Effect of Oils Categories on the Distribution of Polycyclic Aromatic Hydrocarbons and Derivatives in the Environment

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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 derivatives, 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).

Index Terms—Monitoring, water soluble fraction, PAHs, Sorptive Bar Solid Extraction.

I. INTRODUCTION

The application of the European Water Framework Directive [1] and the monitoring obligation on water quality for human consumption and industrial activities has created a need for water quality evaluation and monitoring systems. An evaluation of industrial reject oils (from all industries) led to around 600 tonnes discharged in 2002 in France [2]. Among the accidents identified, we found manipulation errors, accidental leakage of household or industrial tanks, petrol station leakage, wastewater treatment plant overflows, truck accident, fire and deliberate or accidental discharges of

river boats.

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 [3]. Indeed, polycyclic aromatic hydrocarbons (PAHs) are classified as priority hazardous substances and as priority substances by the European Union (Decision 2455/2001/EC). The objectives of the studies were (1) the monitoring of the PAHs in the three compartments (air, water and oil slicks) as a function of the time and (2) the measuring of the studied compounds on final equilibrium. The mass balance was established by quantifying compounds in at least two of the three compartments.

II. MATERIAL AND METHODS

A. 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, acenaphthylene, acenaphthene, 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 d₈, Biphenyl d₁₀, Phenanthrene d₁₀, Chrysene d₁₂ and Benzo[a]pyrene d₁₂ at the concentration of 1 µg/mL in acetone. All the calibrations

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curves were obtained by extracting and analyzing water samples spiked with target molecules and corresponding internal standards.

The calibration solutions were prepared by dilution of a PAHs mix solution in 100 mL Milli-Q water leading to 8 solutions: blank, 0.5 ng.L⁻¹, 1 ng.L⁻¹, 5 ng.L⁻¹, 10 ng.L⁻¹, 100 ng.L⁻¹, 500 ng.L⁻¹, 1 000 ng.L⁻¹. The extraction standard solution was prepared while diluting 1 mL of a The extraction standard solution was prepared while diluting 1 mL of a deuterated PAHs mix solution in 1 L of methanol (ROTISOLV ≥99.98% Ultra LC-MS by Carl Roth). The standard solutions were stored in amber glass bottles at +4 °C.

B. Oils 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 and their possible involvement in freshwater oil spills. 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. Physical and chemical properties of oils are described in Table I.

TABLE I: DESCRIPTION OF THE OILS USED AND THEIR MAIN PROPERTIES

Oils	Physical State	Color	Density (kg/m ³ at 15 °C)	Octanol-water partition coefficient	Viscosity
Heavy fuel	Viscous liquid at 20 °C	Brown/Green. Dark brown/Black	920 - 1060	$2.7 \leq \text{Log Kow} \leq 6$	> 9.5 mm ² s at 20 °C < 40 mm ² s at 100 °C
Domestic fuel	Clear liquid at 20 °C	Characteristic	820 - 860	$3.9 \leq \text{Log Kow} \leq 6$	< 7 mm ² s at 40 °C
Jet A1	Liquid	Colorless to pale yellow	775 - 840	$3.3 \leq \text{Log Kow} \leq 6$	< 7 mm ² s at 40 °C
Gasoline SP98	Clear liquid at 20 °C	Pale yellow	720 - 775	$2.1 \leq \text{Log Kow} \leq 6$	0.5 - 0.75 mm ² s at 20 °C
Gasoline SP95-E10	Clear liquid at 20 °C	Pale yellow	720 - 775	$2.1 \leq \text{Log Kow} \leq 6$	< 1 mm ² s at 40 °C
Diesel fuel	Liquid at 20 °C	Yellow	820 - 845	$3.9 \leq \text{Log Kow} \leq 6$	< 7 mm ² s at 40 °C

C. 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, conducting 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 was sampled with a 100mL volumetric pipette after a given time of exposure to the oil. The sample was separated 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).

D. PAHs analysis

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

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 internal 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 [4].

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 spectrometer (Agilent Technologies, Little Falls, DE, USA). The analytical system was equipped with an automated sampler MPS2 (Gerstel). Desorption was achieved at 300 °C for 10 minutes under an helium flow of 50 mL/min in the splitless mode and with a transfer line maintained at 300 °C. The desorbed compounds were cryofocused in a cooled injection system (CIS-4, Gerstel) at 10 °C 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 °C (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 compounds.

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 (no weathering) relatively to the deuterated 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 T_i ; $C_{Ci/T0}$: target compound concentration in initial oil; $A_{Ci/Ti}$: target compound area at T_i ; $A_{Ci/T0}$: target compound area in initial oil; $A_{H/Ti}$: reference compound area at T_i ; $A_{H/T0}$: reference compound area in initial oil)

III. RESULTS AND INTERPRETATION

A. Fresh Oil Characterization

PAHs levels in the initial oils were presented Fig. 1. The characterization has shown that domestic fuel had the highest PAHs content, gasoline (SP95, SP98) the lowest.

Fig. 1. Initial concentration of the 41 PAHs in oils.

B. Mass Balance of PAHs

The results are presented based on the sum of the 41 PAHs as a global indicator and the naphthalene level (naphthalene + C₁ C₂ C₃ C₄ derivatives). The distribution of PAHs from the 6 oils in the 3 compartments (water, air and oil slicks) is shown in Fig. 2. In all cases, at 48 hours contact time, equilibrium was observed corresponding to three phenomena: dissolution, evaporation and volatilisation (Fig. 3).

Fig. 2. Distribution of PAHs (% in air, % in water and % in slick) as function of time for the 6 oils studied.

Fig. 3. Distribution of PAHs [8]

1) Water dissolution and solubility

The oil quantity affected by the dissolution process is lower than 11% of the initial mass [10]. Due to their physical, chemical properties, only PAHs are assumed to be dissolved in water [9].

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 substitution decreases water solubility of parental PAHs. Naphthalenes are dominating sum of PAHs profile because of their high solubility in water.

2) 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%. Indeed, these oils contain phenanthrene and chrysene, less volatile and less soluble than naphthalene.

If we measure what is remaining in the silk for SP95-E10, SP98 and kerosene, we observe that no PAHs persist in the silk. Although, for domestic fuel, heavy fuel and diesel fuel, we observe a persistence of phenanthrene compounds (Table

II).

TABLE II: PERSENTATION OF PHENANTHRENES AT 48 HOURS

PAHs	Domestic fuel	Heavy fuel	Diesel fuel
Phenanthrene	3.7	2.1	0.2
C ₁ -Phenanthrene	6.8	4.1	0.3
C ₂ -Phenanthrene	2.6	1.9	0.2
C ₃ -Phenanthrene	1.0	1.0	1.0
Σ Phenanthrene	14.1	9.2	1.7

The partitioning between air and water is characterized by Henry's law constant (K_H). The K_H implies higher volatility and results from combination of high vapour pressure and high aqueous solubility (Table III). Volatilisation losses from aqueous phase to the atmosphere are also influenced by the aqueous solubility of the compounds.

TABLE III: CALCULATION OF THE TARGET PAHs IN THE FLOATING FRACTION [5]

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

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 [6]. But, the decrease of oil slick is also due to the increase of hydrocarbons volatility of which form azeotropes with ethanol [7]. The both phenomena explain the difference between the oil slicks of gasoline, while the soluble fractions remain low.

IV. CONCLUSION

Within the Migr'Hycar research project, experimentations at laboratory scale were performed to study the behaviour of hydrocarbons when petroleum products enter surface-water systems. This work required the development of an experimental protocol to evaluate the behaviour of PAHs in the 3 compartments. Data were the results of the equilibrium obtained during the distribution of hydrocarbons in the different phases. Six petroleum oils were studied and 41 polycyclic aromatic hydrocarbons and derivatives (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 addition of water miscible oxygenated compounds, such as ethanol, to fuels increases the global solubility of PAHs. 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.

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- The environmental evaluation such as the Life Cycle Assessment: optimization and objectification of working methodologies by specifying in particular the outlines of the studied systems and the valuation methods of flows and impacts.

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