



Diel cycles of reduced manganese and their seasonal variability in the Marque River (northern France)



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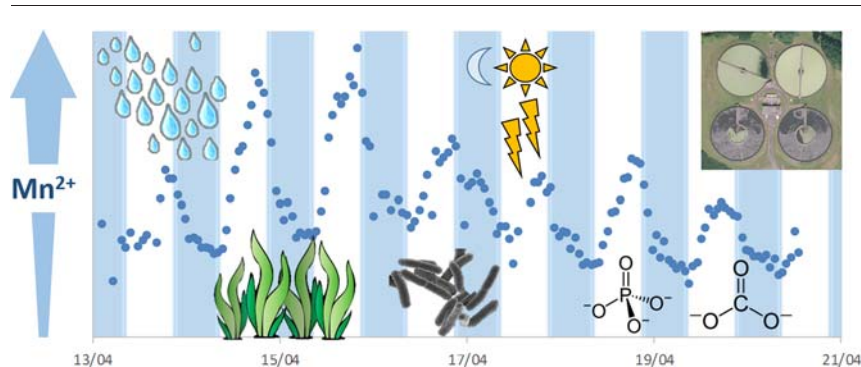
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HIGHLIGHTS

- High frequency monitoring of electrolabile Mn^{2+} in a small river was performed.
- Diel and seasonal variations were observed over two one-month periods.
- Photoreduction of MnO_x and biotic oxidation of Mn^{2+} partly control Mn behaviour.
- Biodegradable organic matter input during storms impacted Mn^{2+} concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrolabile reduced manganese (II) has been monitored by voltammetry during two periods of one month in summer 2014 and at the end of winter 2015 in a small river (the Marque River) located in northern France and going through a suburban area with agricultural activities. Diel variations, evolution within the one-month periods and seasonal differences have been observed. Taking into consideration the multiple physical, biological and chemical reactions regulating manganese speciation in aquatic systems, it has been demonstrated that manganese speciation is probably controlled by the competition of two antagonist reactions: the photoreduction of manganese oxides (in broad sense and represented thereafter by MnO_x) and the biotic oxidation of $Mn(II)$. Depending on the season, the biological activity in the river and the amount of luminosity reaching the MnO_x , either the production of reduced labile $Mn(II)$ or the precipitation of MnO_x can become the dominant process. Other punctual events such as the drop of oxygen concentration due to large inputs of biodegradable organic matter and eutrophication phenomena, rainy events and high luminosity periods can also affect the behaviour of dissolved $Mn(II)$ in the Marque River and so, of other contaminants.

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1. Introduction

Manganese is considered as the 12th most abundant element in the biosphere. Its concentration in the Earth's crust reaches as much as

0.098 mass % (Morgan, 2000). More particularly, it is widely spread in the terrestrial aquatic systems with concentrations in the range of 0.1–10 $g\ kg^{-1}$ in fine sediments, of 0.1–10 $mg\ L^{-1}$ in porewaters (Martynova, 2012) depending on the primary redox reactions promoted by the bacterial activity and the secondary other reactions. In the overlying waters, concentrations up to several hundred $\mu g\ L^{-1}$ can be measured (World Health Organization, 2004).

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Manganese can be assimilated by aquatic organisms mainly under its ionic form Mn^{2+} , as an essential nutrient at low concentrations but also as a toxic element with LC50 (Lethal Concentration) in the $mg\ L^{-1}$ order of magnitude (Howe et al., 2004). However, at high concentration, manganese can also serve as a protection against more toxic elements (Sunda and Huntsman, 1998). Mn is a key element when monitoring trace metal contamination or nutrient bioavailability in aquatic media as it controls partly their speciation. Manganese oxides and oxo-hydroxides (represented thereafter by MnOx) can be efficient adsorption phases for cationic species in the pH range commonly found in waters and sediments (pH 5–9) as its PZC value (Point of Zero Charge) is around pH 5. Mn is also known for co-precipitating with several elements like Fe, Zn, Pb, Co (Hem, 1980; Shope et al., 2006).

The speciation of manganese can be difficult to determine as it is stable or metastable under various forms that can be dissolved, colloidal or particulate, with several oxidation states (Stumm and Morgan, 1996). Considering experimental studies and computing calculations, dissolved Mn(II) is considered as relatively labile and less complexed by organic matter compared to other trace metals like Cu, Co, Ni, Pb or Zn (Abbasse et al., 2002; Charriau et al., 2011). Its speciation can evolve quickly due to chemical, biochemical or physicochemical reaction (e.g. Morgan, 2005). For instance, diel cycles have been observed for manganese redox speciation in different types of waters: Brick and Moore (1996) have monitored the cycles of dissolved Mn in acid mine drainage, highlighting the role of redox reactions in sediments. Another study case by Scott et al. (2002) explained the variations of dissolved Mn(II) concentrations over 30 h monitoring by modelling several aquatic redox mechanisms.

In order to monitor the numerous species of manganese, several methods can be used with more or less relevant discrimination. Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) is relevant to measure total dissolved concentrations but the presence of the colloidal fraction makes difficult the interpretation of the results. Chemiluminescent approach with the Mn(II) catalysed oxidation of 7,7,8,8-tetracyanoquinodimethane (Chapin et al., 1991) allows the specific measurement of dissolved reduced Mn only. Another technique, also selective to dissolved Mn(II) quantification, is the voltammetry that can be used in direct cathodic mode if the concentrations are sufficiently high [like in sediment porewaters (Brendel and Luther, 1995; Pižeta et al., 2003)] or in ASV (Anodic Stripping Voltammetry) for trace levels. One of the advantages of the latter technique is the possibility to carry measurements in field and to perform on-line measurements for observing short time variations like diel cycles (Superville et al., 2011).

This study is part of a large monitoring project of the Marque River (northern France) and focus in this paper on the variation of labile reduced Mn(II) measured every hour during one month in summer 2014 and one month at the end of the winter of 2015. A review of known phenomena potentially affecting Mn in riverine environments is made to give a general explanation of dissolved Mn behaviour in relation with other key parameters controlling the general composition and chemical properties of this riverine water.

2. Experimental

2.1. Site description

The Marque River is a natural watercourse located in northern France that belongs to the Scheldt drainage basin. Upstream the study site in Villeneuve d'Ascq, it mainly runs through an agricultural area with several villages in the vicinities and then continues in the Lille agglomeration, before flowing in the Deûle River (Ivanovsky et al., 2016). The monitoring station has been installed at Hem, upstream the highly urbanised part of the watershed. It is located however just downstream two main anthropogenic discharges (Fig. 1). The first one is the waste water treatment plant (WWTP) of Villeneuve d'Ascq, which has a capacity of 170,000 population-equivalent (including 50,000 population-

equivalent from the nearby industries). Its impact is significant on several parameters bound to the water quality of the river as its flow represents on average 23% of the total river flow. The second one is the Héron Lake, an artificial storm overflow, receiving the rainwater from parks, streets and the motorway, as well as a small fraction of non-treated domestic effluents. When the level of the lake is too high, water is automatically pumped into the Marque River in order to avoid floods in the residential area around the lake. The flow from the lake represents on average 7% of the river flow and the chemical quality of this input is generally better than that of the river (Ivanovsky, 2016).

2.2. Hydrological context of the campaigns

The Marque River was monitored twice during one month: first from June 23rd to July 23rd 2014 and then from March 20th to April 20th 2015, later referred as summer 2014 and winter 2015 respectively. During the two campaigns, significant rainy events and periods of low water flow have been recorded. The Marque River is a very dynamic hydrological system with water levels that can be multiplied by 5 in a few days during storms. The origin of the water in the river has not been deeply studied but the main fraction may come from the surface runoff and external inputs from treated wastewater (especially during rainy periods) whereas a smaller part would come from the surficial aquifer (Craetes de Paulet and Dufrenoy, 2012; Ivanovsky et al., 2016). In the 2014 summer campaign, two main rainy events occurred: one rather limited in time with a big storm, from June 27th to 30th and a longer one from July 5th to 11th. In winter 2015, the campaign is divided between the 2 first weeks when it was raining regularly and the last 2 weeks when the weather was mainly sunny [see Supplementary information (SI)].

2.3. Material and methods

A power supplied monitoring station belonging to the French Water Agency was installed at Hem. After pumping the water, the following parameters were measured online every 10 min: water temperature, pH, conductivity, turbidity, concentrations of dissolved oxygen, nitrates, orthophosphates and ammonium, luminosity and precipitation level.

Inside this station, an automatic trace metal monitoring system was implemented (Superville et al., 2011). Briefly, it is made of a voltammetric system (a μ Autolab III potentiostat with a mercury drop 663VA stand, Metrohm, controlled by GPES 4.9.007 software, Eco Chemie); the flow cell was supplied in river water and cleared with independent peristaltic pumps. The determination of electro-labile concentrations of Mn (El Mn) was performed at natural pH on non-filtrated water as follows. Differential Pulse Anodic Stripping Voltammetry (DPASV) was chosen with a deposition potential at $-1.65\ V$ during 300 s; the redissolution potential ramp is set up with a period of 0.1 s, a modulation time of 0.05 s, a pulse amplitude of 25 mV and a step potential of 2 mV. Calibration steps were performed weekly on site by addition of diluted standard solution (Merck) in UV-digested water from the Marque River.

In parallel, discrete samples were grabbed as well in order to test a possible contamination of the online system towards manganese and to determine Mn, Fe, As and Zn in the total dissolved fraction. After sampling, the water was immediately filtered on a cellulose acetate filter (Alltech; porosity of $0.45\ \mu m$) and acidified at 2% with ultrapure nitric acid (Sigma-Aldrich). The subsequent analyses were performed by ICP-MS (X Series Thermo Elemental) or ICP-OES (Varian Vista, axial view) depending on the concentration levels of the four elements. Calibration standards were prepared from $1000\ mg\ L^{-1}$ standard solutions (Merck) carefully diluted in the range of concentrations present in the samples.

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