

Fate of metal-associated POM in a soil under arable land use contaminated by metallurgical fallout in northern France

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Small POM-derived organic particles may favor long-term metal sequestration in soils.

Abstract

Organic matter is a major metal-retaining constituent in soils. Among the diversity of organic components in soils, particulate organic matter (POM) accumulates large amounts of metals, but the fate of such metal-associated POM is unknown. We studied different POM size fractions and their corresponding mineral size-fractions isolated from the surface horizon of a soil affected by metallurgical fallout. Analyses of total and EDTA extractible metal contents performed on all size fractions demonstrated that with decreasing POM size, larger metal concentrations were observed but they were less extractable. Micromorphological study revealed the occurrence of opaque parts in decaying POM fragments and their individualization as fine, irregularly shaped opaque fragments in the soil matrix. This work suggested a mutual sequestration of metal pollutants and organic carbon as micro-meter sized, metal-enriched organic particles derived from POM, representing an original pathway for natural attenuation of risk related to metal contaminated soils.

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1. Introduction

The increased presence of heavy metals in soils due to human activity (industries, agricultural practices, etc.) is of great concern for sustainable land management, regarding long-term risks of metal for ecosystems and human health. Chemical speciation is a good indicator for metal mobility, availability and toxicity and pertinent for risk assessment. Establishing chemical speciation is yet difficult due to the numerous chemical forms and associations of metals with a wide variety of soil constituents. The role of soil organic matter (SOM) as

a metal sorbing agent is frequently stressed (McBride et al., 1997; Sauvé et al., 2000), and the stability of SOM-metal interactions is recognized to be a crucial factor governing the fate of metals in soils.

In soils contaminated by industrial activity, metal inputs due to atmospheric fallout mainly consist of mineral metal-liferous species, such as sulfides, oxides, and silicates, but also coal and charcoal particles. These initial metal phases are generally unstable in soil conditions, rapidly altered chemically and freed metals redistributed among reactive soil constituents. Among them, particulate organic matter (POM) appears generally metal-enriched compared to other soil constituents (Ducaroir and Lamy, 1995; Balabane and van Oort, 2002). In addition, metal contents in different POM fractions were found to increase with a decreasing

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POM size (Balabane et al., 1999; Besnard et al., 2001; Balabane and van Oort, 2002; Lamy et al., 2002). POM is mainly composed of identifiable animal and plant residues, root fragments, fungal hyphae, spores and fecal pellets (Cambaradella and Elliott, 1992; Gregorich et al., 2006). Based on a separation approach proposed by Balesdent et al. (1991), POM was operationally defined as 50- μm sized light fractions, obtained by floatation in water. However, smaller organic particles occur in soils, and can be isolated in water from fractions $>20\ \mu\text{m}$ (Ducaroir and Lamy, 1995). Recently, Chenu and Plante (2006) identified “free organic” particles in clay-sized fractions after density fractionation using sodium metatungstate solutions. Considering the rapid C-turnover of soil POM fractions (Christensen, 1992; Balesdent, 1996), questions arise about chemical protection of POM from decomposition by metals and about the fate of freed metals. The study of metal distribution among POM is relevant to assess the contribution of labile organic matter to metal retention in comparison to mineral constituents.

Decay of organic plant debris was studied by means of optical microscopy (Gillet and Ponge, 2002; Jongmans et al., 2003) or transmission electron microscopy (Chenu and Plante, 2006). Recently, metal distribution in plant tissues of metallophyte species were studied within the scope of phytoremediation applications based on direct analyses with micro-spectroscopical techniques, such as $\mu\text{-SXRf}$ and/or $\mu\text{-EXAFS}$ (Dahmani-Muller, 2000; Sarret et al., 2002). Thus, distinct Zn-distribution patterns were observed in organic tissues, reflecting a specific strategy of hyperaccumulators regarding uptake, transmission and storage of metals in adapted cells or organs (Küpper et al., 1999; Zhao et al., 2000; Dahmani-Muller et al., 2000). When such plant residues reach the soil's surface, heterogeneous metal distribution patterns already exist. But for low- or moderately contaminated agricultural soils, organic residues mainly originate from agronomic plant species and distribution maps on metal-POM

associations are virtually absent in literature, contrarily to studies on metal distribution patterns in mineral particles and microstructures (Leguédou et al., 2004; van Oort et al., 2006). Hence, knowledge on metal distribution in organic debris helps to unravel the complex fate of metal-OM associations in relation to SOM dynamics in moderately contaminated agrosystems.

The present paper aimed at studying the fate of metals in soils, in terms of distribution of total and extractable metal contents in different POM size fractions compared to corresponding mineral size fractions. For this we used an original approach combining physical fractionation in water, and chemical analyses of total and extractable concentrations of heavy metals. Analyses were performed on mineral and organic fractions from representative samples of a metal contaminated agricultural soil close to a former zinc smelter (van Oort et al., 2002). Complementary, optical microscopy and $\mu\text{-SXRf}$ study on soil thin sections were used to illustrate a natural way of metal immobilization via the presence of very small-sized organo-metallic complexes deriving from soil POM.

2. Material and methods

2.1. Site and soil selection

The study site was located in an area affected by metallurgical activity in Northern France (Fig. 1), subject to detailed pedological survey (van Oort et al., 2002). A soil profile was selected in an arable field, about 750 m from a former zinc smelter. This metallurgical activity generated large amounts of atmospheric fallout with high amounts of Zn, Pb, and Cd. In the period of activity, between 1901 and 1962, no modern filtering systems were used and emitted dust particles sized from a few to several tens of micrometers (Sobanska et al., 1999). The sandy-loam textured soil, classified as a Eutric Cambisol (FAO, 2006) was used for maize-wheat production for at least 35 years. In this work we focused on the plow layer affected mainly by atmospheric deposition of industrial fallout. Representative bulk samples of several kilograms were collected, air-dried, sieved to $<2\ \text{mm}$, homogenized and stored before analyses.

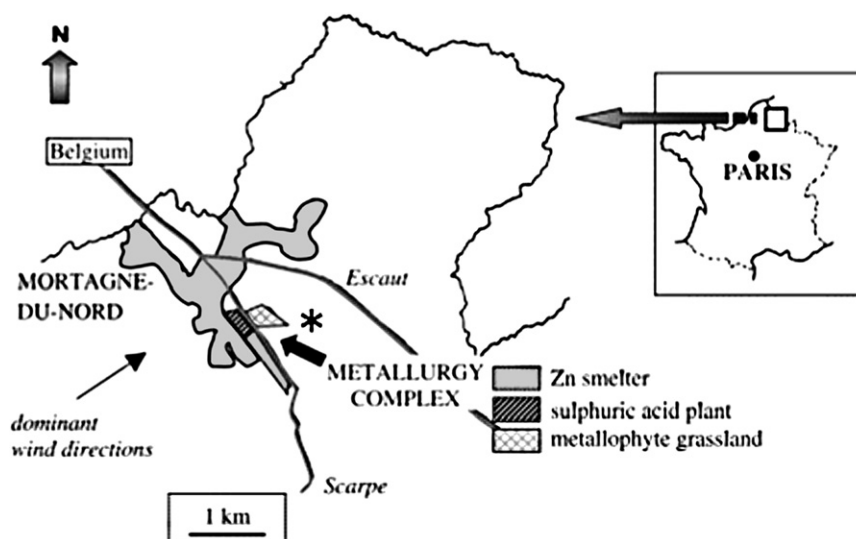


Fig. 1. Location of the study site (*) about 750 m from the former metallurgical plant.

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