Iron speciation at the riverbank surface in wetland and potential impact on the mobility of trace metals

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HIGHLIGHTS

- Fe(II) precipitates as solid Fe(III) at the riverbank surface.
- Ferrihydrite and Fe-OM associations are the main Fe-phases at the riverbank surface.
- Metals bound to Fe oxyhydroxides and OM accumulate at the riverbank surface.
- Fe oxyhydroxides at the riverbank act as seasonal scavenger of metals.
- Riverbank erosion is the key factor of metals mobilization as colloids in the river.

GRAPHICAL ABSTRACT
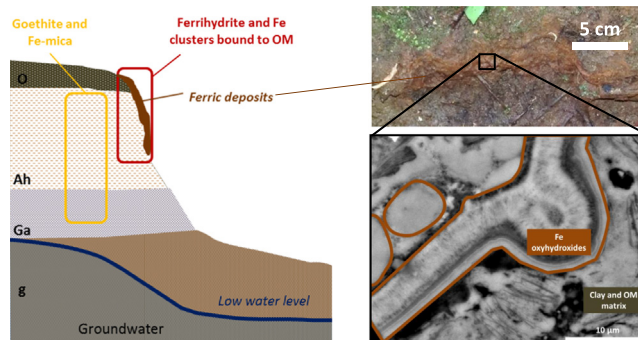
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ABSTRACT

Fe oxyhydroxides in riverbanks and their high binding capacity can be used to hypothesize that riverbanks may act as a "biogeochemical filter" between wetlands and rivers and may constitute a major mechanism in the trapping and flux regulation of chemical elements. Until now, the properties of Fe minerals have been very poorly described in riverbanks. The goals of the present work are to identify Fe speciation in riverbanks where ferric deposits are observed and to determine their impact on the metal behavior (As, Co, Cu, Ni, Pb, Zn, etc.).

At the surface, Fe speciation is mainly composed of small poorly crystalline Fe phases, i.e. ferrihydrite (~30%), Fe-OM associations (~40%) as well as crystalline Fe phases, i.e. goethite (~35%). At the subsurface, the Fe distribution is dominated by goethite (~35%) and Fe-mica (~35%), the proportion of which increases at the expense of ferrihydrite and the Fe-OM associations.

At the riverbank surface, ferrihydrite and the Fe-OM associations are therefore the main Fe hosting phases in response to (i) the fast Fe(II) oxidation induced by the presence of O_2 and (ii) the high amount of OM favoring the formation of nano-phases bound to OM (Fe monomers, polymers and nanoparticles) and preventing mineralogical transformation (ferrihydrite into goethite).

During the high-water level period (high flow), a strong erosion of the riverbank transfers these ferric deposits into the river. However, the physicochemical parameters of the river (pH 6.6–7.6 and continuous oxic conditions) do not promote the dissolution of Fe oxyhydroxides and OM. Ferric deposits and the associated trace metals are therefore maintained as colloids/particles and are exported to the outlet. All of the results presented here

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demonstrate that the ferric deposits trap metals on a seasonal basis and are therefore a key factor in the mobilization of metals during riverbank erosion by river flow.

1. Introduction

In the watershed, the riverbanks are strategic zones between the soil, groundwater, hyporheic zone and river. In wetland, reduction periods occur promoting a strong solubilization of chemical due to the water saturation in soil. Reduced water is charged in chemical and drained by river that is under oxic conditions exhibiting high Eh values (directly in contact with O_2 from atmosphere) (e.g. Dia et al., 2000; Olivie-Lauquet et al., 2001; Grybos et al., 2007; Kerr et al., 2008; Schulz-Zunkel and Krueger, 2009). There is also a formation of a strongly reactive redox interface in riverbank. The redox potential (Eh) and pH variations, as well as the amount of organic matter (OM) and both Fe and Mn oxyhydroxides solubilization/precipitation control the processes that drive the mobility of the associated chemical elements (e.g. McKenzie, 1980; Dzombak and Morel, 1990; Lee et al., 2002; Grybos et al., 2007; Borch et al., 2009; Du Laing et al., 2009). Organic matter and Fe/Mn oxyhydroxides are well-known scavengers of chemical elements because of their high surface-sorption capacity (e.g. McKenzie, 1980; Buffle, 1988; Mustafa and Haq, 1988; Benedetti et al., 1996; Trivedi and Axe, 2001; Grybos et al., 2007; Hassellöv and von der Kammer, 2008; Lynch et al., 2014). In wetlands, under reducing conditions, Fe oxyhydroxides are dissolved by mechanisms that are largely catalyzed by bacteria, releasing Fe(II) in solution and associated elements such as metals or metal-OM complexes (Francis and Dodge, 1990; Chuan et al., 1996; Charlatchka and Cambier, 2000; Dia et al., 2000; Zachara et al., 2001; Davranche et al., 2003; Grybos et al., 2007). Iron(II) released in solution may therefore precipitate as solid Fe(III) in response to the O_2 diffusion in the riverbank porosity.

The variability in physicochemical conditions (temperature, redox potential, pH, O_2, CO_2, nutrients) produces a wide range of Fe oxyhydroxides (i.e. goethite, ferrihydrite, lepidocrocite, hematite, maghemite, etc.) with different morphologies, surface areas and particle sizes (e.g. Roden, 2003; Taylor and Konhauser, 2011). Goethite (α-FeOOH) is the most common Fe oxyhydroxide in environment with respect to its high thermodynamic stability under ambient conditions (Cornell and Schwertmann, 2003; Navrotsky et al., 2008). Ferrihydrite, a hydrated semi-crystalline material ($Fe_5(OH)_8 \cdot 4H_2O$) and lepidocrocite (γ-FeOOH) are also known to exist in wetland environments (e.g. Gault et al., 2012; Guénet et al., 2016). Ferrihydrite is generally the result of the fast hydrolysis of Fe(III) in a poorly crystalline structure, while lepidocrocite develops through the oxidation of Fe(II) from the structure of the minerals (e.g. biotite) or through intermediary mineral transformation, e.g. green rust (Tarzi and Protz, 1978; Schwertmann and Fechter, 1994; Vodyanitskii, 2010). Furthermore, the occasional formation of lepidocrocite in pure Fe(III) systems has been reported (Fordham, 1970) and Guénet et al. (2016) evidenced the formation of nano-lepidocrocite and small Fe nano-oxides bound to OM in a riparian wetland.

Both the presence of such Fe oxyhydroxides at the riverbank surface and their high binding capacity allow hypothesizing that riverbanks may act as a "biogeochemical filter" between wetlands and rivers which could be a major mechanism in the trapping and flux regulation of chemical elements. Some studies have shown the impacts of riverbank sediments on the improvement in water quality in alluvial aquifers (e.g. Bourg et al., 1989; Du Laing et al., 2007), on the redox trapping of As or Zn (e.g. Datta et al., 2009; Stahl et al., 2016; Lynch et al., 2017), or on the distribution of elements (Zn and Fe) along vertical redox gradients of floodplain soil profiles (Shaheen and Rinklebe, 2014; Chen et al., 2017). However, the properties of Fe minerals are very poorly described

in riverbanks. Redox alternations influence the composition and properties of the ferric deposits that can be formed along riverbanks. As a result, it is crucial to better characterize this strategic interface in order to predict the speciation and transport of metals, nutrients or organic compounds. For this purpose, riverbank samples were collected in the Mercy wetland at Naizin (Morbihan region, France). Iron-bearing phases were identified using complementary techniques: X-ray diffraction (XRD) to identifiy Fe oxyhydroxides crystalline structures, scanning electron microscopy (SEM) to unravel poorly crystalline structures and associations with OM and X-ray absorption spectroscopy (XAS) to characterize the Fe solid-phases speciation.

2. Materials and methods

2.1. Sample location and sampling

Riverbank samples were collected from the Mercy riparian wetland of Kervidy-Naizin located in Brittany, Western France (Fig. 1). Numerous hydrological and biogeochemical studies have characterized this area over the past 20 years (ORE AgrHyS). Since redox cycles involving Fe have been highlighted in this wetland (e.g. Dia et al., 2000; Olivie-Lauquet et al., 2001; Grybos et al., 2007), this catchment is particularly suitable for studying solid-phase Fe speciation. The Mercy riparian wetland is regularly altered by drying (in summer) and flooding (in winter) conditions (Lambert et al., 2013; Fig. EA-4). Soils are developed in a colluvio-alluvial formation (Bourrié et al., 1999). The soil displays four horizons (Fig. 1d): (1) from 0 to 10 cm, an organic horizon (O); (2) from 10 to 30 cm, an organo-mineral horizon (Ah); (3) from 30 to 40 cm, an albic horizon (Ga); (4) less than 40 cm, redoxic horizon (g). Soils in the Mercy wetland are considered as organo-mineral soils mainly dominated by clay (42%), quartz (30%) and Fe oxyhydroxides (3.5%). The clay fraction is composed of kaolinite, smectite, mica, hydroxyl-aluminous, vermiculite and interstratified minerals (Pellerin and Van Vliet-Lanoë, 1998). Bourrié et al. (1999) demonstrated the presence of green rusts in these hydromorphic soils between the redoxic horizon and the schistose saprolite.

Samples were collected in December 2016. However, there was no significant water flow in the stream bed. All samples were therefore collected under oxic conditions. Samples were collected at the riverbank surface (Fig. 1d), where ferric deposits are observed over a length of 20–30 m (Surface samples: P1 0–5, P1 5–10, P2A, P2B and P3). Riverbank is in permanence under oxic conditions. The water level bellows the ferric deposit allowing a supply of O_2 regardless the atmosphere and the water is always under oxic conditions (Fig. EA-4). P1 samples include the organic horizon. P2A and P2B include the albic horizon and P3 is a peculiar sample corresponding to a small amount of the observed ferric deposit (Fig. 1c). The ferric deposit is essentially developed on the surface of the organo-mineral horizon (Fig. 1c) making of P2A and P2B the most suitable to represent Fe deposits at the riverbank surface. A profile was also collected below the riverbank surface (horizontal thickness of ~10 cm, subsurface samples) in three horizons: Ah (P4A), Ga (P4B1 and P4B2) and g (P4C) (Fig. 1b and d). Samples were stored in a plastic bag until the laboratory and they were dried at ambient temperature. Then, samples were sieved at 2 mm (bulk fraction). This fraction was disaggregated using an ultrasonic tub and then divided into a fine fraction (<50 μm) by dry sieving and a clay fraction (<4 μm) using the sedimentation technique according to Stokes' law. The amount of P3 and P2A samples did not allow performing size