Influence of Organic Matter from Urban Effluents on Trace Metal Speciation and Bioavailability in River Under Strong Urban Pressure

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Abstract In aquatic systems, dissolved organic matter (DOM) constitutes a key component of the carbon cycle controlling the transport, speciation, bioavailability, and toxicity of trace metals. In this work, we study the spatiotemporal variability of the MO in terms of both quality and quantity from upstream to downstream the Parisian conurbation. Urban discharges which are the main source of allochthonous organic matter into the Seine at low-water periods were also investigated. The DOM collected was fractionated according to polarity criteria into five fractions: hydrophobic, transphilic, hydrophilic acid, hydrophilic basic, and hydrophilic neutral. Due to urban discharges, a strong enrichment in the hydrophilic (HPI) fraction was observed for downstream sites. This hydrophilic fraction presented stronger binding capacities for copper than hydrophobic fraction from less urbanized site (upstream from Paris) and Suwannee river fulvic acid (SRFA). Furthermore, biotests highlighted a significant copper bioavailability decrease in presence of hydrophilic DOM.

Keywords Hydrophilic organic matter • Urban discharges • Trace metals • Speciation and bioavailability

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Introduction

In aquatic systems, dissolved organic matter (DOM) constitutes a key component of the carbon cycle controlling the speciation, bioavailability, and toxicity of trace metals (Buffle 1988; Tessier and Turner 1995). Over the past few decades, many studies have been published regarding the capacity of DOM to complex trace metals. It is interesting to note however that the published data pertain mainly to the so-called humic substances (HS) and demonstrate the ability of these substances to complex metals.

In aquatic system under strong urban pressure, the hydrophobic characteristic of DOM is weaker as a result of various urban DOM discharges and of the strong primary productivity induced by these discharges (Pernet-coudrier et al. 2008). Because of the difficulty in isolating the hydrophilic fraction of DOM, very little information is available regarding its composition and influence on metallic speciation, bioavailability, and toxicity, particularly in anthropized rivers. In previous works, we highlighted the high trace metal-binding ability of DOM from one wastewater treatment plant (WWTP) effluents by dry weather (Pernet-coudrier et al. 2008). In this study, in order to assess the dissolved organic carbon (DOC) distribution between hydrophobic, transphilic, and hydrophilic fractions in river under strong urban pressure, an extensive survey of receiving waters upstream and downstream Paris has been carried out. Urban discharges have also been investigated. The hydrophilic fraction has been especially studied.

Materials and Methods

A monthly sampling campaign (30 samples) has been undertaken over a period of 12 months (October 2010–September 2011) in order to assess the spatiotemporal variability of DOM in receiving waters and the potential impact of urban discharges. Sampling sites were located upstream Paris ("Ussy-sur-Marne" on the river Marne and "Fontaine-le-Port" on the river Seine) and downstream Paris ("Andresy").

Ten campaigns (20 samples) have been carried out in order to sample treated effluents of five different wastewater treatment plants (WWTP with different wastewater treatment methods) in Parisian conurbation.

Furthermore, during rainstorm events, the WWTP capacity may be exceeded, and the water overload is discharged to the river without any treatment. A major wet weather outlet in this system is located on the right bank of the river, at the Clichy pretreatment plant (more than 75% of the sewage water from Paris and its suburb). The combined sewer overflow (CSO) discharge was sampled with an automatic sampler equipped with a cooled (4°C) compartment. An average sample is reconstituted by the assembling of subsamples collected every 6 min over 30 min into glass 1-L bottles. CSO was processed within 3 h after collection of the last sample. Nine discharges were sampled between June 2010 and September 2011.

For all these samples, DOM was fractionated according to polarity criteria. Samples of about 10 L were first filtered (0.45 μm) and then acidified and filtered on nonionic macroporous XAD-8 resins and XAD-4. This allows us to fractionate DOM into different fractions according to polarity criteria: hydrophobic (HPO) and transphilic (TPI) fractions are retained, respectively, onto XAD-8 and XAD-4 resins (Croué 2004). Basic and acid hydrophilic (HPI) fractions are, respectively, retained onto cationic exchange resin (AGMP-50) and anionic exchange resin (AGMP-1). The neutral hydrophilic fraction, not retained by any resins, is in the effluent. This protocol allows us to fractionate DOM into five fractions according to polarity criteria: hydrophobic (HPO), transphilic (TPI), hydrophilic basic (HPI-B), hydrophilic acid (HPI-A), and hydrophilic neutral (HPI-N) fractions. Various physicochemical analyses were carried out to characterize the isolated fractions (DOC, spectrofluorescence, SUVA, etc.).

Copper-binding abilities of each isolated fraction were assessed using potentiometric methods (ISE). Data obtained from DOM titration were modeled with the NICA-Donan model which gives us stability constants and metal-binding site numbers for each fraction. Influence of each isolated fractions onto copper toxicity and bioavailability was assessed with acute toxicity tests. These tests were also carried out in order to compare properties of DOM from nonurbanized areas (upstream Paris and SRFA as a fulvic reference) with DOM collected from urban discharges.

Results and Discussion

At low-water periods, surface waters studied show DOC concentrations varying from 2.2 mg C/L to 3.4 mg C/L from upstream to downstream of the Paris area (Fig. 1). Increase of DOC downstream Paris is principally due to urban discharges (about 10–15 mg C/L for the treated effluent of the main Parisian WWTP). Furthermore, the surface waters DOM displays a more pronounced hydrophobic character upstream (41% HPO and 33% HPI for Ussy-sur-Marne and 39% HPO and 34% HPI for Fontaine-le-Port) than downstream Paris (35% HPO and 45% HPI for Andresy). This increase of the hydrophilicity downstream Paris is attributed to urban discharges. Indeed, the DOM collected from urban discharges (CSOs and WWTP effluents) displays strong hydrophilic characteristics, low humic substance contents (Fig. 1), low SUVA, and high contents of protein compounds. These results highlight the influence of urban discharges on the receiving waters DOM quality.

As it can be seen in Fig. 2, DOM from urban discharges and from downstream sites present high binding capacities for copper compared to DOM from the least urbanized sites (upstream Paris and SRFA). These results also indicate a difference in the copper-binding ability according to the different organic fractions;

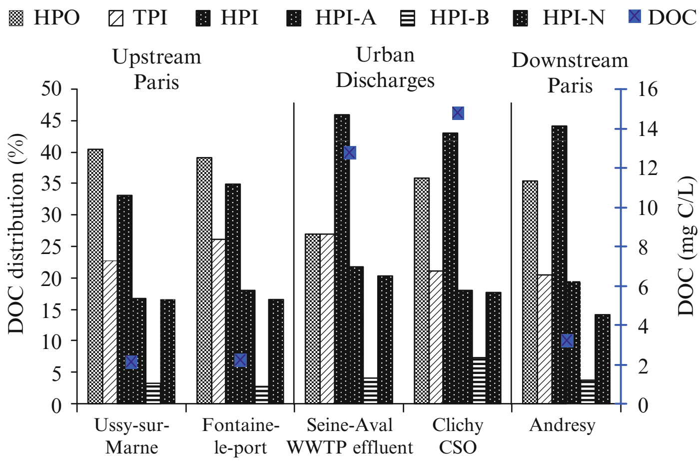

Fig. 1 DOC and distribution of DOC at low-water periods in receiving waters of the Parisian conurbation and urban discharges

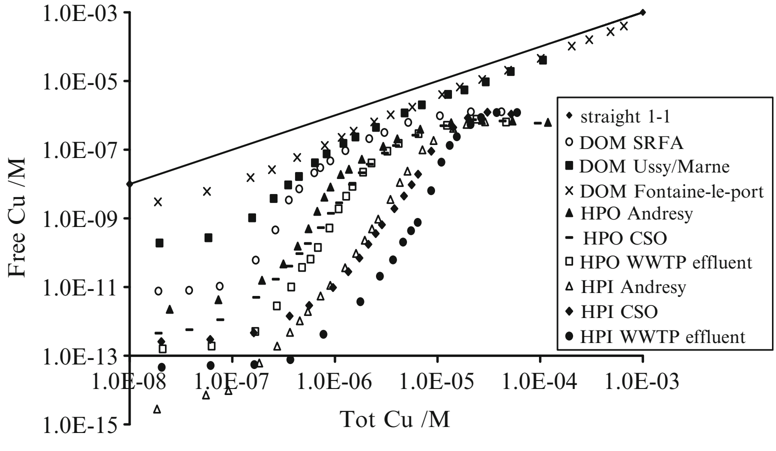

Fig. 2 Copper titrations of different DOM (non-fractionated) and different DOM fractions

hydrophilic fractions have a higher binding ability than hydrophobic and transphilic fractions (Fig. 2). Furthermore, acute toxicity tests highlighted a significant copper bioavailability decrease in presence of DOM especially in presence of hydrophilic DOM from combined sewer overflows.

Conclusion

This study highlights that in rivers under strong urban pressure, the hydrophilic DOM may be the main component of DOM especially at low-water periods. On the opposite, humic substances are a minor part of DOM. This is due, for one part, to urban discharges. This study confirms our first results showing a strong influence of hydrophilic DOM from WWTP effluent on the trace metal biogeochemistry. Furthermore, for the first time, this study demonstrates that DOM from CSOs contains also high proportion of hydrophilic organic matter with high binding capabilities and then with strong influence onto trace metal speciation and bioavailability within aquatic systems. This is why it is essential to also consider the binding capabilities of hydrophilic organic matter when computing trace metal speciation and bioavailability within aquatic system under strong urban pressure.

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References

Buffle, J. 1988. In *Complexation reactions in aquatic systems: An analytical approach*, ed. M. Masson, J.F. Tyson, 124–692. New York: Ellis Horwood.

Croué, J.F. 2004. Isolation of humic and non-humic fractions: Structural characterization. *Environmental Monitoring and Assessment* 92: 193.

Pernet-coudrier, B., L. Clouzot, G. Varrault, M.H. Tusseau-vuillemin, A. Verger, and J.M. Mouchel. 2008. Dissolved organic matter from treated effluent of a major wastewater treatment plant: Characterization and influence on copper toxicity. *Chemosphere* 73(4): 593–599.

Tessier, A., and D.R. Turner. 1995. *Metal speciation and bioavailability in aquatic systems*. Chichester: Wiley.