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Iron mineralogy as a fingerprint of former steelmaking activities in river sediments

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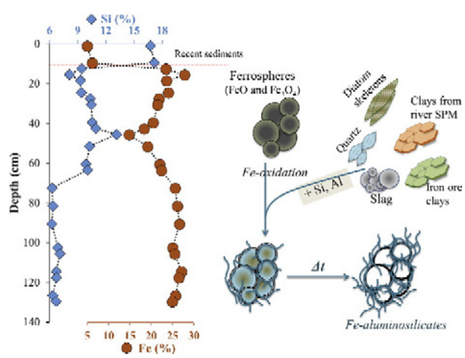
HIGHLIGHTS

- Steelmaking activities strongly modified the composition of riverine sediments.
- Deciphering anthropogenic and natural components via geochemistry and mineralogy.
- Weathered status of steelmaking wastes was evidenced at the micro-scale.
- Fe-aluminosilicates as a fingerprint of steelmaking impact on river.

GRAPHICAL ABSTRACT



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ABSTRACT

Submerged sediment cores were collected upstream of a dam in the Orne River, northeastern France. This dam was built in the context of steelmaking to constitute a water reservoir for blast furnace cooling and wet cleaning of furnace smokes. The dam also enhanced sediment deposition in the upstream zone. This study was performed to unravel the contamination status of sediments and to evidence possible contribution sources. The sediment layers were analyzed for water content, grain size, chemical composition, crystalline phases at a bulk scale and poorly crystalline and amorphous phases at a sub-micrometer scale. Visual aspect, texture, color, and chemical and mineralogical analyses showed that the settled sediments were mainly composed of fine black matter, certainly comprising steelmaking by-products. Those materials were highly enriched with Fe, Zn, Pb and other trace metals, except for a relatively thin layer of surficial sediments that had settled more recently. Bulk mineralogy revealed crystalline iron minerals, such as magnetite, goethite, wuestite and pyrite, in the deep layers of the sediment cores. Furthermore, microscopic investigations evidenced the presence of ferrospheres, goethite nanoparticles and newly formed Fe-aluminosilicates; all originating from the former steelmaking facilities. The variation of iron mineralogy, combined with specific chemical profiles and other sediment features, demonstrate

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the different contributions that constitute the sediment deposit. Furthermore, chemical and mineralogical features of goethite and Fe-aluminosilicates could be used as a fingerprint for such contaminated sediments.

1. Introduction

River sediments are recognized as reservoirs of various pollutants, such as chemicals (e.g. nitrates, pesticides, medical drugs, organic micropollutants and metals) and microbes (e.g. viruses, bacteria and parasites) (Droppo et al., 2009; Grabowski et al., 2011 and references therin; Heise and Förstner, 2007; Hudson-Edwards et al., 2008). Furthermore, surface waters are often the common receptacle of anthropogenic pollutants from diverse origins, which once combined to particulate matter, might settle and enrich the sediment compartment. A concern could arise if contaminated sediments are then translocated further downstream, which might be caused by specific seasonal or hydroclimatic events (Droppo et al., 2009). It is also commonly assumed that the contaminants in sediments can be several orders of magnitude higher than in the overlying water, and consequently constitute a threat for stream quality (Cappuyns et al., 2006; Simpson et al., 1998). In European and North-American countries, studies dealing with sediment cores have shown that contaminant inputs into sediments were maximized in the 1960s, and then decreased due to the improvement in environmental regulations (Ayrault et al., 2012; Dhivert et al., 2016; Ferrand et al., 2012; Wakeham et al., 2004).

Northern and northeastern France had been very active with mining (such as iron, coal and salt) and metallurgical (such as Zn and Fe) activities during the last century (Lesven et al., 2010; Lourino-Cabana et al., 2010; Montargès-Pelletier et al., 2007, 2014; Sterckeman et al., 2000, 2002). Industrial facilities were commonly established close to rivers to ensure a water source for the cooling of furnaces. This was the case in Lorraine, where several rivers in the Moselle watershed, like the Orne, Fensch and Rosselle Rivers, were physically, chemically and biologically modified by steelmaking activities, including iron ore mining and coke production (Garcier, 2007; Picon, 2014). Because they were strongly impacted by the industrial activity, those small valleys were referred to as "steelmaking valleys". Waste products, furnace smokes, dust and sludge from wet cleaning of furnace smokes had been introduced in the aqueous media, transported as suspended particulate matter (SPM) or stored more or less definitely in river sediments. The possible metal release due to re-suspension upon flooding (Vdović et al., 2006; Zebracki, 2008) or sediment dredging (Lesven et al., 2010), as well as selective remobilization of metal bearing phases (Montargès-Pelletier et al., 2014) were studied and reported to evidence the possible impact of contaminated sediments. Furthermore, polluted sediment remobilization was shown to cause socioeconomic, ecological and environmental problems (e.g. Fernandes et al., 2016; Macklin et al., 1997; Maclin and Sicchio, 1999). For example, the removal of the Fort Edward Dam (Hudson River) caused the remobilization of polluted sediments for tens of kilometers in the downstream area. As a result, >40 distinct "polluted sites" had formed and the biota and water quality were severely damaged for a period of nearly thirty years (Maclin and Sicchio, 1999).

Many studies focused on speciation and evolution of elements in contaminated river sediments (e.g. Van Damme et al., 2010; Roberts et al., 2002; Spadini et al., 2003; Sterckeman et al., 2000; Zeng et al., 2013), or the speciation of metals in weathered blast furnace sludge from landfills or ponds (e.g. Huot et al., 2013; Kretzschmar et al., 2012; Mansfeldt and Dohrmann, 2004). In order to understand the fate of steelmaking by-products, there is a need for detailed knowledge of the raw materials used, the processes undertaken, and the possible ageing and transformations taking place within the sediment matrix. Therefore, this study focuses on the mineralogy of river sediments that have accumulated upstream of a dam in an area that was highly influenced by steelmaking processes during the last century. The objectives of the study are to i) characterize the sediments that had settled upstream of the dam, ii) identify the layers and phases of lithogenic and anthropogenic sources and iii) follow the Fe-bearing mineral species in the vertical sediment profile. For that purpose, the present study investigates global parameters, chemical composition, as well as iron mineralogy of the sediments. The objectives are attained by using a combination of techniques, mainly X-ray diffraction and scanning and transmission electron microscopies.

2. Materials and methods

2.1. Study area

During the 20th century, steelmaking activities were very intense in the Lorraine region, and in 1938, as much as 67% of the total French steel was produced in Lorraine. In 1974, when the French steel production was at its maximum (25 million tons per year "Mt/yr"), the production in Lorraine was about 8 Mt/yr. The steel or iron basin in Lorraine covered a 60 km long and 40 km wide area, subdivided into several compartments, one of which was the Orne valley. The Orne River, a tributary of the Moselle River, flows in northeastern France (Fig. 1a), is 90 km long, has a drainage basin of 1226 km^2, and displays a mean discharge of 12.2 m^3/s at the junction with the Moselle River. Several small sized dams were built on the Orne River to create water reservoirs for industrial purposes. The production of steel encountered the highest expansion period from 1954 to 1960. Thus, at the end of the 50′s, two new blast furnaces were installed on the left bank of the Orne River, located within the limits of Moyeuvre-Grande city area, and close to the iron mine of Jœuf «Mine du Haut Fond» (Fig. 1b). Those two blast furnaces were active from 1960 until 1988, with a steel production of about 1.3 Mt/yr (Freyssenet, 1979). In the same period, Beth dam was built to provide high volumes of water for the general functioning of steelmaking facilities (Fig. 1b and Supplementary material 1 "SM 1"). Two other sets of blast furnaces were previously installed along the Orne River, one set at the exit of Jœuf city (active from 1882 to 1970), and another set in the center of Moyeuvre-Grande city (active from 1918 to 1975) (Fig. 1b). The blast furnaces were fed with ore extracted from the nearby iron mine; the ore was partially sintered before its introduction in the furnace (about 64% in 1967), producing about 2.4 Mt/yr.

Generally speaking, for this part of the Orne valley, the steelmaking activities and related industrial activities (iron mining, coke and gas production) resulted in a strong contamination of soils and aqueous media, with the spreading of materials enriched in iron, other metallic elements and persistent organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs). In 1988, dredging of the Orne River was performed from Jœuf to Moyeuvre, stopping at the limit of Moyeuvre city area. Thus, the dredging operation removed most of the highly contaminated sediments (Garcier, 2007; Picon, 2014), but did not concern the sediment deposits in the upstream part of the Beth dam. This dam should be partially modified or completely removed in the coming decade, with consequent questioning about the fate of the highly anthropogenic sediments located on the right bank of the river.

2.2. Sediment coring

Three sediment cores were collected at distinct locations upstream of the Beth dam. The lengths of the cores were 96 (BETH1302), 131 (BETH1402) and 18 cm (BETH1507). The submerged sediments were cored with a piston corer (or Beeker corer) directly from the bank (in