Mass Balance of Polycyclic Aromatic Hydrocarbons and Derivatives after Oils Spill in Water

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Abstract. Context and objective: The Migr'Hycar research project was initiated to provide decisional tools for risks connected to oil spill drifts in continental waters. This paper focuses on the distribution of polycyclic aromatic hydrocarbons (PAHs) from oils in water, air and oil slicks.

Material and methods: Six petroleum oils covering a representative range of commercially available products were tested. Dynamic tests at laboratory scale were performed to study 41 PAHs and derivates, among them 16 EPA priority pollutants. Water soluble fraction protocol, stir bar sorptive extraction (SBSE) and high performance gas chromatography mass spectrometry (HPGC-MS) was used. Limit of quantification were lower than 1 ng.L^{-1} for each compounds.

Results: A large variation in composition of the water soluble fraction depending on oil type and mixing time has been highlighted. Results have shown that evaporation is the primary mechanism of PAHs loss from spilled oil. The subsequent fate of hydrocarbons deposited in surface water is further influenced by volatilisation behaviour because of possible slick loss to the atmosphere. The water soluble fraction remains very low and is dominated by low molecular weight PAHS (e.g. naphthalenes).

Keywords: Monitoring, Water soluble fraction, PAHs, Sorptive Bar Solid Extraction

1. Introduction

The Migr'Hycar research project (www.migrhycar.com) was initiated to provide decisional tools, and satisfy operational needs, for risks connected to oil spill drifts in continental waters (rivers, lakes, estuaries). These tools aim to serve in the decision-making process once oil spill pollution occurs and/or as reference tools to study scenarios of potential impacts of pollutions on a given site. Within the framework of the Migr'Hycar project, experiments on situations under controlled conditions were conducted in order to evaluate the dissolved, floating and evaporated oil fractions. The water soluble fraction protocol is of special interest because such components dissolved (e.g. naphthalenes, phenanthrenes and dibenzothiophenes) from an oil slick are known to have a high bio-availability to marine organisms, and therefore have a potential to cause toxic effects (Neff et al., 2000). Indeed, polycyclic aromatic hydrocarbons (PAHs) are classified as priority hazardous substances and as priority substances by the European Union (Decision 2455/2001/EC). The objective of the study was the monitoring of the PAHs in the three compartments: air, water and oil slicks. The mass balance was established by quantifying compounds in at least two of them.

2. Material and Methods

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2.1. Material and Reagents

Glassware was cleaned carefully with water, Milli-Q water and acetone HPLC grade. Methanol Ultra LC-MS grade was purchased by Carl Roth (France).

The solutions were prepared from certified reference material purchased from LGC Standards (Molsheim, France) as regards semi-volatile compounds: CUS 9305, which contains 21 PAHs (naphthalene, benzothiophene, biphenyl, acenaphtylene, acenaphtene, fluorine, phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benzo [a] anthracene, chrysene, benzo [b] fluoranthene, benzo [k] fluoranthene, benzo [e] pyrene, benzo [a] pyrene, perylene, indeno [1, 2, 3-cd] pyrene, dibenz [a, h] anthracene and benzo [g, h, i] perylene) at the concentration of 1 µg/mL in methanol, and CUS 9207, which contains the corresponding internal standards: Naphthalene d_8, Biphenyl d_{10}, Phenanthrene d_{10}, Chrysene d_{12} and Benzo [a] pyrene d_{12} at the concentration of 1 µg/mL in acetone. All the calibrations curves were obtained by extracting and analyzing water samples spiked with target molecules and corresponding internal standards.

2.2. Oil Studied

Six different oils, supplied by TOTAL, were studied: Heavy fuel, Domestic fuel, Jet A1, Gasoline (SP98), Gasoline (SP95-E10) and Diesel fuel. They were selected because of their common use. The oil storage was performed at +4°C. Before use, light oils were conserved at room temperature during 12 h. The use of heavy oils was made after a reheat at 70°C during 1h.

2.3. Water-Soluble Fraction

Water-soluble fraction protocol was performed in darkness at 20°C. 2000g of Milli-Q water were introduced in a 3L glass beaker. 200mg of oil were deposited on water surface, conducing to about a 10% surface ratio. A gentle stirring without vortex was ensured to allow the diffusion of molecules. C20 standard (500µg/mL, LGC Standards) was added in order to evaluate evaporation part. Mixing times were fixed to 1h, 3h, 6h, 10h, 24h and 48h. First, totality of the slick was sampled with a 100mL volumetric pipette after a given time of exposure to the oil. The sample was treated in a separating funnel in order to recover the oil fraction. Separating funnel was rinsed with 10mL of dichloromethane. An aliquot of 2mL was then sampled and stored at +4°C for GC/MS analysis. Then, the soluble fraction was sampled with a 100mL volumetric pipette in order to take a water sample free from oil after a given time of exposure to the oil. This fraction was extracted by sorptive bar solvent extraction (SBSE).

2.4. PAHs Analysis

This analytical method was used to analyze the 15 PAHs from the EPA priority pollutants list, plus 26 PAHs derivates which are more soluble compounds.

2.4.1. PAHs in *Water (Soluble Fraction)*: SBSE-TD-GC-MS

100 mL water samples were added with 10 mL of methanol containing the 5 deuterated internals standards at the concentration of 1 ng/mL (final concentration of 100ng/L relatively to water). Stir bars (Twister® 20 mm x 0.5 mm PDMS by Gerstel) were then added to the water samples and stirred at 700 rpm for two hours. Stir bars were then recovered by using tweezers, dried over plot paper and stored in a vial at +4°C for subsequent GC/MS analysis (Guyomarch and Van Ganse, 2010).

The analyses were performed using a Thermal Desorption Unit combined with a Cooled Injection System from Gerstel (Mülheim an der Ruhr, Germany) mounted on a 7890 Agilent GC system coupled to an Agilent 5975 mass spectrometrer (Agilent Technologies, Little Falls, DE, USA). The analytical system was equipped with an automated sampler MPS2 (Gerstel). Desorption was achieved at 300 ºC for 10 minutes under an helium flow of 50 mL/min in the splitless mode and with a transfer line maintained at 300 ºC. The desorbed compounds were cryofocused in a cooled injection system (CIS-4, Gerstel) at 10 ºC and then transferred to the HP-5MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness, constant helium flow of 1 mL/min) by a rapid increase of the CIS temperature (from 10°C to 300°C at 12°C/s). For the analysis of PAHs, the oven program of temperature was: from 50 ºC (1 min) to 150°C at 10°C/min, and then to 320°C (5 min) at 5°C/min. The mass spectrometer was operated in Selected Ion Monitoring (SIM) with a minimum

of 2 cycles/s. The quantification was performed by using the molecular ion of each PAH. The target molecules were quantified relatively to the deuterated PAHs (internal standards) using a calibration curve (from 0.1ng/L to 100ng/L) with regression coefficient > 0.99. Limit of quantification were lower than 1 ng.L^{-1} for each compound.

2.4.2. PAHs in *Oils (Initial and Slick Fraction)*: GC-MS

The analysis was performed as described previously except the injection technique. The split/splitless injector was used in the pulse splitless mode (pulse pressure: 15 psi, splitless time: 1 min, flow 50 mL/min). The injector temperature was maintained at 300°C. PAHs were quantified in the oil in their initial state relatively to the perdeuterated PAHs (internal standards) using a calibration curve (from 0.1ng/L to 100ng/L).

A semi-quantitative method was applied to the slick. In this view, the fraction of molecules disappearing from the slick was assessed relatively to a compound or group of compounds present in the slick, sufficiently abundant, poorly volatiles and of low solubility. In the case of products characterized by a residue at 250°C higher than 30%, compounds with a molecular weight equal or higher than C3-phenanthrenes were chosen. For lighter products (gasoline and kerosene), as no compound meets these requirements, oils were spiked with a linear alkane (nC20) at the concentration of 500 µg/mL. This method was adopted as the amount of oil sampled at the water surface could not be determined precisely (presence of water). In the case of oils sampled during the experiment at T_i, the calculation of the target compounds concentrations was performed according equation 1.

$$C_{Ci/Ti} = C_{Ci/T0} \times \frac{A_{Ci/Ti}}{A_{Ci/T0}} \times \frac{A_{H/Ti}}{A_{H/T0}}$$

Eq. 1: Calculation of the target PAHs in the floating fraction.
($C_{Ci/Ti}$: target compound concentration at Ti ; $C_{Ci/T0}$: target compound concentration in initial oil ; $A_{Ci/Ti}$: target compound area at Ti ; $A_{Ci/T0}$: target compound area in initial oil ; $A_{Hi/Ti}$: reference compound area at Ti ; $A_{Hi/T0}$: reference compound area in initial oil)

3. Results and Interpretation

The results are presented based on the sum of the 41 PAHs as a global indicator. The distribution of PAHs from the 6 oils in the 3 compartments (water, air and oil slicks) is shown in figure 1.

3.1.1. Volatilisation

When petroleum products enter surface-water systems, the lighter aliphatic and aromatic hydrocarbons spread out along the surface of water and evaporate. In general, evaporation is the primary mechanism of loss of volatile and semi-volatile compounds of spilled oil. As it is shown in figure 1, evaporation is almost total in the case of gasoline, diesel fuel and kerosene, which are rich in naphthalenes which easily sublimates in the air and presents the highest water solubility in water. For the heavy and domestic fuels, the oil slick remains around 20%, especially for the domestic fuel which contains phenanthrene and chrysene, less volatile and less soluble than naphthalene. The partitioning between air and water at equilibrium is characterized by Henry's law constant (K_H). An increasing K_H implies higher volatility and results from combination of high vapour pressure and low aqueous solubility (table 1). Volatilisation losses from aqueous phase to the atmosphere are also influenced by the aqueous solubility of the compounds.

Table 1: Calculation of the target PAHs in the floating fraction (source: Mackay et al., 2006)

PAHs	Water Solubility [mg/L]	Vapor Pressure [mmHg at 25°C]	Henry constant [bar at 298K]
Naphthalene	32	$8.2 \ 10^{-2}$	23.796
Phenanthrene	1.0	$6.8 \ 10^{-4}$	1.771
Chrysene	0.006	$6.3 \ 10^{-7}$	0.036

3.1.2. Water Dissolution and Solubility

Analysing the water soluble fraction, we observed that water solubility of PAHs tends to decrease with increasing molecular weight. Moreover, linear fused PAHs (e.g. naphthalene and anthracene) also tend to be

more soluble than pericondensed structures (e.g. phenanthrene and pyrene). Furthermore, alkyl substation decreases water solubility of parental PAHs. Naphthalenes are dominating sum of PAHs profile because of their high solubility in water.

3.1.3. Ethanol Influence

We can observe that gasoline SP95-E10 presents a reduced oil slick compared to gasoline SP98. Indeed, the addition of ethanol in gasoline increases PAHs solubilisation (Corseuil et al., 2004). But, the decrease of oil slick is also due to the increase of hydrocarbons volatility of which form azeotrops with ethanol (Muzicova et al., 2009). The both phenomena explain the difference between the oil slicks of gasoline, while the soluble fractions remain low.
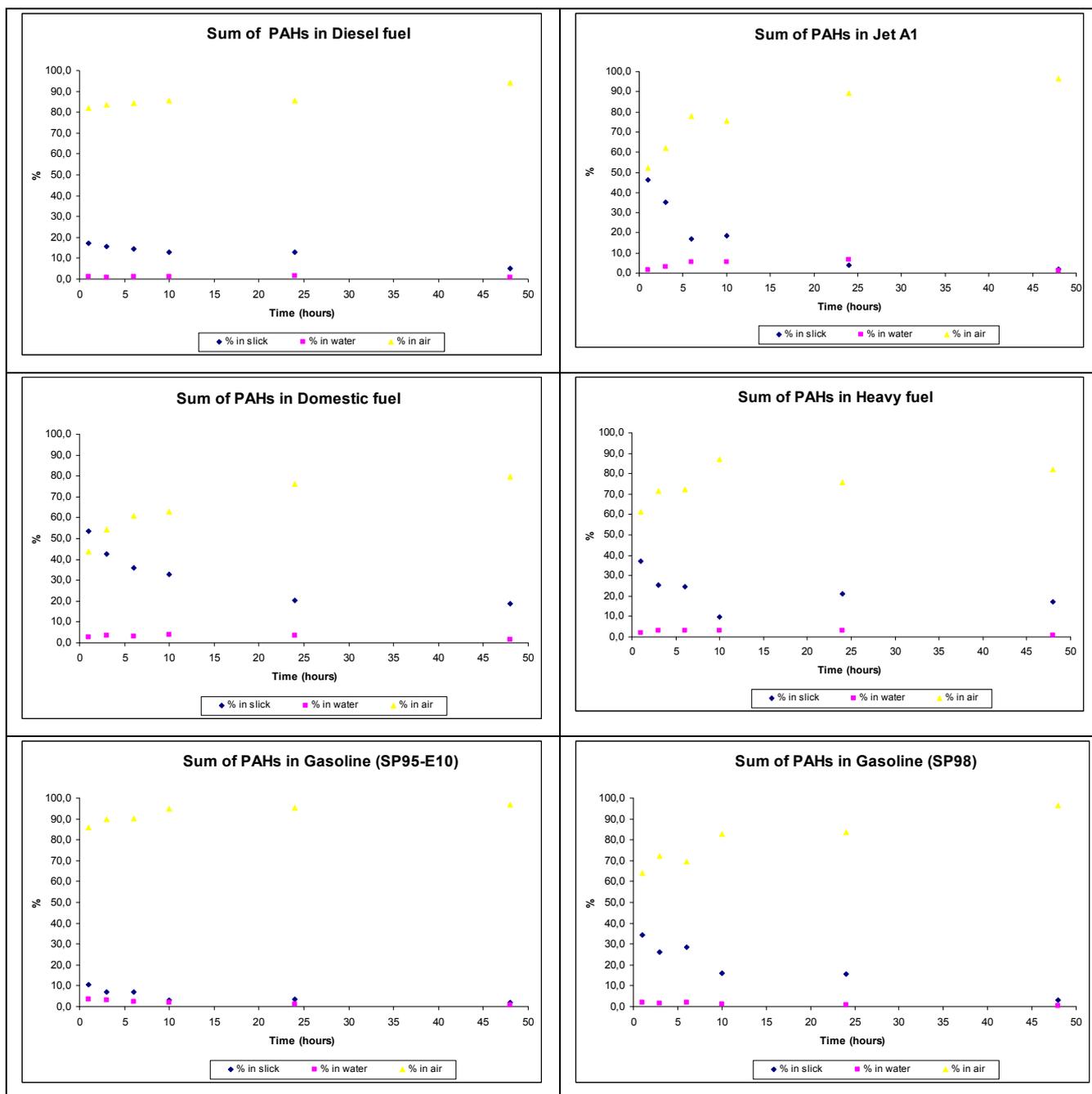

Fig. 1: Distribution of PAHs (% in air, % in water and % in slick) as function of time for the 6 oils studied.

4. Conclusion

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Whithin the Migr'Hycar research project, experimentations at laboratory scale were performed to study the behaviour of hydrocarbons when petroleum products enter surface-water systems. Six petroleum oils were studied and 41 polycyclic aromatic hydrocarbons and derivates (PAHs) were monitored. The mass balance in the 3 compartments (air, water and slick) was established by quantifying compounds in water and slick. Results have shown that evaporation is the primary mechanism of PAHs loss from spilled oil. The subsequent fate of hydrocarbons deposited in surface water is further influenced by volatilisation behaviour because of possible slick loss to the atmosphere. The water soluble fraction remains very low and is dominated by low molecular weight PAHS (e.g. naphthalenes). In spite of their low solubility, dissolution is an important media exchange process leading to the primary destruction pathway of hydrocarbons in aquatic systems via biodegradation.

5. Acknowledgements

6. References

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