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Characterization of organic matter in aquatic systems under strong urban pressure: Sources, physico-chemical properties and interactions with organic pollutants

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Abstract

Many organic pollutants are toxic for the aquatic biota but their fate in urban systems is still little studied, especially regarding Dissolved Organic Matter (DOM) effect on their distribution. Strong interactions with DOM play a key role in the speciation, bioavailability and toxicity of micropollutants. Understanding of the interaction processes, their dependence on local conditions and their temporal and spatial variations are needed for a sound risk assessment of micropollutants in Seine river basin.

We make the characterization of the DOM present in surface water in the Seine river basin and its evolution to the crossing of the Paris agglomeration and the characterization of the interactions between the urban DOM and organic micropollutants and the characterization of the interactions between the DOM and the suspended solids (mineral and organo-mineral complexes).

Interactions between organic pollutants and mineral and organo-mineral complexes are being investigated. Several DOM samples from Seine Basin are being studied and their evolution in the crossing of the Paris Metropolitan Area, agricultural and forest zones are investigated. The Seine river basin, along an urban/industrial gradient, provide an interesting study site for DOM characterization and can show the predominant role of DOM in mitigating the contaminants fate and bioavailability in aquatic ecosystems.

Keywords

Dissolved organic matter; organic pollutants; organo-mineral complexes

INTRODUCTION

The fate and behavior of organic pollutants in the environment have been studied in recent decades. The interest is justified by the harmful effects of many organic chemicals that may constitute serious risks to human health and other living organisms.

Nowadays, water in France is managed under regulations established at European level: the EU Water Framework Directive (WFD) of 23 October 2000 establishing the goal of achieving good status waters by 2015. This European Directive was transposed into French law: the LEMA (Law on Water and Aquatic Environments) of December the 30th 2006.

Our study of organic pollutant fate in the basin of the Seine, as well as their behavior in the environment and their bioavailability, is highly relevant and current source of concern: to

evaluate the status of water bodies, to improve scientific and technical knowledge and to monitor progress to accomplish many of the objectives of EU Water Framework Directive.

When a compound is introduced into the environment, it tends to diffuse from phase to phase, until equilibrium is reached between the phases (Figure 1). The main mechanisms, by which contaminants are removed from the system, include processes of biodegradation, photolysis, oxidation and transport processes. The mobility depends on the speciation of the pollutant. Dissolved form (including colloids) will promote transport over long distances and particulate form will promote sedimentation.

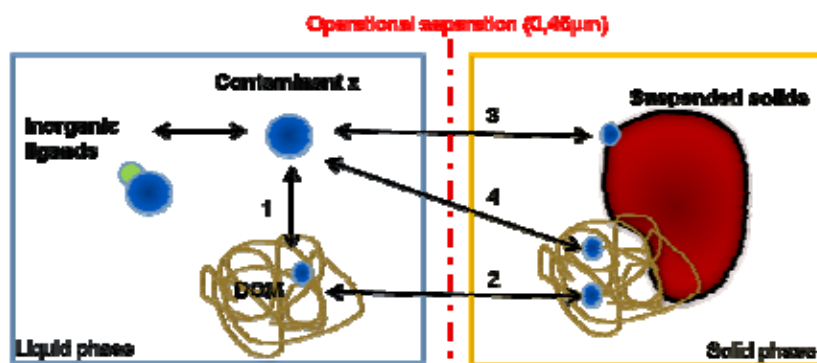


Figure 1: The way in which contaminants are sorbed into, MO and solid phase. The arrows indicate interactions between pollutants and mineral surface and organic surface. The contaminant may be sorbed on the surface and mineral complex MOD-Suspended solids. (TREMBLAY et al., 2005)

Dissolved organic matter is from different sources: natural autochthons from the biota (algae, bacteria, macrophytes), natural allochthonous of soil, anthropogenic allochthonous and urban domestic and industrial source. The composition of the DOM is very heterogeneous due to the diversity of its sources, its age and the different processes affecting their composition. The description of DOM compounds and their composition are dependent on the analytical protocol used (Table 1).

Table 1: Type of molecules observed in MOD (IMAI et al., 2001).

Fraction		Types of compounds observed fractions
Humic substances	Acids Hydrophobic	fulvic acid (soluble at any pH) humic acids (precipitated at pH <2)
	Neutral Hydrophobic	hydrocarbons, detergents, pigments (including chlorophyll)
Non humic substances	Bases Hydrophobic	Surfactants and proteins
	Acids Hydrophilic	sugars, amino acids
	Neutral Hydrophilic	Oligosaccharides and polysaccharides,
	Bases Hydrophilic	Proteins, amino acids

MATAR (2012) did a great advance for the comprehension of the origin and characteristics of the DOM of the Seine river basin. Her results showed that the DOM in receiving water, after urban water discharges, presents a high percentage of hydrophilic DOM, a low degree of hydrophobicity and aromaticity. In contrast, a greater functional diversity of DOM from urban versus natural DOM has been demonstrated with a particularly strong presence of protein structures. On low-flow conditions, the high proportion of hydrophilic DOM in urban discharges impacts receiving water. In this period the impact of urban discharges is highest due to a lower dilution, the DOM is mainly non-hydrophobic in highly urbanized rivers.

Dissolved organic matter plays an important role. Its role is particularly important in the biogeochemistry of metal and organic micropollutants potentially influencing their speciation and bioavailability. Excess biodegradable form of DOM in surface waters can lead to oxygen deficiencies in its mineralization. In addition, in operational perspective, the organic matter is a key parameter in the purification of water.

There are several modes of interaction of organic pollutants as described by HAV-ACHA and REBHUN (1992), shown in Figure 2. The presence of DOM in aquatic systems induces a decrease in the bioavailability and the bioaccumulation of hydrophobic organic contaminants (denoted HOC), PAHs, PCBs, ... (AKKANEN and KUKKONEN, 2003). It has been shown that decrease is due to the formation of complexes MOD-COH too large or too polar to cross biological membranes (HAITZER et al., 1998). Interactions MOD-organic contaminants are generally relatively low (RABER and KOGELKNABNER, 1997). It is mainly hydrophobic interactions, "Van der Waals" or $\pi - \pi$.

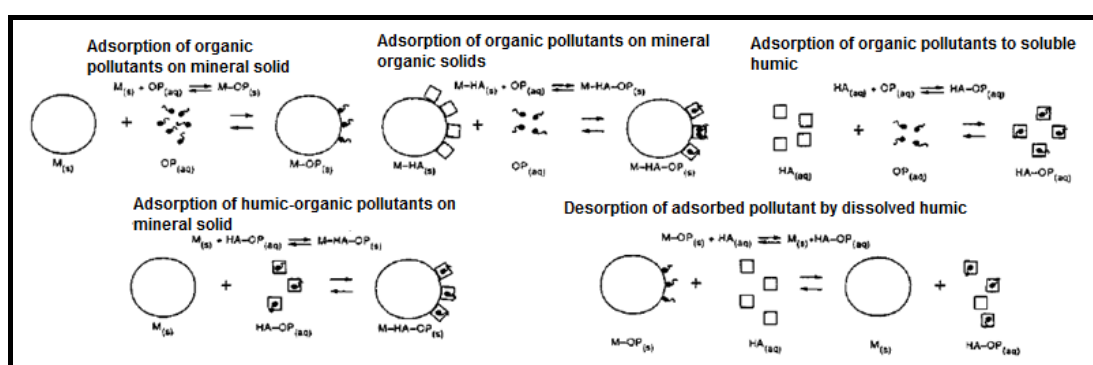


Figure 2: Possible adsorption mechanisms of organic pollutants on solid mineral dissolved organic matter and organic-mineral complexes.

The partition coefficient and Henry's law are important to determine where the solute will tend to accumulate and also calculate the transfer rate between the phases. It is also necessary to determine a number of parameters, mainly: water solubility, vapor pressure, constant Henry's law, the octanol / water coefficient of adsorption and bioconcentration factor (DEARDEN et al, 2003). These parameters can be obtained with a series of experimental methods. Values for a large number of organic pollutants have been collected and are available in the literature.

To characterize the DOM present in urban waste but also to quantify the proportion of hydrophilic DOM in the receiving water to the crossing of the Paris Metropolitan Area our sampling strategy will take place in various hydrological situations (floods, drought) including periods of algal bloom. Will also be affected urban discharges of dry weather or wet weather. For the sorption study of interaction of OPs and dissolved and particulate phase we will choose the sites with a very different typology of DOM, humified substances from the DOM to very hydrophilic and to compare their behavior of sorption of contaminants and particles and DOM. The campaigns will be conducted and funded under the program Piren-Seine (2011 and 2015) and are conducted in collaboration with other researchers of other laboratories (LGE, Sisyphe, EPOC, LSCE, Cemagref Antony and University of Illinois, Chicago).

My study is divided in two chapter: in the first one we study the influence of suspended particulate fraction (mineral and organo-mineral complexes) in the sorption of organic pollutants. In the second one we will develop new methods to study the interactions of different typology of dissolved organic matter and organic pollutants. The objectives of this research project are to assess the transport and fate of OPs and to continue and expand the efforts to

investigate the source–receptor relationships, temporal and spatial trends, determination of free OPs concentration (indicator of bioavailability) and the response to the implementation of better management of aquatic systems under strong urbanization with the key role of urban DOM.

MATERIAL & METHODS

Sampling campaigns of DOM:

The location of sites sampled during snapshot campaigns of August / September 2012 and February 2013 is presented respectively in figure 3. These two campaigns have been made in different flow conditions ($100 \text{ m}^3 \cdot \text{s}^{-1}$) at Austerlitz to August / September 2012 and $900 \text{ m}^3 \cdot \text{s}^{-1}$ at Austerlitz for February 2013 (Figure 3). We have analyzed 38 sites in different location of the basin of Seine (9 on the Seine upstream, 10 on the Marne, 13 on the Oise and 6 on Seine downstream). There are two kinds of sites, for the non-priority sites only 250ml were sampled and on the priority sites 10L were sampled.



Figure 3: Location of stations sampled during the snapshot campaign August / September 2012 (low water period) and February 2013 (BONNOT- LGE, 2013).

Characterization of DOM

Analyses are made in collaboration with other researchers of other laboratories. Two kinds of analyses were made: Physics-chemical characterization of dissolved organic matter in aquatic systems urbanized and determination of its sources (absorption spectroscopy UV-visible, spectrofluorimetry, Asymmetric Field Flow Fractionation (AFFF), fractionation according DOM hydrophobicity, biodegradable dissolved organic carbon (BDOC) and the role of Dissolved Organic Matter (DOM), on the study of the interactions between the DOM, the mineral particles and organic contaminants and metal. Urban DOM origin is particularly studied.

Fractionation of dissolved organic matter

Fractionation is the separation of the DOM according to its hydrophobicity. We used the resins having the best adsorption DAX-8 and XAD-4. Dissolved organic matter will interact with adsorbent resins, and nonionic macroporous (styrene - divinylbenzene or polymers of methyl methacrylate). The hydrophobic moiety of the organic matter is retained on the resin DAX-8, the fraction called "transphilic" is retained on the resin XAD-4 and the hydrophilic fraction, is not retained for any resin.

The fractionation of the MOD was performed according to the protocol of MATAR (2012). The samples before fractionation are filtered with a GF/F filter, concentrated on ROTAVAP and acidified to pH 2 (Figure 4).

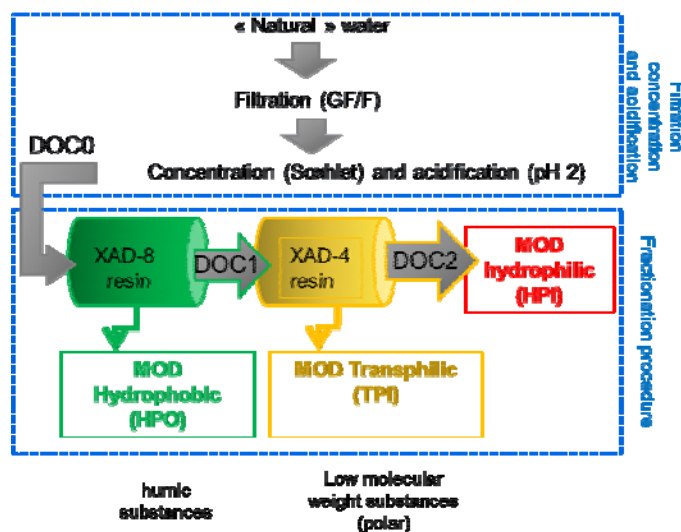


Figure 4: The analytical procedure for preparative DOC from natural waters and wastewaters.

Once passed through the MOD resins (DAX-8 and XAD-4) for the division of each sample, the composition of the effluent obtained outputs of each resin is as follows:

Output-1 (DAX-8) is: $DOM1 = DOC_{total} - HPI = HPO + TPI$

Output-2 (XAD-4) is: $DOM2 = DOC_{total} - (HPO + TPI) = HPI$

The relative proportions of each fraction were determined by measuring the COD input and output column fractions and the percentages are calculated as follows:

$$\% HPO = 100 * [(DOC0 - DOC1) / DOC0]$$

$$\% TPI = 100 * [(DOC1 - DOC2) / DOC0]$$

$$\% HPI = 100 * [(DOC0 - DOC2) / DOC0]$$

The resins were washed before utilization, this step can take more than a month. The non-ionic resins, DAX-8 and XAD-4 were washed 2 times with sodium hydroxide (0.1 mol.L⁻¹) under stirring for a week and the second washing is done in a solid-liquid extraction (Soxhlet) with dichloromethane for 24 hours and then with acetonitrile for 48 hours. Between each wash with solvent, cleaning with Milli-Q water and filtration with GF/F was done. The resins were washed with Milli-Q water until the concentration in dissolved organic carbon was under 0,5mgC/L. For each output of resin the DOC was measured, a blank (output 2-Milli-Q water) and total (concentrated sample) was analyzed.

Analytical procedure to study the sorption of organic pollutants onto mineral and complex organo-mineral

The organo-mineral complexes can influence the surface characteristics and consequently the possible sorption of pollutants onto particulate fraction. For example, the water-solid distribution of OP in the presence of humic acid (HA), are going to depend on the hydrophobicity of AH coated in iron oxide. Iron oxide has a preference for the sorption of less hydrophobic AH, the concentration of hydrophobic AH solution will increase and consequently the sorption of pollutants in the particulate and dissolved fraction is going to be different (MITSUNOBU and TAKAHASHI, 2006).

Several authors have studied the interaction of organic compounds with suspended particulate material to better quantify these pollutants in wastewater systems (AVISAR et al, 2010, BAKER et al, 2012) to study the bioavailability of pollutants (MACKENBACH et al, 2012) in the environment (SITHOLE and GUY (1986); FUKUSHIMA et al (1997); WU et al (2011)). But any study has been conducted in aquatic environments highly urbanized and even less sure the role of the DOM of urban origin in the fate of organic pollutants in the basin of the Seine.

Several study like YOUNG BELL et LEBOEUF (2013), GHOSH et al (2009), FENG et al (2006), have developed a protocol for the sorption of humic acids onto mineral. In the literature there are very few studies about any works with urban DOM for the coating of the mineral surfaces. The studies are made especially for the study in the soil. In our case, we want to see the influence of the DOM (from urban, sub-basin forest and output WWTPs) in the fate of organic pollutants in the basin of the Seine. It is for this reason that we started a protocol to isolate the DOM with different backgrounds and physico-chemical characteristics to do the kinetic and isotherms of sorption.

The adsorption isotherms of organic solutes are divided into four categories, the main categories are as follows (GILES et al, 1960): The S-curves, indicating the vertical orientation of molecules adsorbed on the surface, "S" curves is characteristic of adsorption: (a) monofunctional (no adsorption shaped micelle) (b) shows moderate intermolecular attraction (c) strong competition for substrate sites. The "L" curves (Langmuir) generally representative of molecules adsorbed on the surface, or, occasionally, vertically with a strong intermolecular attraction oriented adsorbed ions. The "H" curves, often given by solutes adsorbed as ionic micelles. And the "C" curves, linear curves given by solutes entering the solid more easily than does the solvent, availability of sites remains constant at all concentrations up to saturation.

For the sorption of DOM onto mineral the clay Montmorillonite (MMT) was chosen like a model of smectite clay. The Na-MMT (SWy-2) was obtained from the Clay Minerals Society's Source and the DOM was sampled from a forester site (Forêt de Compiègne). The clay was adapted of the protocol of purification of CARRADO et al (2000). Carbonates are decomposed by the addition of dilute hydrochloric acid. pH Stat was used to take care that the pH does not drop below 4.5 and to avoid any attack on the clay mineral structure. Decomposition of high carbonate concentrations requires significant time (up to 2 days), we did our decomposition of carbonate for 5 days. We will stabilize the pH until pH 8 (pH of Seine river) we will centrifuge (10000 rt/min 2 hours) and the DOC will be analyzed to determine possible contamination of the Na-MMT. The pellet will be deep-frozen and lyophilized to the future adsorption experiments. The mineral and organo-mineral are going to be characterized with several technics (Table2). These characterizations will help us to better understand our possible interaction and possible changes on aromaticity, specific surface area, morphology, availability of surface sites or Blocking "cavities".

Table 2: Characterization of clays, DOM and organo-clays complexes:

Characterization of solid:	Characterization of DOM:	Characterization of organo-clay complex
Carbon-13 MR (some samples)	COD	COD and COP Point of zero charge
Carbon and nitrogen analysis	Ultraviolet-visible spectroscopy	Brunauer-Emmett-Teller (BET)
Brunauer-Emmett-Teller (BET)	High performance size exclusion chromatography	Scanning Electron Microscope (SEM)
Point of zero charge		
Scanning Electron Microscope (SEM)	Fluorescence Spectrometry	
X-ray scattering techniques		

Analytical procedure to study sorption of organic pollutants onto DOM

The objective is to develop one protocol of extraction adapted for the analysis of organic pollutants on the dissolved organic carbon, to characterize the interactions between MOD and urban organic micropollutants to promote better understanding of the behavior of organic pollutants in the basin of the Seine and their bioavailability with the estimation of KDOC (free OPs).

Sampling sites will be selected to access DOM with very different typologies. We privileged to work on samples of marked typologies will be privilegedly marked of like urban DOM (hydrophilic component) and or humic certain humic (forest). Contaminants will necessarily have different characteristics: hydrophobic compounds (PAHs, PCBs), and polar compounds loaded. We will work at different concentrations of contaminants. The KDOC organic contaminants will be measured directly in filtered samples. We are going to use the technique of micro-solid phase extraction (SPME) to determine the “free” organic pollutant fraction.

The technique of micro-solid phase extraction (SPME) has been developed in the 90s by the research team of Dr. Pawliszyn Januz (ARTHUR and PAWLISZYN, 1990). Recent years, several publications have been made and suitable for organic pollutant analysis, initially developed for the analysis of trace organic compounds trace in water (volatile organic compounds, polycyclic aromatic hydrocarbons, pesticides, surfactants, organometallic, organochlorines, amines ...), the SPME sampling technique was then adapted to the analysis of other matrices such as air (KOZIEL et al 2000), soil, biological and food materials (BELTRAN et al 2000, KATAOKA et al 2000).

The SPME has two steps: First, analyte organic pollutants are extracted by a fiber from a sample matrix for a predetermined time. Secondly, the fiber is removed from the sample and the analyte is desorbed kept in an analytical instrument to be separated and quantified. The desorption step is usually carried out by thermal desorption, by placing the fiber in an injector of a gas chromatograph (GC) or in the desorption chamber a SPME / HPLC (ALPENDURADA, 2000). The parameters that must be applied to develop a method SPME are proposed by RISTICEVIC et al (2010) to develop a common protocol SPME. Several other studies have been carried out with the same goal by different research groups: WARDENCKI et al, 2007; RISTICEVIC and al 2010, OUYANG et al 2005, 2006 and 2008, DUGUAY et al, 1998. The organic pollutant studied was PAHs because it is one of the priority substances (water framework directive, DCE - good chemical status) and is also a specific pollutant for assessing the ecological status of aquatic systems.

We tested the better extraction temperature (natural temperature and 40°C), the extraction time and the temperature of desorption were optimized and better different fibers (PDMS or PDMS-DVB) were tested for extraction of PAHs. Accuracy and repeatability were tested too in the GC/FID assessed.

RESULTS AND DISCUSSION

Characterization of DOM for the Seine river basin

The concentration of the different sites is represented on the Figure xxx5. In the basin of Seine river basin have a gradient of DOM concentration were observed with the upstream sites of upstream more concentrated than downstream. and the strongest concentration was for Forest de

Compiègne (Oise River) (Figures 5). The strongest concentration was for the Forêt de Compiègne (Oise River) site and Senuc (Aisne River) for the campaign of February 2013. These two sites are being selected to the future procedure of coating mineral to the analyses of sorption with OPs.

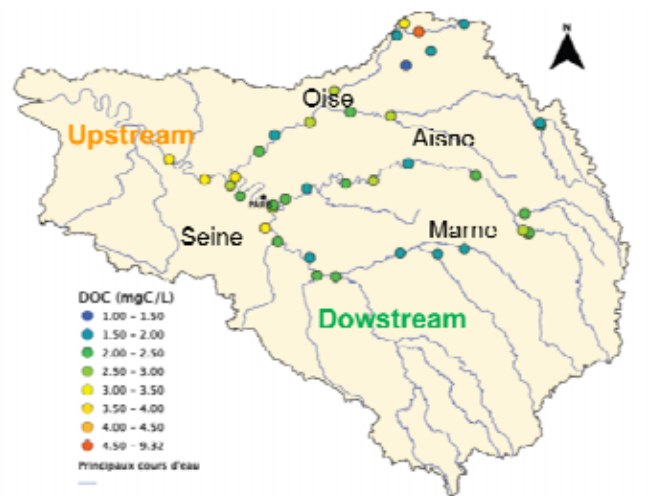


Figure 5: Concentrations of dissolved organic carbon (DOC) for sites sampled during the campaign in August / September 2012. (BONNOT- LGE, 2013)

The results of fractionation of the DOM samples for the campaign August/september 2012 and February 2013 are represented on the Figure 7. The results from August/september 2012 confirm the distribution between the different DOC fractions, hydrophobic (HPO) transphilic (TPI) and hydrophilic (HPI) which represent respectively 32%, 27% and 41%, these values changed little from one station to another and also little from upstream to downstream (for the champagne of August/september 2012). This low hydrophobicity is quite consistent with the results obtained in the framework of the thesis Zeinab Matar (MATAR, 2012). This confirms the low proportion of humified DOM at this time and a preponderance of fresh organic matter little mature probably due to indigenous production. Greater hydrophobicity is representative during floods (February 2013) with hydrophobic DOC values reaching well over 50% because of terrigenous source.

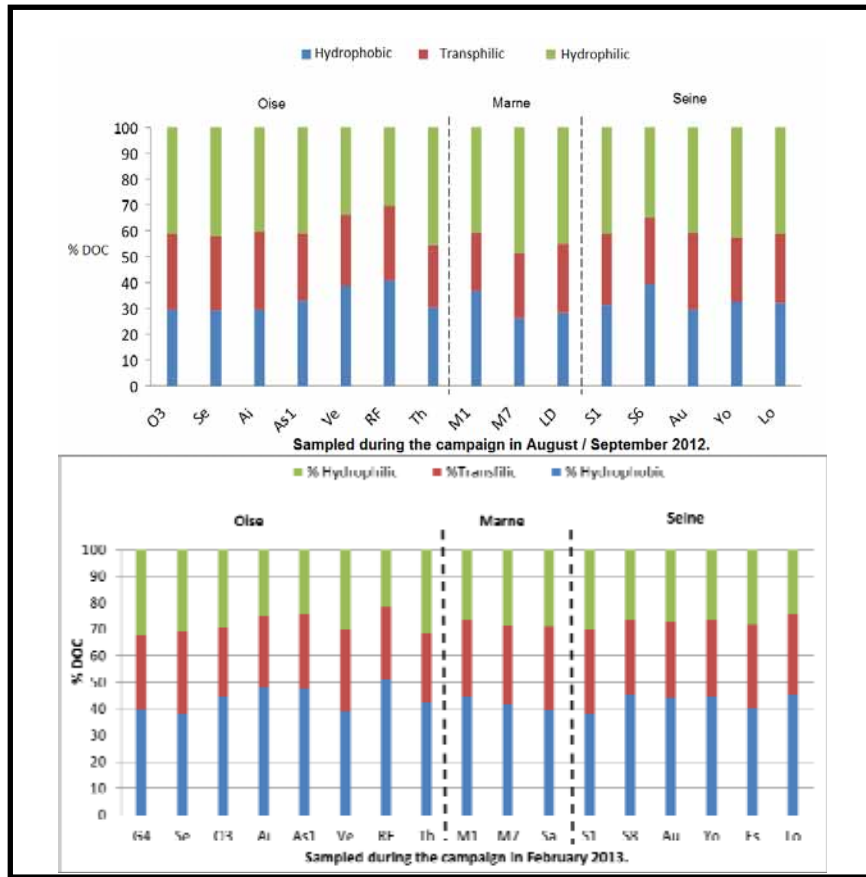


Figure 7: Distribution of dissolved organic carbon (mgC.L-1) by fractions hydrophobic, and hydrophilic and transphilic fractions for priority sites sampled during the campaign in August / September 2012 and February 2013.

Development of analytical procedure to study sorption of organic pollutants onto DOM

The extraction temperature is not a parameter that have a strong effect on the extraction of light PAHs. For heavy PAHs there is a better extraction and greater signal at 40°C (Figure 8). The temperature has a strong influence on the desorption of high molecular weight molecules. For PDMS fiber, the signal of PAHs is directly proportional to the increase in temperature. The better temperature of desorption is 270°C.

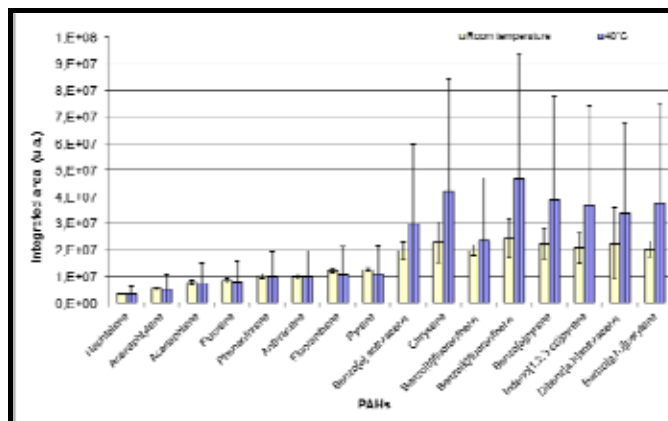


Figure 8 : Difference in the extraction of PAH as a function of temperature, at room temperature and at 40°C.

SPME technique has good robustness (variability = 24-37%) for PAHs with molecular weight less than or equal to $178 \text{ g}\cdot\text{mol}^{-1}$, while the detection limits vary considerably for heavier compounds (mean = variability 61% . Results of DE PERRE (2009) confirm these results.

Agitation has a strong influence on the repeatability. For the analysis without agitation, an error of 70% was observed for the heavier PAHs. With agitation the PDMS fiber has a maximum error for fluoranthene (40%) and the PDMS-DVB fiber of for dibenz [a,h] anthracene (55%).

The performance of SPME can be affected by many physical-chemical parameters and these results are important to choose the better parameters to have great repeatability, robustness and limit of detection. The selected parameters are : 60 minutes of extraction, with stirring and at 40°C , 30 minutes of desorption at 270°C , 10 minutes of conditioning to eliminate possible contamination, and time of purge (4 minutes). These results are important to help us to better understand this new technique in our laboratory, and to adapted our study to environmental concentration, for that we will make tests extraction/desorption on GC/MS.

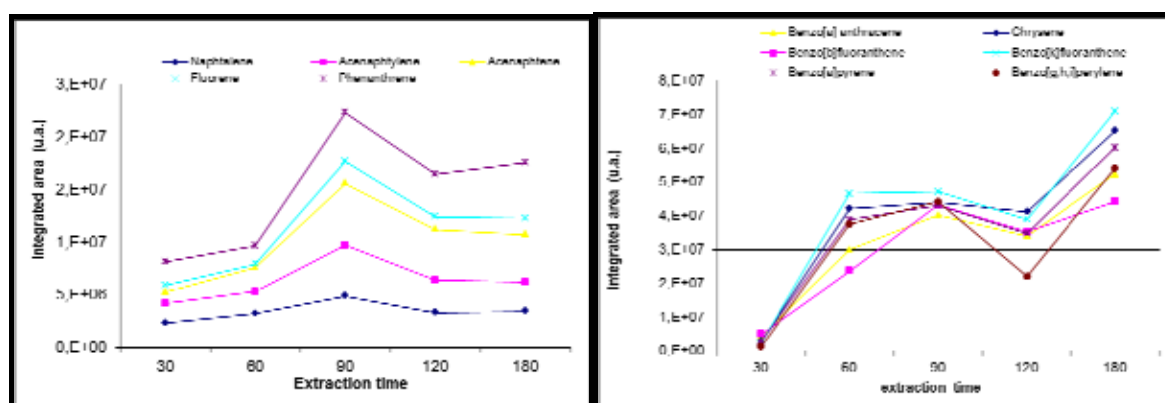


Figure 9: Results of PAH extraction time with the PDMS fiber

CONCLUSIONS

The physico-chemical characteristics influence of urban DOM on sorption of organic contaminants has not taken into account in study of surface water. Based on its affinity for contaminants, can change the speciation of dissolved phase contaminants and thus affect their bioavailability. It can also modify the adsorption properties of particles (suspended or in sediment) and therefore strongly influence the distribution dissolved / particulate with all that flows in terms of contaminant transport.

My research perspectives are to elucidate the influence of the DOM of urban origin on the biogeochemistry of OPs. For first I will take into account the role played by the particles in the speciation and biogeochemistry of these contaminants and on the last year of my thesis projects the dissolved phase.

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