Science of the Total Environment 472 (2014) 425–436

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Impact of historical mining assessed in soils by kinetic extraction and lead isotopic ratios

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HIGHLIGHTS

- Trace-metal behaviour is estimated in soils affected by past mining and metallurgy.
- Kinetic extractions of soils are modelled by two first-order reactions.
- Lead origin can be estimated in kinetic extracts by isotopic composition.
- Stable organo-metallic complex remains but anthropogenic metal may have percolated.
- Kinetic results suggest that metals do not threaten biota, in these soils at least.

ARTICLE INFO

Article history:
Received 12 July 2013
Received in revised form 26 October 2013
Accepted 27 October 2013
Available online 1 December 2013

Keywords:
Mining
Bioavailability
Trace metals
Forest soil
Spatial distribution
EDTA

ABSTRACT

The aim of this study is to estimate the long-term behaviour of trace metals, in two soils differently impacted by past mining. Topsoils from two 1 km^2 zones in the forested Morvan massif (France) were sampled to assess the spatial distribution of Cd, Cu, Pb and Zn. The first zone had been contaminated by historical mining. As expected, it exhibits higher trace-metal levels and greater spatial heterogeneity than the second non-contaminated zone, supposed to represent the local background. One soil profile from each zone was investigated in detail to estimate metal behaviour, and hence, bioavailability. Kinetic extractions were performed using EDTA on three samples: the A horizon from both soil profiles and the B horizon from the contaminated soil. For all three samples, kinetic extractions can be modelled by two first-order reactions. Similar kinetic behaviour was observed for all metals, but more metal was extracted from the contaminated A horizon than from the B horizon. More surprising is the general predominance of the residual fraction over the "labile" and "less labile" pools. Past anthropogenic inputs may have percolated over time through the soil profiles because of acidic pH conditions. Stable organo-metallic complexes may also have been formed over time, reducing metal availability. These processes are not mutually exclusive. After kinetic extraction, the lead isotopic compositions of the samples exhibited different signatures, related to contamination history and intrinsic soil parameters. However, no variation in lead signature was observed during the extraction experiment, demonstrating that the "labile" and "less labile" lead pools do not differ in terms of origin. Even if trace metals resulting from past mining and metallurgy persist in soils long after these activities have ceased, kinetic extractions suggest that metals, at least for these particular forest soils, do not represent a threat for biota.

1. Introduction

Elevated trace-metal (TM) concentrations in soil surface horizons represent a potential threat to terrestrial and aquatic ecosystems. The accumulation of metals in soils may sometimes be of natural origin, but is often related to human activity. Many recent studies have focused on the characterisation of metal contamination in soils or sediments near to metallurgical industrial sites, whether previously or currently active (Aleksander-Kwaterczak and Helios-Rybicka, 2008; Chopin and Alloway, 2007; Douay et al., 2009; Ettler et al., 2005; Hudson-Edwards et al., 2001; Kochem Mallmann et al., 2012; van Oort et al., 2009).

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http://dx.doi.org/10.1016/j.scitotenv.2013.10.103

Much less attention has been paid to archaeological mining activity, which is nonetheless known to be responsible for elevated TM levels in ecosystems (Macklin et al., 1997; Pyatt et al., 2000). It is therefore essential to assess long-term metal dynamics and bioavailability in soils from historically contaminated sites.

Soils are highly complex, requiring sophisticated modelling of pollutants, focusing particularly on their incorporation into biota (van Oort et al., 2006; Pajak and Jasik, 2011). Several methods based on the use of chemical reagents have been developed to estimate the chemical forms (speciation) by which TMs are associated to soil constituents. Chemical extractions often include several sequential steps with increasing extraction strength (Bade et al., 2012; Tessier et al., 1979; Ure et al., 1993). They have nonetheless been criticised because of their poor selectivity (Bermond, 2001; Gleyzes et al., 2002; Nirel and Morel, 1990). Other authors have hypothesised that kinetic metal extraction might better reflect the dynamics of TMs in soils. Among chemical reagents, ethylenediaminetetraacetic acid (EDTA) has been widely used to estimate the total extractable metal pool (Bermond et al., 1998; Brunori et al., 2005; Fonseca et al., 2011; Gismera et al., 2004; Jalali and Tabar, 2013; Labanowski et al., 2008; Leleyter et al., 2012; Manouchehri and Bermond, 2009; Manouchehri et al., 2006). It is a strong non-specific reagent, reported to remove organically bound metals, as well as those associated to oxides or secondary clay minerals (Lo and Yang, 1999). Even though this method does not mimic metal behaviour under natural conditions, EDTA-based kinetic extraction still provides two types of pertinent data: (*i*) the proportion of potentially extractable metals to total metal content in the sample, and (*ii*) the kinetic extraction behaviour of metals (Labanowski et al., 2008). It has been suggested that kinetic extractions can be efficiently modelled by the sum of multiple first-order reactions, generally reduced to two (Gutzman and Langford, 1993). The first, or "labile", pool is composed of the readily extracted metal fraction. The second, "less labile" pool is composed of more slowly removed metal, reasonably attributed to the metal fraction which is only "potentially mobile" (Bermond et al., 2005; Fangueiro et al., 2005). The third pool consists of a fraction that is non-extractable using EDTA. It is composed of strongly bound metals, or elements occurring in the lattice network of minerals, not readily transferred to biota. Although EDTA-based kinetic extractions provide no information about TM origin, such information can be obtained by stable lead isotope analysis. This method has frequently been used to trace Pb sources in surface environments, and more particularly in soils (Cloquet et al., 2006; Erel and Patterson, 1994; Ettler et al., 2004; Izquierdo et al., 2012; Kylander et al., 2008; Reimann et al., 2011, 2012), but has never been applied specifically to kinetic extractions. Complementary information about the fundamentals of the Pb isotope method can be found in Komárek et al. (2008).

Here, our main objective is to examine the kinetic behaviour of metals in a context of historical mining, and hence to assess their potential bioavailability. Such past contamination is less frequently studied than contamination from modern urban and industrial areas, or from agricultural practices (amendments). As pointed out by Ettler et al. (2012), most metal mobility studies have been performed on soils with circum-neutral or alkaline pH, particularly on the plough layer of agricultural soils (Labanowski et al., 2008; Manouchehri et al., 2006). The behaviour of metals in forest soils is less well known, although acidic conditions have been shown to favour the migration of more mobile elements, such as Zn and Cd (van Oort et al., 2009), as well as less mobile elements, such as Pb (Semlali et al., 2001). The forest soils of the Morvan region (north Burgundy) are particularly well adapted to that aim. The Morvan is today one of the least inhabited regions in France, yet this area has experienced several phases of mining and smelting, identified as early as the Bronze Age, and throughout the Iron Age (Forel, 2009; Jouffroy-Bapicot et al., 2007; Monna et al., 2004). Even though all such activity finally ceased during the 20th century, lasting TM soil contamination has resulted. In this study, the area affected by historical mining was estimated using the spatial distribution of Cd, Cu, Pb and Zn in acidic topsoils collected from both contaminated and non-contaminated forest sites. Possible discrepancies in metal fates according to depth were studied by performing kinetic extractions. EDTA was used as the chemical reagent for extractions, as it allows total fractions of potentially mobile metals to be assessed and hence compared between soils. In a context of moderate contamination, as is the case here, EDTA was preferred to other chemicals (e.g. $CaCl_2$ or citrate), which are expected to extract exchangeable fractions only, or to present a moderate metal complexation strength. The origin of the lead in the extracted pools was then determined from the lead isotopic compositions of the resulting extracts. Kinetic extractions are used for the first time on forested soils in a regional nature park, erroneously thought to be free of any anthropogenic contamination, but in reality affected by past mining. Using lead isotope analysis in this context is also an innovation since, to our knowledge, this method has never been combined with kinetic extractions until now.

2. Materials and methods

2.1. Study area

The Morvan, located in the north-east part of the Massif Central, France (Fig. 1), is a Hercynian middle-altitude mountain (elevation 200–900 m, a.s.l.), mainly composed of granitic and volcano-sedimentary rocks (rhyolites and conglomerates). The entire massif is crosscut by micro-granitic or quartz veins. Three main types of mineral deposits have been identified: (*i*) hydrothermal mineralised quartz veins, typically with U, F–Ba, Pb–Zn–Ag, or Sn–W, (*ii*) abundant polymetallic mineralisation in NNW–SSE and NNE–SSW veins, and, (*iii*) stratiform F–Ba ore deposits in Early Mesozoic formations (Delfour, 2007; Gourault, 2009).

The study of several peat archives has shown that local metallurgy started as early as the Late Bronze Age (ca. 1300 cal BC) and peaked during the Iron Age, when the Celts occupied the area (Monna et al., 2004). A mining trench, recently excavated by Cauuet and Boussicault (2006) at the archaeological site of Bibracte, seems to extend underneath the walls of the oppidum. It is filled by material dating from the 1st century BC, demonstrating unambiguously the existence of local metal exploitation during the Celtic period. Many other geomorphological anomalies, such as wide trenches, gullies and pits have been discovered and interpreted as being remains of mining works (Jouffroy-Bapicot et al., 2007). Radiocarbon dating of six pieces of charcoal trapped in iron tap slags indicates periods of activity lasting from the 2nd to the 6th centuries AD, while one piece yielded a mediaeval date in the 12th century AD (Monna et al., submitted for publication). Concerning more recent times, textual archives indicate that mining continued sporadically until its final collapse during the 20th century AD. Nowadays, the area is a supposedly pristine, protected nature park.

Two study sites (~1 km^2) were selected: a non-contaminated reference area free of mining and a historical mining area. The first, located near Gien-sur-Cure, is presumed to have been affected only by long-range diffuse anthropogenic inputs. This historically non-contaminated site should therefore represent the local geochemical background. The second site, La Ruchette, is located about 7 km S-W of the Bibracte oppidum. It is considered to be a contaminated site, since mining for pyrite and iron oxides occurred there from the 19th century to the early 20th century AD (Delaville, 1858; Gourault et al., 2012). Two pieces of charcoal trapped in iron slags were also dated by radiocarbon at around 130 AD–426 AD, proving the interest of early societies for mineral resources in this specific area (Monna et al., submitted). Both sites are located in forested areas.

2.2. Soil sampling

2.2.1. Bulk analysis for topsoil mapping

The grid for the non-contaminated Gien-sur-Cure site was composed of 24 plots, 200 × 200 m^2, while the contaminated La Ruchette