

Effect of Environmental Parameters on the Water Solubility of the Polycyclic Aromatic Hydrocarbons and Derivatives Using Taguchi Experimental Design Methodology

P. Pimsee, C. Sablayrolles, P. de Caro, J. Guyomarch, N. Lesage, M. Montréjaud-Vignoles

Abstract—The MIGR'HYCAR research project was initiated to provide decisional tools for risks connected to oil spill drifts in continental waters. 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. This paper focuses on the study of the distribution of polycyclic aromatic hydrocarbons (PAHs) and derivatives from oil spill in water as function of environmental parameters. Eight petroleum oils covering a representative range of commercially available products were tested. 41 polycyclic aromatic hydrocarbons (PAHs) and derivatives, among them 16 EPA priority pollutants were studied by dynamic tests at laboratory scale. The chemical profile of the water soluble fraction was different from the parent oil profile due to the various water solubility of oil components. Semi-volatile compounds (naphthalenes) constitute the major part of the water soluble fraction. A large variation in composition of the water soluble fraction was highlighted depending on oil type. Moreover, four environmental parameters (temperature, suspended solid quantity, salinity and oil: water surface ratio) were investigated with the Taguchi experimental design methodology. The results showed that oils are divided into three groups: the solubility of Domestic fuel and Jet A1 presented a high sensitivity to parameters studied, meaning they must be taken into account. For Gasoline (SP95-E10) and Diesel fuel, a medium sensitivity to parameters was observed. In fact, the four others oils have shown low sensitivity to parameters studied. Finally, three parameters were found to be significant towards the water soluble fraction.

Keywords—Monitoring, PAHs, SBSE, water soluble fraction, Taguchi experimental design.

I. 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

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impacts of pollutions on a given site. The water soluble fraction protocol is particularly interesting because components dissolved (e.g. naphthalenes, phenanthrenes and dibenzothiophenes) from an oil slick are known to have a high bio-availability to marine organisms, and thus potentially cause toxic effects [1]. Therefore, polycyclic aromatic hydrocarbons (PAHs) raise considerable environmental concerns, mainly due to their relative persistence, carcinogenic and mutagenic potential, and their possible indication of anthropogenic pollution [2]. Indeed, polycyclic aromatic hydrocarbons (PAHs) are classified as priority hazardous substances by the European Union (Decision 2455/2001/EC). Relatively few published studies focus upon PAH dissolved in the continental water integrating environmental factors such as temperature or salinity.

Taguchi method, based on orthogonal arrays, has been chosen as a screening method to identify relevant parameters and their influence on the response studied (soluble fraction). It reduces significantly the number of tests while maintaining good accuracy [3], [4]. The parameters selected are variables which are believed to affect the soluble fraction of hydrocarbons, namely temperature of the medium, suspended solid quantity, salinity of the water and surface ratio occupied by the product. So there are four variable parameters, in addition to the type of hydrocarbon which is a discrete variable.

II. MATERIALS 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 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 curves were obtained by extracting and analyzing water samples spiked with target molecules and corresponding internal standards. The calibration solution was prepared by dilution of a PAHs mix

solution in 100mL Milli-Q water leading to 8 solutions: blank, 0.5ng.L⁻¹, 1ng.L⁻¹, 5ng.L⁻¹, 10ng.L⁻¹, 100ng.L⁻¹, 500ng.L⁻¹, 1000ng.L⁻¹. The extraction standard solution was prepared while diluting 1mL of a deuterated PAHs mix solution in 1L of methanol (ROTISOLV \geq 99.98% Ultra LC-MS by Carl Roth). The standard solution was stored in amber glass bottles at +4°C [5], [6].

B. Oil Samples

Eight petroleum oils covering a representative range of commercially available products were tested: Bitumen (Azalt 35-50), Heavy fuel (IFO 380), Domestic fuel, Jet A1, Gasoline (SP98), Gasoline (SP95-E10), Gasoline (E85), and Diesel fuel. The oil storage was performed at +4°C. Before their use, light oils were stored at room temperature during 12h. Heavy oils were used after a reheat at 70°C during 1h.

C. Experimental Design

Four environmental parameters (temperature, suspended solid quantity, salinity and oil: water surface ratio) were investigated. Each of these parameters presents three different levels in order to be representative of the physical-chemical conditions of the receiving environment (continental waters), during the seasons (see Table I).

TABLE I
PARAMETERS WITH THEIR RESPECTIVE LEVELS

Parameter	Level 1	Level 2	Level 3
Temperature	5°C	17°C	28°C
Surface ratio	10%	25%	50%
Suspended solid	0 mg/L	300 mg/L	1000 mg/L
Salinity	0 g/L	10 g/L	35 g/L

The number of variable parameters studied (4) would require a considerable number of experiments to cover all combinations of levels of possible parameters ($3^4 = 81$ experiments for each oil studied). With 4 parameters at 3 levels, a L₉ (orthogonal array) Taguchi generates the experimental design presented in Table II. For each oil, the experiments were carried out in duplicate, in accordance with the assignment of parameters.

TABLE II
TAGUCHI EXPERIMENTAL DESIGN

Number	Temperature	Surface ratio	Suspended solid	Salinity
1	5°C	10%	0	0
2	5°C	25%	300 mg/L	10 g/L
3	5°C	50%	1000 mg/L	35 g/L
4	17°C	50%	300 mg/L	0
5	17°C	10%	1000 mg/L	10 g/L
6	17°C	25%	0	35 g/L
7	28°C	25%	1000 mg/L	0 g/L
8	28°C	50%	0	10 g/L
9	28°C	10%	300 mg/L	35 g/L

D. Water Soluble Fraction

Model water samples were prepared from water "ultrapure" to which is added, suspended solids collected from the

Garonne River and, then, aquarium "Instant Ocean" salts, at the desired levels.

Water-soluble fraction protocol was performed in darkness at the temperature selected. 150g of model water samples were added in a 250mL glass beaker. The amount of oil is deposited on water surface, corresponding to about a 10%, 25% and 50% surface ratio. A gentle stirring without vortex was ensured to achieve the diffusion of molecules. Mixing times were set at 1h for light oils and 2h for heavy oils. 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).

E. PAHs Analysis: SBSE-TD-GC-MS

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

100mL water samples were added with 10mL of methanol containing the 5 deuterated internal standards at the concentration of 1ng/mL. Stir bars (Twister® 20mm x 0.5mm 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 [5], [6].

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 a helium flow of 50mL/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 (30m x 0.25mm i.d. x 0.25µm film thickness, constant helium flow of 1mL/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 (5min) 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 [5]-[7].

III. RESULTS AND DISCUSSIONS

Equation (1) represents the responses as a function of environmental parameters:

$$R = a0 + a1 * T + a2 * Ratio + a3 * S + a4 * Salinity \quad (1)$$

where, R is the response (soluble fraction),

a1, the coefficient of temperature,
 a2, the coefficient of surface ratio,
 a3, the coefficient of suspended solid,
 and a4, the coefficient of salinity

A large variation in composition of the water soluble fraction was highlighted depending on oil type. The chemical profile of the water soluble fraction was different from the parent oil profile due to the various water solubilities of oil components. Semi-volatile compounds (naphthalenes) constitute the major part of the water soluble fraction. The impact coefficients connected to the four parameters are presented in Fig. 1. According to negative or positive values for impact coefficients, three behaviours were observed: the solubility of Domestic fuel and Jet A1 presented a high sensitivity to parameters studied, leading to consider them as influential. For Gasoline (SP95-E10) and Diesel fuel, a moderate sensitivity to parameters was observed, while the four others oils have shown low sensitivity towards the same parameters. Infact, these are products which present the lowest global soluble fraction [8].

For each oil, as expected, the water soluble fraction is minimized with the minimal temperature. This behavior was also observed by Brian G., Whitehouse, in the case of PAHs [2].

Except for Heavy fuel, the water soluble fraction was surprisingly minimized with the maximal surface ratio. This result may be explained by the solubilization of the more volatile compounds from the slick.

An increasing solubility of products with suspended solid may be explained by the affinity between suspended solid and PAHs, thus shifting the solubility limit. As for salinity, its effects vary with the products, and so depend of their composition.

Finally, all parameters except salinity should be thus taken into account.

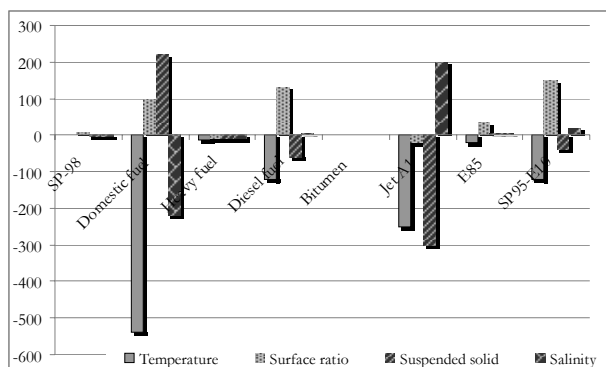


Fig. 1 Coefficients of environmental impacts towards water soluble fraction (sum of PAHs)

As the naphthalenes, semi-volatile compounds, constitute the major part of the water soluble fraction, the impact coefficients are also presented in Fig. 2.

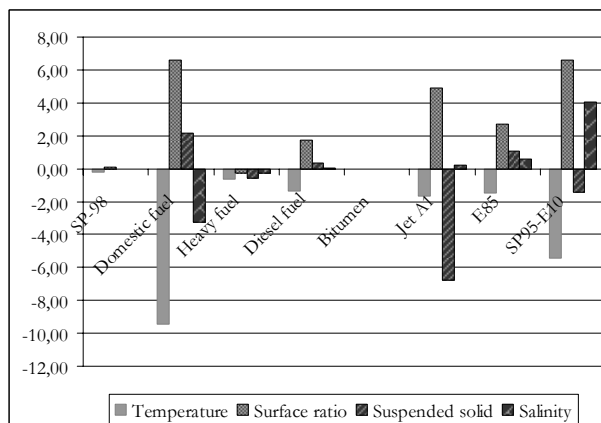


Fig. 2 Coefficients of environmental impacts towards water soluble fraction (Naphthalenes)

The influence of the temperature and of the surface ratio on the soluble naphthalenes is confirmed: the same effects are observed for the different oils. Furthermore, the effect of suspended solids on the solubility of total PAHs and of naphthalenes is similar.

IV. CONCLUSION

Dissolution is an important media exchange process leading to the primary destruction pathway of hydrocarbons in aquatic systems via biodegradation. Within the Migr'Hycar research project, experimentations at laboratory scale were performed to study the effect of four environmental parameters (temperature, suspended solid quantity, salinity and oil: water surface ratio) on the solubility of PAHs when petroleum products are spilled in water systems. The development of an experimental protocol to evaluate the behavior of PAHs solubility has been performed. Eight petroleum oils were studied and 41 polycyclic aromatic hydrocarbons and derivatives (PAHs) were monitored by quantifying soluble compounds in water. The water soluble fraction remains very low and is dominated by low molecular weight PAHs (e.g. naphthalenes).

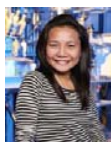
Taguchi methodology have led to discriminate oils according to three groups; (i) Domestic fuel and Jet A1 whose solubility presents a high sensitivity to four parameters studied; (ii) Gasoline (SP95-E10) and Diesel fuel with a solubility moderately sensitive to parameters, (iii) Gasolines (SP98 and E85), Heavy fuel and Bitumen with a solubility slightly depending to the same parameters. Eventually, temperature of water, surface ratio of oil deposit and suspended solid in water, appear as parameters affecting the soluble fraction of PAHs, especially for Domestic fuel, Jet fuel, Diesel fuel and Gasoline E10. Results were thus interpreted according to different processes involved; solubilization of oil spill, volatilization of soluble fraction and adsorption of soluble fraction on suspended solids.

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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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