral phases, confirmed by DRX analyses (not shown), was observed after the thermal pretreatment.

Relative standard deviation and validation of the design of experiments

Based on the results of the triplicates analyzed during the DOE, relative standard deviations (RSD) were calculated for DOC, PAHs, O-PACs, and N-PACs and expressed in percentage (Table S2). Globally, the RSD could be considered as acceptable considering the multiple steps required from the start of the batch leaching test to the final analysis. Naphthalene was excluded from the monitored PAHs as it is the most volatile of the studied PACs and the most sensitive to the number of experimental and analytical steps performed for the DOE. This was confirmed by the lower RSD found when considering 15 PAHs compared to the 16 PAHs (respectively 8 and 10% for COK1 and 4 and 8% for COK2). These low RSD validated the DOE and the comparison of the different responses obtained from the different conditions of the batch leaching tests.

Influence of availability, ionic strength, and temperature on DOC, PAH, O-PAC, and N-PAC release

To highlight the main trends, the DOC and PAC concentrations in the leachates were compared to those obtained under “raw” conditions defined as low-level conditions: availability (initial soil (a)), ionic strength (without CaCl₂ addition (s)), temperature (3 °C (t)).

Table 2 : DOC, Σ 15 PAH, HWM PAH, LMW PAH, Σ 11 O-PAC and Σ 5 N-PAC concentration differences (in percentage) induced by the temperature (ast vs. asT), the ionic strength (ast vs. aSt) or the availability (ast vs. Ast) modifications in COK1 and COK2 leachates (upper and lower cases of a, s and t correspond to high and low parameter levels respectively)

Parameter Modification	Soil	DOC (mg/L)		Σ 15 PAHs ($\mu\text{g/g}$)		LMW PAHs ($\mu\text{g/g}$)		HWM PAHs ($\mu\text{g/g}$)		Σ 11 O-PACs ($\mu\text{g/g}$)		Σ 5 N-PACs ($\mu\text{g/g}$)	
		Conc. Diff (%)	RSD (%)	Conc. Diff. (%)	RSD (%)	Conc. Diff. (%)	RSD (%)	Conc. Diff. (%)	RSD (%)	Conc. Diff. (%)	RSD (%)	Conc. Diff. (%)	RSD (%)
ast→asT (increase in Temperature)	COK1	33,9	1,2	16,7	2,8	6,0	1,0	89,1	7,2	-2,9	-0,7	16,7	0,3
	COK2	45,1	4,0	21,9	1,8	20,5	1,7	100,5	20,5	24,4	3,2	42,3	3,4
ast→aSt (increase in Ionic Strenght)	COK1	-33	-1,2	-26,6	-4,5	-19,3	-3,3	-76,6	-6,2	-10,4	-2,5	-3,2	-0,1
	COK2	-7,6	-0,7	-3,9	-0,3	-3,3	-0,3	-38,9	-7,9	-0,8	-0,1	-10,4	-0,8
ast→Ast (increase in Availability)	COK1	177,2	6,2	153,8	25,7	177,3	30,2	-5,0	-0,4	153,2	36,2	397,9	7,5
	COK2	194,8	17,4	365,3	29,7	368,4	30,2	192,1	39,2	446,4	59,4	694,1	55,6

Σ 15 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA except naphthalene. LMW-PAHs: Sum of low molecular weight PAH concentrations (acenaphthylene to pyrene). HWM-PAHs: Sum of high molecular weight PAH concentrations (benzo(a)anthracene to benzo(ghi)perylene). Σ 11 O-PACs: Sum of the concentrations of the 11 O-PACs quantified in this study. Σ 5 N-PACs: Sum of the concentrations of the 5 N-PACs quantified in this study. The Relative Standard Deviations (RSD) are calculated from the results of the three replicates.

In order to clarify experimental conditions used in the text, the following nomenclature will be used:

- Availability: initial soil (a), preheated soil (A)
- Ionic strength: without CaCl₂ addition (s), with CaCl₂ addition (S)
- Temperature: 3 °C (t), 28 °C (T)

The effect of temperature (28 °C) was evaluated by comparing (ast) with (asT), the effect of ionic strength was evaluated by comparing (ast) with (aSt) and the influence of the availability level was evaluated by comparing (ast) with (Ast) (Table 2). The effects of the three parameters were then expressed in proportion of change (percentage of increase or decrease).

Availability For both soils, the increase in pollutant availability induced a strong increase in DOC, PAH, O-PAC, and N-PAC concentrations in water (Table 2). The effect of the increase in availability on DOC was similar for both soils (+ 177 and + 195% in COK1 and COK2, respectively). This increase was also observed in the same range for PAH and O-PAC concentrations for COK1 leachates (+ 154 and + 153%, respectively) and more pronounced for COK2 leachates (+ 365 and + 446% for PAH and O-PAC contents, respectively). N-PACs exhibited the more important increase in their water concentrations due to the enhanced availability (+ 398 and + 694% in COK1 and COK2, respectively) (Table 2). In COK2, LMWPAHs were more affected by the availability increase than HMW-PAHs (+ 368% for LMW and + 192% for HMW), whereas in COK1, LMW-PAHs increased by 177% while HMW-PAHs remained stable (Table 2).

Ionic strength For both soils, an increase in ionic strength caused lower DOC release, – 33 and – 8% in COK1 and COK2, respectively (Table 2). The same trend was observed for PAH, O-PAC, and N-PAC contents in both samples with a less pronounced decrease, except for N-PAC content in COK2 leachates. The effect of ionic strength was globally higher on COK1 compared to COK2. HMW-PAH concentrations were mostly affected by the increase in ionic strength with a 77 and 39% decrease for COK1 and COK2 leachates, respectively, while LMW-PAH quantities were reduced of 19 and 3% in COK1 and COK2 leachates, respectively (Table 2).

Temperature An increase in temperature (from 3 to 28 °C) induced higher DOC, PAH, O-PAC, and N-PAC releases into water, except for O-PACs in COK1 leachates where a minor decrease was observed (Table 2). The temperature effect was more intense on COK2 compared to COK1. For COK2, temperature increase had a similar effect on PAH and O-PAC mobilization (+ 22 and + 24%, respectively), and on DOC and N-PAC mobilization (+ 45 and + 42%, respectively). For COK1, temperature increase led to an increase in PAH and N-PAC contents (+ 17%), whereas O-PAC concentration remained stable (– 3%). For both samples, the increase in temperature induced a much higher effect on HMW-PAHs than on LMW-PAHs (89 and 6% for COK1 and 100 and 20% for COK2 for HMW and LMW-PAHs respectively—Table 2).

Discussion

Global behavior and mechanisms involved in the release of PACs

PACs vs. DOC in water PAH and polar PAC concentrations which represent 0.5 to 2% of the DOC content were linearly correlated to the DOC into leachates (Fig. 1). A linear correlation between DOC and PAHs is also observed by Benhabib et al. (2006) and Totsche et al. (2006) and suggests a link between DOC and PAH content as well as between DOC and polar PACs. Although the PACs analyzed in this study represented a tiny proportion of the DOC, it shows that PACs behave similarly to the other organic compounds released into water. The specific organic composition of our soils mainly inherited from coal transformation industries (Table 1) with marked polycyclic aromatic signature can explain the linearity observed between DOC and studied PACs

Polar PACs vs. PAHs in water In both coking plant soils, the polar PAC proportions comprised between 13.0 and 16.1% (raw and preheated COK1, respectively) and between 15.1 and 19.1% (raw and preheated COK2, respectively) of the total PAC content (Table S4). Whatever the conditions applied to the leaching experiment (temperature, ionic strength, and availability), the polar PACs in the leachates

represented 52 to 62% (COK1) and 51 to 58% (COK2) of the total PACs (Table S1). This difference of polar-PAC proportion between soils and leaching waters clearly indicates a preferential mobilization of polar PACs (enrichment by a factor 2 to 4 for O-PACs and 5 to 14 for N-PACs) compared to PAHs. Lundstedt et al. (2007) also showed through column experiments the preferential mobility of O-PACs compared to PAHs. The presence of heteroatoms (O or N) in the structure of the polar PACs induces a higher solubility. Consequently, the final concentration of an individual PAC into water seems to be controlled by the combination of its water solubility and its initial soil concentration.

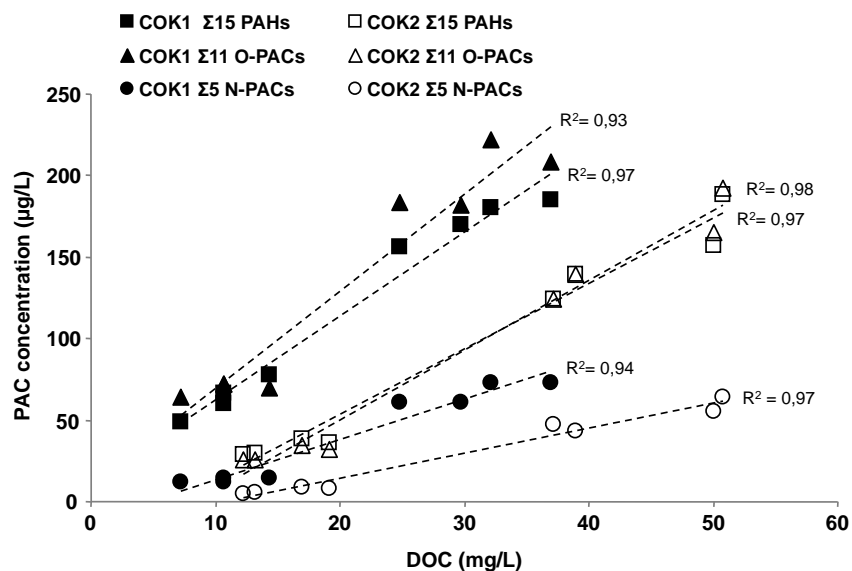


Figure 1: Σ 15 US-EPA PAH, Σ 11 O-PAC and Σ 5 N-PAC concentrations in the leachates as a function of dissolved organic carbon (DOC) content in COK1 and COK2 leachates whatever the temperature (t or T), the ionic strength (s or S) and the availability (a or A) level. Σ 15 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA except naphthalene. Σ 11 O-PACs: Sum of the concentrations of the 11 O-PACs quantified in this study. Σ 5 N-PACs: Sum of the concentrations of the 5 N-PACs quantified in this study.

PAC release by dissolution

In coal-tar-contaminated soils, the main mechanism involved in the PAH release is known to be dissolution and is described by Raoult's law (Endo et al. 2008; Mahjoub et al. 2000). This law defines the equilibrium concentration of a compound in water as function of the compound water solubility and its molar fraction in the initial phase in contact with water. Recent studies showed that Raoult's law could also describe the concentrations of O-PACs and N-PACs at equilibrium (Endo et al. 2008). Raoult's law is defined and simplified (Endo et al. 2008) as follows:

$$C_{w-dissolution} = (C_0 \times MW_{ct} \times S_{PAC}) / (MW_{PAC} \times EOM)$$

With $C_{w-dissolution}$, the compound concentration in water in equilibrium with the soil (mg/L), C_0 , the initial compound concentration in soil (mg/g soil), MW_{PAC} and MW_{ct} , the PAC and coal-tar molecular weights occurring in soil respectively (g/mol), EOM, the extractable organic matter content (mg/g soil) and S_{PAC} , the PAC solubility in the aqueous phase (mg/L) (Table S4). For compounds that are solid at ambient temperature (all studied PACs except quinoline), the subcooled solubility must be used instead of the crystal solubility as these compounds are already dissolved in the coal-tar phase (Lee et al. 1992). For the calculations, the MW_{ct} was determined by size exclusion chromatography (Table S4).

The PAC concentrations found in leachates, whatever the conditions of availability and ionic strength applied on the leaching experiment, were plotted and compared to those predicted by Raoult's law (Fig. 2). To be consistent with the solubility data found in the literature (25 °C), only the

leachates obtained at 28 °C (T) were considered. Whatever the soil, the concentrations obtained for high availability level show reasonable agreement with Raoult's law prediction for soluble compounds including LMW-PAHs and O-PACs (solubility > 0.2 mg/L). At low availability level, Raoult's law prediction overestimates the concentrations for these compounds. Raoult's law does not allow good prediction for N-PACs whatever the level of availability probably linked to the higher polarity of these compounds than PAHs and the studied O-PACs. Indeed, Raoult's law is generally applied to predict solubility of apolar compounds such as PAH (Schwarzenbach 1993).

Raoult's law predicts well the concentration of HMW-PAH leachates whatever the ionic strength in the case of COK2 leachates but only at high ionic strength levels for COK1 leachates (Fig. 2). This clear distinction observed for COK1 leachates at low ionic strength between soluble compounds (solubility > 0.2 mg/L) and HMW-PAHs (solubility < 0.2 mg/L) reveals two different mechanisms of PAC release into water according to their solubilities.

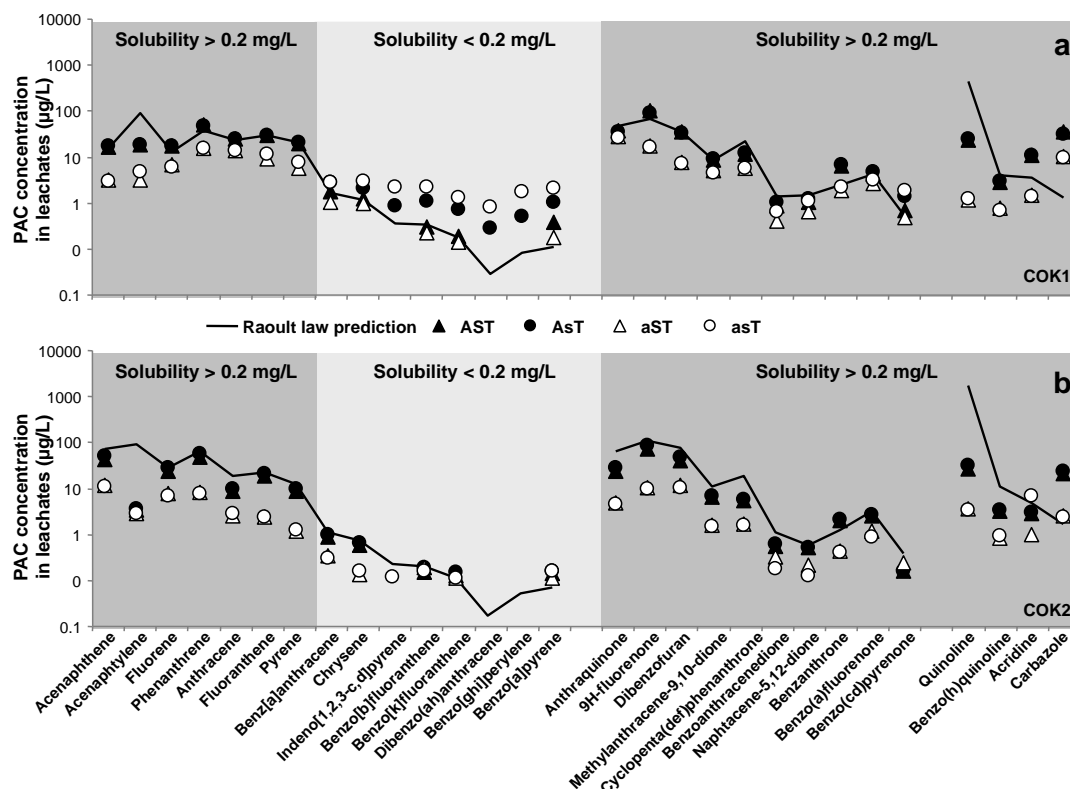


Figure 2: Individual PAC ($\mu\text{g/L}$) concentrations (in Log scale) in leachates from (a) COK1 and (b) COK2 soils for AST (\blacktriangle), AsT (\bullet), aST (\triangle) and asT (\circ) conditions. Upper and lower cases correspond to high and low parameter levels, respectively. PACs are classified depending on their solubility (grey background: > 0.2 mg/L and white background: < 0.2 mg/L). The black line corresponds to the PAC concentrations deduced from the Raoult law. Perinaphtenone and benzo(a)acridine are not considered due to the lack of reliable data about their respective solubilities

PAC mobilization by colloid release

To distinguish the two mechanisms involved in the release of HMW-PAHs identified previously, only the results of COK1 are discussed.

The ionic strength increase induced a decrease in PAC concentration (Table 3). The presence of ions in solution is known to reduce the solubility of neutral or nonpolar compounds like PAHs (Schwarzenbach 1993). During dissolution processes, a reduced PAH mobilization is observed as ions increase the polarity of the aqueous phase and repel PAHs from water molecules (Mahjoub et al.

2000). In our experiment, this effect was increasingly marked with the decrease in PAC polarity (N-PACs < O-PACs < PAHs) (Table 3). It is consistent with previous works of Mahjoub et al. (2000) and reveals that more soluble compounds like polar PACs are less affected by ionic strength modification.

The increase in ionic strength caused mainly a reduction of the PAH release which was much higher for HMW-PAHs than for LMW-PAHs (Table 3). The clear distinction between these two classes of compounds, in regard to ionic strength changes, suggests different release mechanisms as previously discussed. Moreover, at low ionic strength, the HMW-PAHs were released in water above their solubility limits (Fig. S1), implying another mechanism than dissolution for HMW-PAH mobilization as already shown by the Raoult law prediction (cf. § 4.2).

It is known that low ionic strength can favor the mobilization of colloids or soil particles in water (Ryan and Elimelech 1996). In our experiments, the increase in ionic strength stabilized the colloids or particles in soil by neutralizing the negative charges of mineral or organic particles and consequently decreased the repulsion between each other. In addition, the cations control the configuration of the colloids or soil particles by binding them to the solid phase through ternary surface complexes or by condensing them through intramolecular cation bridging (Marschner 1998). All these processes tend to decrease the release of colloids or soil particles into water (Kanti and Khilar 2006). On the opposite, the leaching with low ionic strength solution induced a release of cations from soil particles to the water leading to surfaces negatively charged, causing repulsion but also breaking of the ternary surface complexes and intramolecular cation bridging (Marschner 1998).

In our case, the good correlation between HMW-PAH concentrations in water at low ionic strength and their concentrations in soil (Fig. S2) is compatible with a mobilization of these compounds in association with colloids or soil particles. Other authors already identified this mechanism as the main release mechanism for HMW-PAHs (Chin et al. 1997; Lundstedt et al. 2007).

Thus, due to their low solubilities, HMW-PAHs are mainly released in association with colloids, and this release is controlled by ionic strength. Simultaneously, a part of polar PACs and LMW-PAHs is also probably released in association with colloids but the dissolution process conceals this mechanism due to their higher solubility compared to HMW-PAHs. Additionally, it has to be pointed out that mechanisms involved in the release of PACs depend on the soil characteristics, as shown by the differences of behavior between COK1 and COK2 due to different levels of initial ionic strength (initial ionic strength in COK2 leachates is four times higher compared to COK1 leachates).

Table 3 : Influence of ionic strength modification on the DOC, PAH, LMW-PAH and HMW-PAH, O-PAC and N-PAC concentrations released in COK1 leachates at low (t) and high (T) temperature conditions and at low (a) and high (A) availability level.

Parameter Modification	DOC		Σ 15 PAHs		LMW PAHs		HMW PAHs		Σ 11 O-PACs		Σ 5 N-PACs	
	Conc. Diff (%)	RSD (%)	Conc. Diff (%)	RSD (%)	Conc. Diff (%)	RSD (%)	Conc. Diff (%)	RSD (%)	Conc. Diff (%)	RSD (%)	Conc. Diff (%)	RSD (%)
ast→aSt	-33,0	-1,2	-26,6	-4,5	-19,3	-3,3	-76,6	-6,2	-10,4	-2,5	-3,2	-0,1
asT→aST	-25,4	-0,9	-23,2	-3,9	-7,0	-1,2	-84,5	-6,8	3,2	0,7	2,7	0,1
Ast→AST	-16,5	-0,6	-7,7	-1,3	-5,2	-0,9	-58,1	-4,7	1,0	0,2	0,4	0,0
AsT→AST	-13,0	-0,5	-2,7	-0,5	0,3	0,1	-58,9	-4,8	6,5	1,5	1,0	0,0

Σ 15 PAHs: Sum of the concentrations of the 16 PAHs listed by the US-EPA except naphthalene. Σ 11 O-PACs: Sum of the concentrations of the 11 O-PACs quantified in this study. Σ 5 N-PACs: Sum of the concentrations of the 5 N-PACs quantified in this study. The Relative Standard Deviations (RSD) are calculated from the results of the three replicates.

Effect of aging on PAC dissolution

In this section, results obtained at high ionic strength were selected (i) to focus on the effect of availability on PAC dissolution and (ii) to overcome the bias induced by colloid mobilization.

As discussed earlier, polar PACs and LMW-PAHs were mainly released according to a dissolution process described by Raoult's law. The log-log plot of the partitioning coefficient K_d (division of the PAC concentration in soil by the PAC concentration in water) and the solubility of the polar PACs (O-PACs and N-PACs) and PAHs indicate good correlations for both soils whatever the availability level (Fig. 3). These results show that dissolution processes occur at high and low availability. For both soils, when availability is low, higher K_d values (lower concentrations in the leachates) are obtained for the most soluble PACs while K_d values for less soluble PACs are less impacted. This was previously observed (Table 2) especially in the case of COK2 for which increasing effect of availability lead to increasing solubility (with N-PACs > O-PACs > PAHs). Although the dissolution process did operate at low availability level, these observations tend to show that aging impacted the most soluble PACs (polar PACs and LMW-PAHs) by decreasing their concentrations in water to a higher extent compared to less soluble PACs (HMW-PAHs).

The K_d values measured at high availability present similar values to those predicted by Raoult's law (Fig. 3), while K_d values obtained for leachates with low availability present higher deviation, the deviations being higher for COK2 leachates. Luthy et al. (1993) reported a deviation from the concentration at equilibrium predicted by Raoult's law in the case of aged coal tars. Our results (Fig. 3) show increasing deviation to Raoult's law from high to low availability and are thus confirming their observations. Considering the lower deviation at high availability level, we can consider that the operated thermal pretreatment allowed erasing or partially erasing the effect of aging.

Some authors studied the influence of aging on the DOM and PAH transfer to water (Ghoshal et al. 2004; Luthy et al. 1993; Mahjoub et al. 2000; Totsche et al. 2003). The authors observed the formation of a higher viscosity film at the interface after only few hours of contact between the fresh coal tar and water. Ghoshal et al. (2004) attribute the film formation to interactions between the constituents of the coal-tar and the water molecules. Under soil conditions (vadose zone), oxidation and polymerization processes can occur and be responsible for the formation of a film at the water/coal-tar interface (Totsche et al. 2003). In addition, the fast dissolution of the most soluble compounds outcompetes their diffusion within the coal tar. This prevents their renewal at the coal-tar water interface and is responsible for the depleted zone. It also explains the formation of the film and the higher viscosity at the interface (Mahjoub et al. 2000). The film occurrence at the interface mainly causes a decrease in diffusion and mass transfer coefficients rather than a decrease in the partitioning between the two phases (Ghoshal et al. 2004). Inversely, Benhabib et al. (2006) observed a decrease in the PAH equilibrium concentration with aging of coal-tar particles without any contribution of a film at the interface. The decrease in the partitioning is attributed to limitation in PAC diffusion within coal-tar particles that depends only on the particle size and on temperature. The main difference between these studies is the history of the material used for the experiments, namely the time scale of the contact between coal tar and water. Ghoshal et al. (2004) and Luthy et al. (1993) used fresh liquid NAPL or coal tar aged for few days in laboratory, while Benhabib et al. (2006) used aged solid-like coal tar sampled on former coking plants. Liu et al. (2009) observed an important depletion of the most soluble compounds after a 5-year in situ aging period which induced a solidification of the coal tar. These authors observed also a large decrease in the equilibrium concentration. Thus, while a viscous interfacial film controls the release of PAHs into water in the case of freshly aged liquid coal tars, the influence of this film becomes negligible in regard to the increased viscosity of the coal tar that occurs after larger aging periods. After such aging period, the diffusion within the coal-tar particles becomes the main process controlling the PAC release into water. This was confirmed by Ortiz et al. (1999).

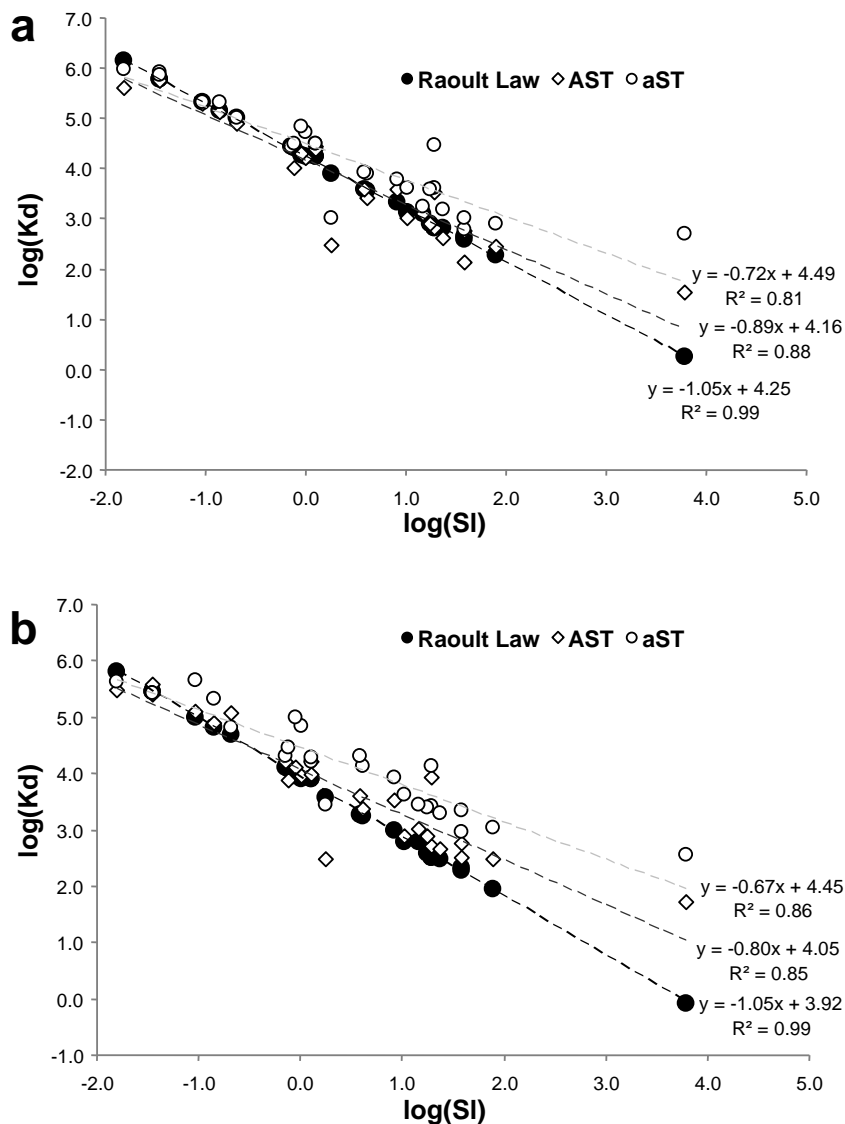


Figure 3: Log – log plot of solubility (SI) of PACs (including 15 US-EPA PAHs, 10 O-PACs and 4 N-PACs) and partitioning coefficient (Kd) deduced from experimental concentrations measured during leaching experiments in (◇) AST and (○) aST conditions and calculated from (●) Raoult law for (a) COK1 and (b) COK2 soils. Upper and lower cases correspond to high and low parameter levels respectively. Perinaphtenone and benzo(a)acridine are not considered due to the lack of reliable data about their respective solubilities.

Thus, as real soils aged for decades were used in our experiments, the PAC release into water is probably limited by the low diffusion within the solid-like coal-tar particles. This would explain the important decrease observed in the equilibrium concentration at low availability level compared to Raoult's law prediction.

However, a more pronounced decrease in water concentration for polar PACs and LMW-PACs than for HMW-PACs was observed with aging (Fig. 3). It may actually be explained by a two-film model (Schwarzenbach 1993). This model considers the presence of an aqueous (water-side) boundary layer and nonaqueous (coal-tar side) boundary layer in coal-tar water systems (Fig. 4). The release into water is controlled by diffusion within these two boundary layers. Ortiz et al. (1999) and Schluep et al. (2001) evidenced a contribution of the coal tar side boundary layer higher for the most soluble compounds than for the less soluble compounds. Due to their higher solubilities, the diffusion of LMW-PAHs and polar PACs to the water phase is faster than for HMW-PAHs. Conversely, their diffusion within coal-tar particles is more limited. The diffusion limitation within the coal tar creates a depleted zone at the

interface (Ortiz et al. 1999) that we assume to be more developed in the case of LMW-PAHs and polar PACs compared to HMW-PAHs. As the depletion zone size increases with aging (Ortiz et al. 1999) alongside with viscosity, the most soluble PACs are increasingly impacted and their release into water presents even higher deviation to Raoult's law compared to less soluble PACs.

It can then be assumed that the application of the thermal pretreatment allowed erasing the effect of aging, by redistributing the contaminants at the interface between tar and water and removing the depleted zone. It led to a higher equilibrium concentration for high availability conditions, close to Raoult's equilibrium concentration. However, assuming that the coal-tar viscosity is not changed by the thermal pretreatment once back at room temperature, the diffusion limitation concerns also the thermally pretreated particles. This is why, even if the deviation to Raoult's law prediction is lower than in the case of low PAC availability, a deviation is still observed in high availability conditions.

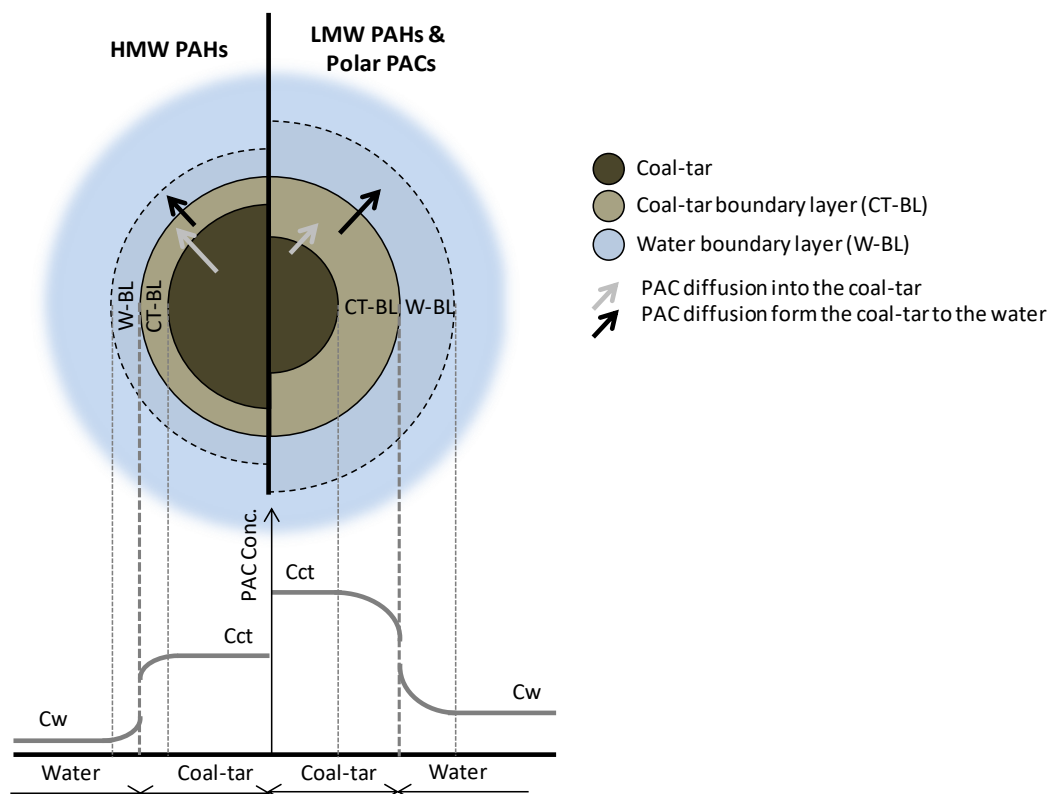


Figure 4: Schematic representation of the interface between coal-tar particles and water with two boundary layers. With C_w : PAC concentration in water, C_{ct} : PAC concentration in coal tar, LMWPAHs: low molecular weight PAHs (from naphthalene to pyrene), HMW PAHs: high molecular weight PAHs (benzo(a)anthracene to benzo(ghi)perylene), polar PACs: oxygenated and nitrogenated PACs (O-PACs and N-PACs)

Effect of temperature

The effect of temperature enhancement was similar on polar PACs and PAHs with a global increase of concentrations in the water.

Case of dissolution (Raoult's law) Higher temperatures induce an increase in aqueous solubilities of PACs (Feitkenhauer and Märkl 2003) and higher diffusion coefficients (Benhabib et al. 2006; Schlupe et al. 2001). Benhabib et al. (2006) and Schlupe et al. (2001) observed an enhancement of the PAH diffusion through coal tar or coal-tar particles at higher temperature leading to higher mobilization into water according to dissolution processes. The stronger influence of temperature on most soluble PACs (highly limited by diffusion within the coal tar) compared to less soluble PACs (less

limited by diffusion) (Table 2) could be an evidence of higher diffusivities at more elevated temperature. However, while this seems clear for COK2 leachates, it is not so for COK1 leachates.

Case of colloids When plotting the HMW-PAH concentrations in COK1 soil and leachates under low ionic strength conditions (s), similar slopes (Fig. S2) were obtained for low temperature (Ast and ast). A higher slope ($\times 2$) was obtained for high temperature and low availability (asT) suggesting a higher amount of mobilized colloids not observed in the case of high availability (AsT). As mentioned in “Preheated soil characteristics” the procedure used to increase the availability induced a modification of the coal-tar surface within the soils (coal-tar melting) and could lead to an artifact limiting the effect of temperature on colloid generation. On the contrary, results from asT conditions (Fig. S2) reveal an increase of colloid release induced by a higher temperature. The lower salt (anions and cations) dissolution from soil to water at low temperature (attested by the lower ionic strength obtained at low temperature than at high temperature) (Table S1) could be an explanation for the lower release of colloids. As a matter of fact, low ionic strength combined with high temperature resulted in a higher release of HMW-PAHs in association with colloids.

Conclusion

This study confirms a preferential release into water of polar PACs (O-PACs and N-PACs) compared to PAHs whatever the PAC availability level and whatever the conditions of ionic strength and temperature applied during the leaching test. PAHs and polar PACs were released according to a dissolution mechanism except under low ionic strength where HMW-PAHs were mainly released in association with colloids. Due to the higher solubility of polar PACs, their release into water was less affected by an increase in ionic strength than PAHs. Raoult’s law overpredicted the equilibrium concentrations obtained at low availability level of the contamination (aged soils). Reasonable prediction of the equilibrium concentrations could be obtained under high availability level of the contamination (thermally pretreated soils in our work). The deviation observed at low availability was explained by a limitation of the PAC diffusion within the coal-tar particles that become more and more viscous with aging by depletion of the most soluble compounds. LMW-PAHs and polar PACs were more affected by aging than HMW-PAHs due probably to a difference in the extent of their depleted zone at the coal-tar particle surface. Higher temperature increased the dissolution process as well as colloidal mobilization. Polar-PACs mobilization seems to be more sensitive to temperature.

In real-aged soils, Raoult’s law is not able to take into account all the involved mechanisms. For most soluble compounds mainly released in dissolved form, aging is the main parameter controlling their release into water while for less soluble compounds, mainly released in association with colloids, ionic strength is the main parameter. The history (aging) and the properties (especially ionic strength) of the soil are important parameters to take into account as they control the mechanisms involved in PAC release. To predict the equilibrium concentrations and the PAC behavior in aged soils, it would be necessary to add to the prediction laws a correcting factor that would take into account aging (availability).

Our batch leaching tests allowed identifying the mechanisms involved in the release of PACs and evaluate the influence of several parameters (temperature, ionic strength) influencing their release. The thermal pretreatment applied on soils allowed partly erasing the effect of aging and allowed studying the mechanisms at different aging levels. The next step is to study these mechanisms under dynamic conditions via column leaching tests to understand the processes occurring at more complex scale.

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