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Fate of cadmium in the rhizosphere of *Arabidopsis halleri* grown in a contaminated dredged sediment

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HIGHLIGHTS

• Cd was present as a mixed Zn, Cd, Fe sulfide in the sediment before culture.
• After culture Cd-bearing sulfides were mostly oxidized, Cd-O species were predominant.
• These changes in Cd speciation were slightly enhanced in the presence of plant.
• Cd mobility and bioavailability were not affected by the changes in Cd speciation.

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ABSTRACT

In regions impacted by mining and smelting activities, dredged sediments are often contaminated with metals. Phytotechnologies could be used for their management, but more knowledge on the speciation of metals in the sediment and on their fate after colonization by plant roots is needed. This work was focused on a dredged sediment from the Scarpe river (North of France), contaminated with Zn and Cd. Zn, Cd hyperaccumulating plants *Arabidopsis halleri* from metallicolous and non-metallicolous origin were grown on the sediment for five months in a pot experiment. The nature and extent of the modifications in Cd speciation with or without plant were determined by electron microscopy, micro X-ray fluorescence and bulk and micro X-ray absorption spectroscopy. In addition, changes in Cd exchangeable and bioavailable pools were evaluated, and Cd content in leachates was measured. Finally, Cd plant uptake and plant growth parameters were monitored. In the original sediment, Cd was present as a mixed Zn, Cd, Fe sulfide. After five months, although pots still contained reduced sulfur, Cd-bearing sulfides were totally oxidized in vegetated pots, whereas a minor fraction (8%) was still present in non-vegetated ones. Secondary species included Cd bound to O-containing groups of organic matter and Cd phosphates. Cd exchangeability and bioavailability were relatively low and did not increase during changes in Cd speciation, suggesting that Cd released by sulfide oxidation was readily taken up with strong interactions with organic matter and phosphate ligands. Thus, the composition of the sediment, the oxic conditions and the rhizospheric activity (regardless of the plant origin) created favorable conditions for Cd stabilization. However, it should be kept in mind that returning to anoxic conditions may change Cd speciation, so the species formed cannot be considered as stable on the long term.

1. Introduction

The North of France hosts one of the oldest and largest industrial areas in Europe, with a large concentration of non-ferrous metal processing activities. The Scarpe river is strongly impacted by these activities, and sediments are contaminated by many metals including Zn (about

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7000 mg kg^{-1}) (Isaure et al., 2002) and Cd (about 600 mg kg^{-1}) (Alary and Demougeot-Renard, 2008). The maintenance of waterways such as the Scarpe river by regular dredging generates large volumes of metal-polluted sediments. Land disposal of these sediments may present some risks in the environment. Sediments with contaminant levels above guidelines are usually stored in landfill sites. Over the last decade, a substantial body of research has been conducted on the fate of metals in the lower Scarpe river. Studies have focussed on the speciation of Zn (Isaure et al., 2002, 2005) and other metals (Thiry et al., 2002) and on their availability (Piou et al., 2009; Lions et al., 2010). Chemical extractions suggested that Cd was mostly present in the oxidable fraction, likely polymetallic sulfides, but no direct methods such as EXAFS spectroscopy was used to determine Cd overall speciation in this sediment. Chemical extractions suggested that after land disposal of the sediment, the sulfidic pool progressively decreased in favor of exchangeable forms (Piou et al., 2009). Secondary Cd species formed after release of Cd^{2+} in a soil may include O-coordinated Cd adsorbed to iron oxihydroxides, clay minerals, carbonates and COOH/OH groups of organic matter, and S-coordinated Cd complexed by reduced organic S groups of natural organic matter or bacterial cell walls or Cd adsorbed to metal sulfides (O'Day et al., 1998; Karlsson et al., 2005; Karlsson and Skyllberg, 2007; Sajidu et al., 2008; Mishra et al., 2010; Fulda et al., 2013). To our knowledge, there is no study on Cd speciation in dredged sediments after land disposal using direct methods.

Phytotechnologies have been proposed as alternative management methods for these sediments (Bert et al., 2009; Bolan et al., 2011). In a previous work, the fate of Zn after a phytostabilization treatment with graminaceous plants was studied (Panfili et al., 2005). Results showed a clear impact of the rhizospheric activity on Zn speciation, regardless of the plant species (*Festuca rubra* or *Agrostis tenuis*) and of the addition of amendments. Zn sulfide, present as major Zn species in the original sediment, was almost completely oxidized and replaced by secondary forms including Zn phosphate, Zn phyllosilicates and Zn-sorbed ferrihydrite. The rhizosphere is a zone of intense and dynamic exchanges between the soil, the root, and the microbial and fungal communities which colonize this zone. Exchanges in gas, water, solutes, large and small organic molecules are supposed to influence the chemistry of metals, although it is difficult to know exactly the role of each parameter in this complex interplay (Hinsinger et al., 2006; Wenzel, 2009). The rhizosphere of metal hyperaccumulating plants has been the subject of many studies. Enhanced metal uptake by these species does not seem to be related to specific phenomena, but to the enhancement of processes common with non-accumulators. They include a highly developed root system, enhanced transport activity at the soil–root interface, and possibly enhanced release (or release of different types) of organic ligands (Wenzel et al., 2003; Li et al., 2013; Tsednee et al., 2014). *Arabidopsis halleri* is a model of Zn, Cd hyperaccumulating plant, and it has been intensively studied for the genetics and physiology of metal tolerance and hyperaccumulation (Roosens et al., 2008; Sarret et al., 2009; Huguet et al., 2012; Verbruggen et al., 2013; Isaure et al., 2015; Meyer et al., 2015). It is a pseudo-metallophyte, which means that it is found both on metal-rich and normal environments. Previous studies suggested some variations in metal tolerance and accumulation between and within populations (Meyer et al., 2010, 2015). Despite these numerous studies, data concerning the impact of *A. halleri* on the speciation and availability of Cd in the soil are lacking.

The aim of this work was to determine the speciation of Cd in a dredged sediment, to assess its fate after land disposal, and to evaluate the influence of the rhizospheric activity on Cd speciation. The Cd tolerant and hyperaccumulating species *A. halleri* was chosen as model plant for this study because this species is naturally present in metal-contaminated soils of this studied area. Moreover, we have some knowledge on Zn and Cd tolerance and accumulation (Sarret et al., 2009 and Isaure et al., 2015, respectively), and on rhizospheric processes (Barillot et al., 2013) for *A. halleri* from the same metallicolous origin. Thus, this species was not chosen as a candidate for phytoextraction (which it is not), but as a model plant to study rhizospheric processes.

Information on Cd solid phase speciation, on Cd extractability and leachate composition, and on Cd transfer in the plant was obtained. Such combined approach provides key information on metal dynamics in soil–plant system both on the short and long term. Such knowledge is essential for the management and phytomanagement of dredged sediments after land disposal. In this aim, a 5-month pot experiment was conducted on a Zn- and Cd-contaminated dredged sediment with *A. halleri* of two origins, metallicolous (MET) and non-metallicolous (N-MET). Plants originating from a contaminated site and a non-contaminated site were compared to examine potential differences between MET and N-MET plants in Cd uptake and Cd behavior in rhizosphere. The speciation of cadmium in the sediment before and after culture and its relationships with other elements were studied by a combination of bulk and microanalyses including scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS), micro X-ray fluorescence (μXRF) coupled with Cd L_{III}-edge and S K-edge micro X-ray absorption near edge structure (μXANES) spectroscopy, and bulk Cd K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. The mobility and bioavailability of cadmium in the sediment were studied by $Ca(NO_3)_2$ extractions and diffusive gradient in thin films (DGT), and measurement of Cd content in the leachates. In addition, plant growth parameters and Cd accumulation were monitored.

2. Materials and methods

2.1. Sediment

The sediment was collected from the lower Scarpe river in the North of France (about 30 km south of Lille). In this study, 500 kg of surface sediment from an area containing 150 mg kg^{-1} Cd (Alary, 2001) was dredged with a mechanic shovel. The sediment was then mixed, spread as a 20 cm-thick layer and dried outdoor for 7 months until the water content was 20% in mass. The sediment was mechanically homogenized several times and sieved (<5 mm with a Cross Beater Mill SK — RETSCH). Characteristics of the sediment at this time, "initial time" *ti* (Fig. 1), just before plant culture, are given in Table 1. Particle size distribution was analyzed following methods described in Isaure et al. (2002). Pseudo-total elements concentrations (Cd, Zn, Cu, Pb, Ni, and As) were quantified in sediment and in the different granulometric fractions. Aliquots of 0.5 g of samples were dried and sieved (100 μm) and then digested by aqua regia micro-waves assisted dissolution. Metal concentrations were determined by ICP-AES. Quality control was based on the use of sediment certified standard samples (NWRI TH-2) and internal control samples.

The pH of the sediment before culture was about 7.48 ± 0.01. The sediment was relatively rich in organic matter and had a relatively high cation exchange capacity (Table 1). As expected the metal concentrations in sediment were high with 141 ± 24 mg kg^{-1} Cd, and other metals (Table 1). The Cd content was higher in finest fractions (e.g. 290 ± 10 mg kg^{-1} Cd for <2 μm fraction). Sediment was mainly composed by <50 μm fractions (Table 1), which concentrated 72% Cd.

2.2. Plant material

A. halleri develops natural populations on both metal contaminated and uncontaminated soils in Europe (Bert et al., 2002). Viable seeds of *A. halleri* were collected in a smelter-impacted site (Bois des Asturies — Auby, France) and in an uncontaminated site (Hautes Fagnes, Belgium). The soil of Bois des Asturies has been characterized in several studies (Bert et al., 2000; Cuny et al., 2004; Sarret et al., 2004; Pauwels et al., 2006; Farinati et al., 2011; Gomez-Balderas et al., 2014). The data from Sarret et al. (2004) are given in Fig. SI-1. The topsoil (0–20 cm) in which *A. halleri* developed roots was collected, and characterized as previously described for the sediment (Fig. SI-1).