



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



E. Camizuli <sup>a,\*</sup>, F. Monna <sup>a</sup>, A. Bermond <sup>b</sup>, N. Manouchehri <sup>b</sup>, S. Besançon <sup>b</sup>, R. Losno <sup>c</sup>, F. van Oort <sup>d</sup>, J. Labanowski <sup>e</sup>, A. Perreira <sup>a</sup>, C. Chateau <sup>f</sup>, P. Alibert <sup>g</sup>

<sup>a</sup> UMR 6298, ArTeHiS, Université de Bourgogne – CNRS – Culture, 6 bd Gabriel, Bat. Gabriel, 21000 Dijon, France

<sup>b</sup> Institut des sciences et industries du vivant et de l'environnement (AgroParisTech), Laboratoire de Chimie Analytique, 16, rue Claude Bernard, 75231 Paris Cedex 05, France

<sup>c</sup> UMR 7583, LISA, Universités Paris 7-Paris 12 – CNRS, 61 av. du Gal de Gaulle, 94010 Créteil Cedex, France

<sup>d</sup> UR 251, Pessac, Institut National de la Recherche Agronomique, Centre de Versailles-Grignon, RD 10, 78026 Versailles Cedex, France

<sup>e</sup> UMR 7285, IC2MP, Université de Poitiers – CNRS, 4, rue Michel Brunet, 86022 Poitiers, France

<sup>f</sup> UFR SVTE, Université de Bourgogne, 6 bd Gabriel, Bat. Gabriel, 21000 Dijon, France

<sup>g</sup> UMR 6282, Biogeosciences, Université de Bourgogne – CNRS, 6 bd Gabriel, Bat. Gabriel, 21000 Dijon, France

### 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 xxxx

#### 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<sup>2</sup> 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.

© 2013 Elsevier B.V. All rights reserved.

### 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).

\* Corresponding author. Tel.: +33 3 80 39 36 26; fax: +33 3 80 39 57 87.

E-mail address: [estelle.camizuli@u-bourgogne.fr](mailto:estelle.camizuli@u-bourgogne.fr) (E. Camizuli).

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; Fanguero 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<sub>2</sub> 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 Cauet 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<sup>2</sup>) 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<sup>2</sup>, while the contaminated La Ruchette

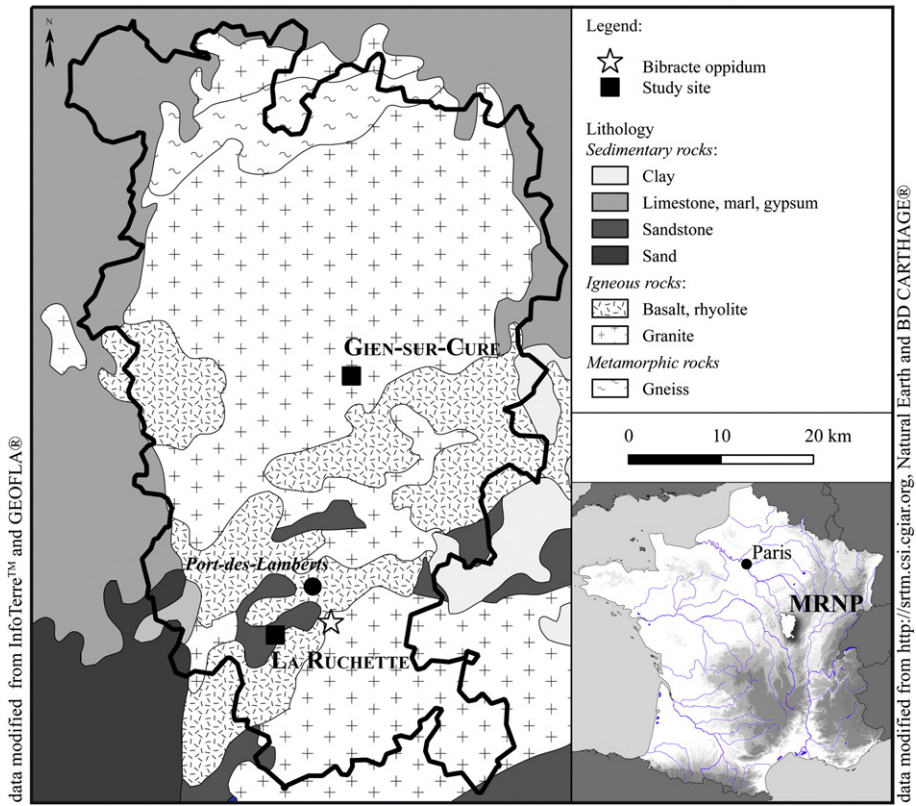


Fig. 1. Location of the study area with simplified lithology of the Morvan Regional Nature Park (MRNP).

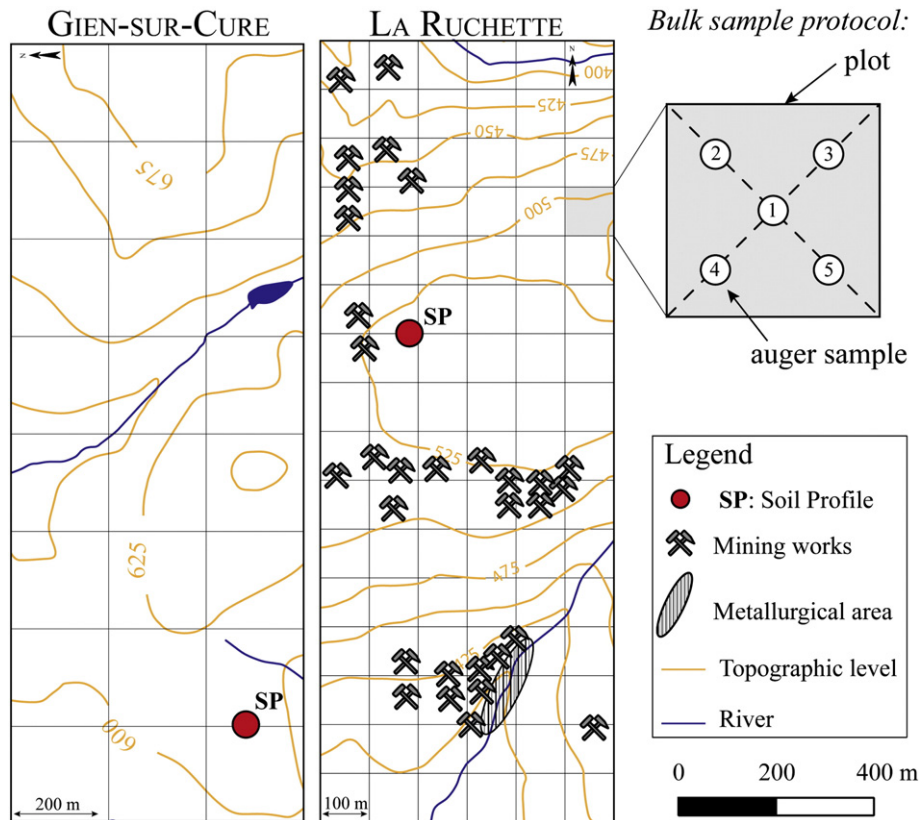


Fig. 2. Topsoil sample protocol for the two study sites and location of the soil horizon profile (SP), solid red circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

site was divided into 96 plots,  $100 \times 100 \text{ m}^2$  (Fig. 2). Fresh grass cover and litter were removed before topsoil sampling. At La Ruchette, 96 (~1 kg) geo-referenced bulk samples were collected, while only 24 samples were collected at Gien-sur-Cure. For each plot, a single bulk sample, stored in a hermetic polyethylene bag, was prepared from 5 auger samples (0–20 cm depth), following a 20 m cross-shaped pattern (Fig. 2). A pedestrian prospection campaign was systematically undertaken at La Ruchette to obtain the most exhaustive inventory possible of the zones where mining and metallurgical activities had taken place in the past (Gourault, 2009; Tamas, 2004). Each discovery was geo-referenced using a GPS device (Fig. 2). In the laboratory, all bulk samples were air-dried, sieved to 2 mm, and carefully quartered. Sub-samples of the 120 topsoils were finely ground in an acid-cleaned agate mortar for elemental analyses. Concentrations in Cd, Cu, Pb, and Zn for the 120 topsoils were measured by ICP-AES after pseudo-total aqua regia digestion at Actlabs (Ontario, Canada). Analytical quality control from Actlabs was performed by measuring 8 replicates, 5 blanks and several certified reference materials (CRMs). To verify this quality control, an additional 12 replicates, together with JSD-1, JSD-2, BCSS-1 and PACS-1 CRMs (stream, estuarine, and harbour sediments) were included as blind samples. The Actlabs protocol set the limits of detection (LOD) at  $0.5 \text{ mg kg}^{-1}$  for Cd,  $1 \text{ mg kg}^{-1}$  for Cu,  $2 \text{ mg kg}^{-1}$  for Pb and  $2 \text{ mg kg}^{-1}$  for Zn. All replicates are typically within  $\pm 5\%$  ( $\pm 18\%$  at worst). Recovery for measured concentrations of reference materials fluctuates between 79 and 105% of certified values (Table 1). Reference samples were digested by aqua regia alone, with no HF, which explains why recovery percentages are often below 100%. However, our results are quite comparable to those reported in the literature for BCSS-1 and PACS-1 after partial digestion (Dunn et al., 1996; Gali Navarro et al., 2011). The relatively low recovery of Pb for JSD-1 could be due to the low Pb concentration or perhaps its deep strong-binding in minerals like silicates, not well dissolved by aqua regia.

### 2.2.2. Horizon sampling for kinetic extraction

In order to collect a sample from each soil horizon, a soil profile pit was dug at each of the two sites, in a fairly flat area close to the summit, so that any anthropogenic inputs would be of atmospheric origin (Fig. 2). The sampling location for the pit at La Ruchette was chosen to

**Table 1**

Reference materials measured (after aqua regia digestion) and corresponding certified values (obtained after total digestion). For BCSS-1 and PACS-1, indicated values after partial digestion are also provided: <sup>a</sup> for mean BCSS-1 results after aqua regia extraction (Dunn et al., 1996) and <sup>b</sup> for mean PACS-1 results after aqua regia +  $\text{H}_2\text{O}_2$  extraction (Gali Navarro et al., 2011). For these two CRMs, recovery percentages are also reported. LOD stands for "limit of detection".

	Cd	Cu	Pb	Zn
LOD ( $\text{mg kg}^{-1}$ )	0.5	1	2	2
JSD-1 ( $\text{mg kg}^{-1}$ )				
Measured	<LOD	22	6	93
Certified	–	22.2	14	99
Recovery	–	99%	43%	94%
JSD-2 ( $\text{mg kg}^{-1}$ )				
Measured	3.3	1070	133	1860
Certified	–	1114	151	2070
Recovery	–	96%	88%	90%
BCSS-1 ( $\text{mg kg}^{-1}$ )				
Measured	<LOD	15	18	110
Certified	0.25	18.5	22.7	119
Recovery	–	81%	79%	92%
Aqua regia <sup>a</sup>	0.29	17	17.9	93.5
Recovery	–	88%	101%	117%
PACS-1 ( $\text{mg kg}^{-1}$ )				
Measured	2.5	397	358	767
Certified	2.38	452	404	824
Recovery	105%	88%	89%	93%
Aqua regia + $\text{H}_2\text{O}_2$ <sup>b</sup>	–	380	294	726
Recovery	–	104%	121%	106%

avoid the immediate proximity of mining works, while representing to some extent plots with metal inputs predominantly derived from short-range atmospheric deposition of past mining activities. The site of Gien-sur-Cure is far from any mining activity and therefore presumed to be affected only by anthropogenic deposition from distal or regional sources. The colour of the soil horizons in each profile was determined using the Munsell soil colour chart (Table 2). The soil at La Ruchette is a Cambic Umbrisol (IUSS Working Group WRB, 2006). Two horizons were sampled there: the A horizon, between 2.5 and 6 cm (RuA), and the B horizon, from 6.5 to 36 cm in depth (RuB). The soil at Gien-sur-Cure is a Cambisol (IUSS Working Group WRB, 2006). Here, the A horizon alone was collected, as it extends downward from 2.5 to 47 cm (GiA). Each of these three bulk-horizon samples weighed several kilogrammes, and was stored in a hermetic polyethylene bag. In the laboratory, samples were air-dried, sieved to 2 mm, and carefully quartered, but not ground, in order to preserve original field properties. Physico-chemical parameters such as particle size distribution expressed in five fractions (0–2  $\mu\text{m}$ , 2–20  $\mu\text{m}$ , 20–50  $\mu\text{m}$ , 50–200  $\mu\text{m}$ , and 200–2000  $\mu\text{m}$ ), C/N (using a Thermo NA-2000 CHN analyser), organic matter content (via loss-on-ignition at 550 °C),  $\text{CaCO}_3$  content (using a Bernard calcimeter), pH (water medium with a 1:5, v:v, ratio), and CEC (using cobalthexamine extraction), were determined at the INRA national soil analysis laboratory, COFRAC certified, using standard AFNOR and ISO methods (AFNOR, 2004; more details about procedures and quality control can be found at <http://www5.lille.inra.fr/las>). This laboratory also measured total Cd and Pb contents by ICP-MS (Thermo X7), and total Cu and Zn contents by ICP-AES (Varian 720), after total digestion by  $\text{HNO}_3$ , HCl, and HF (ISO 14869–1). Certified reference materials and intra-laboratory reference soils routinely processed during each set of analyses, together with inter-laboratory

**Table 2**

Main physico-chemical characteristics of soil horizons sampled for kinetic extraction.

	Gien-sur-Cure	La Ruchette	
Coordinates (centroid in WGS84, EPSG 4326)			
Lon	4.06425	3.95629	
Lat	47.16339	46.91637	
Soil horizon	A <sub>1</sub>	A	B
Label	GiA	RuA	RuB
Depth (cm)	2.5–47	2.5–6	6.5–36
Colour <sup>a</sup>	7.5YR4/4	10YR4/5	7.5YR5/8
Soil type <sup>b</sup>	Cambisol	Cambisol	Cambisol
Particle size distribution ( $\text{g kg}^{-1}$ )			
Clay (<2 $\mu\text{m}$ )	226	295	231
Fine silt (2–20 $\mu\text{m}$ )	212	243	234
Coarse silt (20–50 $\mu\text{m}$ )	66	110	107
Fine sand (50–200 $\mu\text{m}$ )	75	82	86
Coarse sand (200–2000 $\mu\text{m}$ )	421	269	342
C/N	16	18	22
OM ( $\text{g kg}^{-1}$ )	87	136	39
$\text{CaCO}_3$ ( $\text{g kg}^{-1}$ )	<1	<1	<1
pH (water medium)	4.7	4.2	4.5
Exchange capacity ( $\text{cmol} + \text{kg}^{-1}$ )			
CEC	5.0	8.6	4.5
Ca exch	0.06	0.44	0.08
Mg exch	0.12	0.34	0.07
Na exch	0.03	0.04	0.07
K exch	0.10	0.37	0.06
Fe exch	0.02	0.06	0.02
Mn exch	0.04	1.19	0.17
Al exch	4.59	6.30	4.26
Total metal ( $\text{mg kg}^{-1}$ )			
Cd	0.16	0.17	0.19
Cu	11.5	19.7	21.7
Pb	65.1	106.8	101.7
Zn	72	110.9	131.2

<sup>a</sup> Munsell soil colour chart.

<sup>b</sup> WRB (IUSS Working Group WRB, 2006).

comparisons, indicate that deviations from expected values for Cd, Pb, Cu and Zn do not exceed  $\pm 10\%$ .

### 2.3. Kinetic extractions

The extraction protocol applied here is adapted from the methodology described in Fangueiro et al. (2002). Metals were extracted from an aliquot soil sample of 45 g in an initial volume of 450 mL of extracting solution, composed of  $0.05 \text{ mol L}^{-1}$   $\text{Na}_2\text{H}_2\text{-EDTA}$ , adjusted with NaOH at pH = 6.5. The pH was checked at the end of the experiment and ranged from 6 to 6.23. Such conditions guarantee a proper extraction process (Bermond et al., 2005). The mixture was continuously agitated using an overhead shaker. At selected times of 4, 8, 12, 15, 20, 30, 45, 60, 90, 120, 150, 200, 250, 300, 500, and 1440 min, an aliquot of 2 mL was removed from the mixture with a syringe, and immediately filtered through a Millipore syringe filter membrane of  $0.45 \mu\text{m}$ , except for the 1440-min solution, which was first centrifuged for 10 min at 4000 rpm, before filtration. The filtrates were kept in polyethylene micro-tubes at  $4^\circ\text{C}$  before elemental analysis. The entire operation was reproduced twice for each soil-horizon sample.

Concentrations in Cu, Cd, Pb, and Zn were determined using a Hitachi Z-5000 atomic absorption spectrometer. Zinc was measured with an air-acetylene flame and a micro-sampling kit, while Cd, Cu, and Pb were determined by electrothermal atomic absorption spectroscopy (ETAAS). A matrix modifier,  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ , was used to overcome possible matrix interferences (Abi-Ghanem et al., 2009). All reagents were of analytical quality, from Merck. Water of high purity ( $18 \text{ M}\Omega \text{ cm}$ ) was obtained from a Millipore apparatus. Each solution was measured three times after the establishment of a calibration curve absorbance =  $f(\text{conc})$  with three standards. The final relative standard deviation (RSD%) was generally below 10%. Blanks appeared to be insignificant, whatever the metal measured, with respect to the elemental composition of the solutions analysed, and did not require further correction. Lead isotopic compositions ( $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios) were measured for soil solutions sampled at 4, 8, 12, 15, 20, 45, 90, 150, 250, and 500 min, using a high resolution-inductively coupled plasma-mass spectrometer (HR-ICP-MS) Element 2. Instrumental mass bias was corrected by sample-standard bracketing techniques, using a NBS 981 lead solution as the bracketing standard (Monna et al., 1998, 2000). Precisions to the third decimal place are typically of 2–4 for  $^{206}\text{Pb}/^{207}\text{Pb}$  and 4–7 for  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios.

### 2.4. Kinetic modelling and data processing

Several models have previously been used to describe chemical kinetic behaviours (e.g. Bermond et al., 2005; Fangueiro et al., 2005; Yu and Klarup, 1994). Among them, the widely used multiple first-order reactions model is assumed to have a good physical meaning (Gutzman and Langford, 1993):

$$Q_M(t) = \sum_{i=1}^n Q_{Mi} \left(1 - e^{-\lambda_{Mi}t}\right) + \varepsilon_t \quad (1)$$

where  $Q_M(t)$  corresponds to the amount of metal  $M$  extracted per weight unit at time  $t$ , and  $Q_{Mi}$  the amount of the pool  $i$  per weight unit, which is extracted following a decreasing rate,  $\lambda_{Mi}$ . The term  $\varepsilon_t$  is the error. The above equation is generally simplified as a two first-order reactions model:

$$Q_{M,i}(t) = Q_{M1,i} \left(1 - e^{-\lambda_{M1}t}\right) + Q_{M2,i} \left(1 - e^{-\lambda_{M2}t}\right) + \varepsilon_{t,i} \quad (2)$$

with here  $i = 1, 2$  and  $t \in [4, 8, 12, 15, 20, 30, 45, 60, 90, 120, 150, 200, 250, 300, 500, 1440]$  where, as previously defined by Fangueiro et al. (2005),  $Q_{M1}$  corresponds to the “labile”, readily extractable metal fraction, associated to the constant  $\lambda_{M1}$ , and  $Q_{M2}$  to the “less labile”, less

readily extractable metal fraction, associated to the constant  $\lambda_{M2}$ . The term  $i$  corresponds here to the duplicates ( $i = 1$  or  $i = 2$ ).

To better perceive the relevance of this two first-order reactions model, the variation in extraction rate ( $A_M(t)$  [ $\text{mg kg}^{-1} \text{ min}^{-1}$ ]) can be plotted over time (cf. Labanowski et al., 2008, for details). Note that  $Q_M(t)$  is linked to  $A_M(t)$  as follows:

$$Q_M(t) = \int_0^t A_M(t) dt \quad (3)$$

Another important parameter is the amount of metal not extractable by EDTA,  $Q_{M3}$ . It is simply obtained by:

$$Q_{M3} = Q_{\text{tot}} - Q_{M1} - Q_{M2} \quad (4)$$

where  $Q_{\text{tot}}$  is the total metal concentration. Because the experiment was repeated twice, the values of  $Q_{M1}$ ,  $Q_{M2}$ ,  $\lambda_{M1}$ ,  $\lambda_{M2}$ , were estimated using a non-linear mixed model (Pinheiro et al., 2013), where the fixed effects are the four parameters to be determined, and the random effects are  $Q_{M1i}$  and  $Q_{M2i}$  (Eq. 2). Although the original sample was homogenised by quartering, this precautionary measure served to eliminate all possibility of inter-replicate heterogeneity.

Statistical treatment, including non-linear regression analysis, used the free R software (R Development Core Team, 2008) with the nlme package (Pinheiro et al., 2013). Graphics were generated using the ggplot2 package (Wickham, 2009). Mapping was performed with Quantum GIS free software (Quantum GIS Development Team, 2010).

## 3. Results

### 3.1. Mapping of trace-metal concentrations in topsoils

While minimum TM concentrations are comparable whatever the site studied:  $<0.5 \text{ mg kg}^{-1}$  for Cd (LOD),  $\sim 5 \text{ mg kg}^{-1}$  for Cu,  $\sim 35 \text{ mg kg}^{-1}$  for Pb, and  $\sim 30 \text{ mg kg}^{-1}$  for Zn, maximum contents are found in sub-surface soils from La Ruchette (Table 3). This site also clearly exhibits the greatest geochemical heterogeneity, as illustrated by inter-quartile ranges (Table 3) and trace-metal spatial distributions (Fig. 3). Metal concentrations in La Ruchette soils locally exceed maximum reference limits, as defined in sludge-spreading regulations for France (France, 1998):  $2 \text{ mg kg}^{-1}$  for Cd,  $100 \text{ mg kg}^{-1}$  for Cu,  $100 \text{ mg kg}^{-1}$  for Pb and  $300 \text{ mg kg}^{-1}$  for Zn. In contrast, metal contents in Gien-sur-Cure soils are well below these limits, and correspond to assessed values for non-polluted Cambisols:  $0.08\text{--}1.61 \text{ mg kg}^{-1}$  Cd,  $7\text{--}140 \text{ mg kg}^{-1}$  Cu,  $1.5\text{--}70 \text{ mg kg}^{-1}$  Pb,  $9\text{--}362 \text{ mg kg}^{-1}$  Zn (Kabata-Pendias, 2011).

**Table 3**

Descriptive statistics: min, median, mean, max and inter-quartile range for Cd, Cu, Pb and Zn in the two sectors where topsoils were sampled. LOD stands for “limit of detection”.

Concentration ( $\text{mg kg}^{-1}$ )	Cd	Cu	Pb	Zn
LOD	0.5	1	2	2
Sector: Gien-sur-Cure ( $n = 24$ )				
Min.	0.5	2	34	35
Median	0.5	5.5	50	62
Mean	0.5	6.2	53	61
Max.	0.5	11	90	90
Inter-quartile range	-	4.3	16	24
Sector: La Ruchette ( $n = 96$ )				
Min.	0.5	6	41	31
Median	0.5	16	129	86
Mean	0.63	29	377	134
Max.	3.2	212	4520	835
Inter-quartile range	-	18	177	60

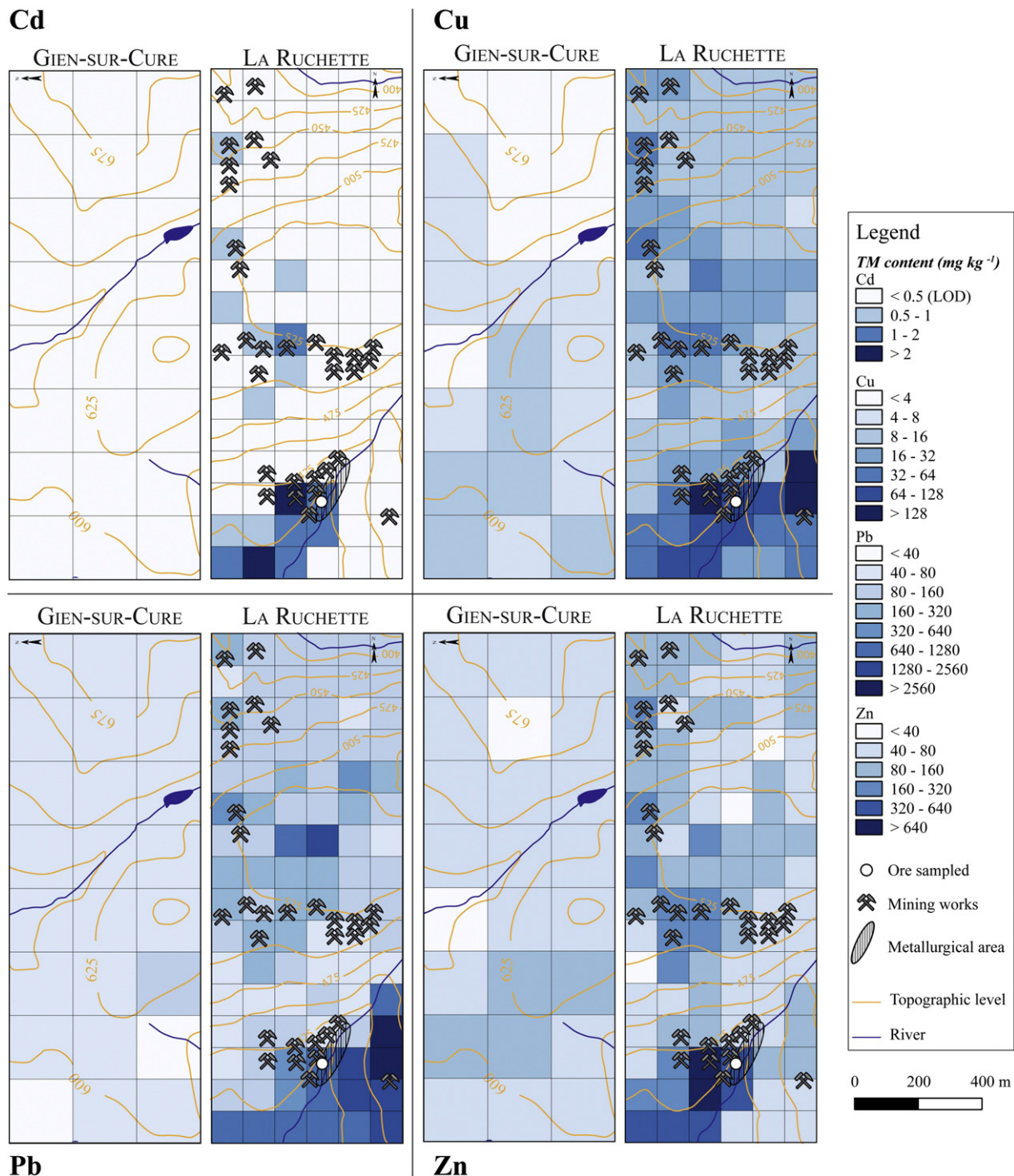


Fig. 3. Spatial distribution of Cd, Cu, Pb and Zn concentrations in topsoils for Gien-sur-Cure and La Ruchette.

### 3.2. Soil profiles and kinetic extractions

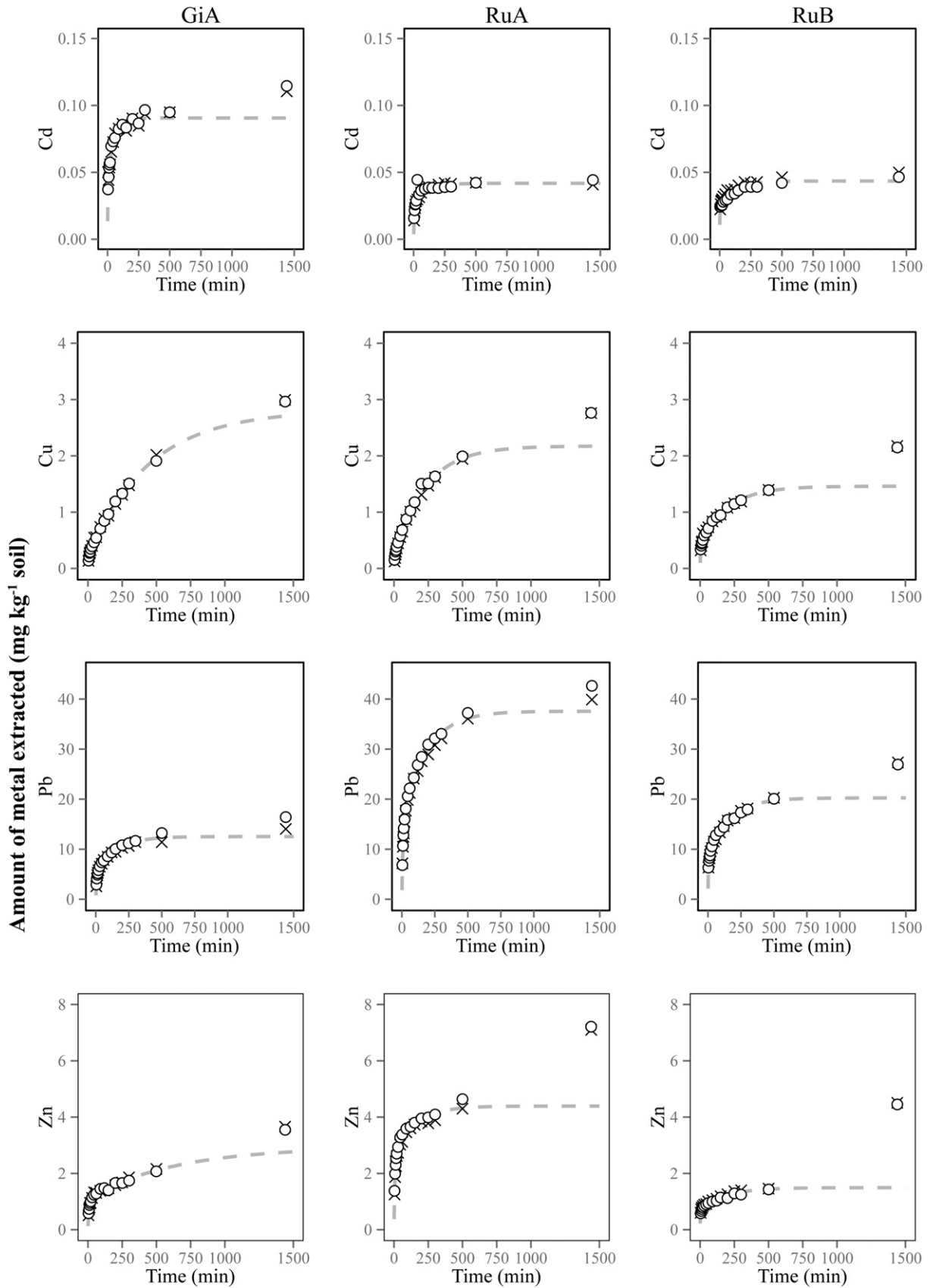
#### 3.2.1. Physico-chemical characteristics of soil horizons

The three soil horizons GiA, RuA and RuB, all sampled in a forest context, are heterogeneous in terms of particle size (Table 2). These acid soils, with no carbonate content, have a low pH (4.2–4.7) and are rich in organic matter, with high C/N values, typical of forest stands. The exchange complex is predominantly compensated by  $Al^{3+}$  ions. At Gien-sur-Cure, considered here as a reference area, total metal concentrations in the A horizon are about  $0.15 \text{ mg kg}^{-1}$  for Cd,  $12 \text{ mg kg}^{-1}$  for Cu,  $65 \text{ mg kg}^{-1}$  for Pb and  $72 \text{ mg kg}^{-1}$  for Zn. In contrast, levels of total trace metals in horizons A and B from La Ruchette are about

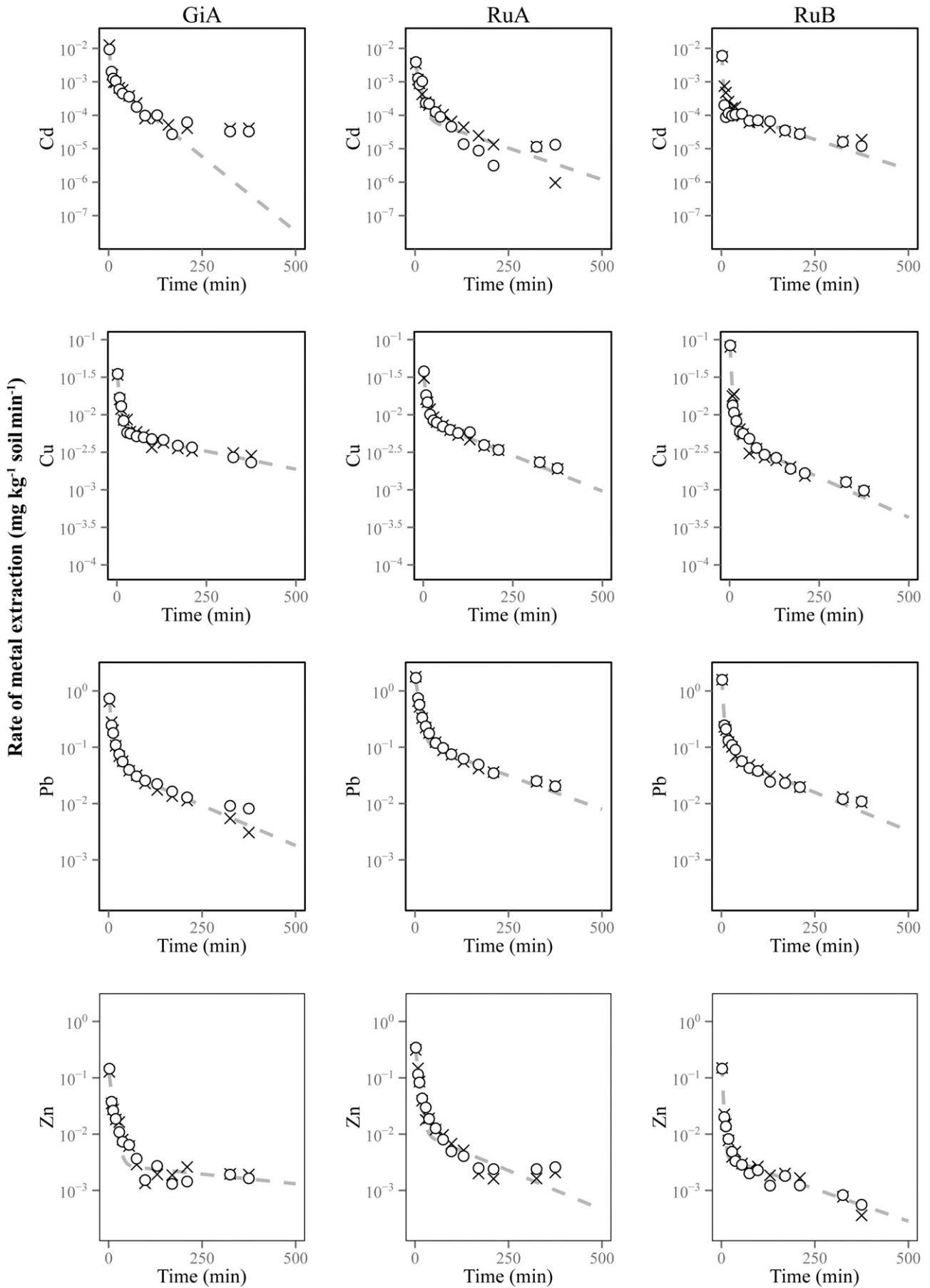
160–170% of those measured in the A horizon of Gien-sur-Cure, except for Cd content which is fairly similar (Table 2).

#### 3.2.2. Kinetic aspects

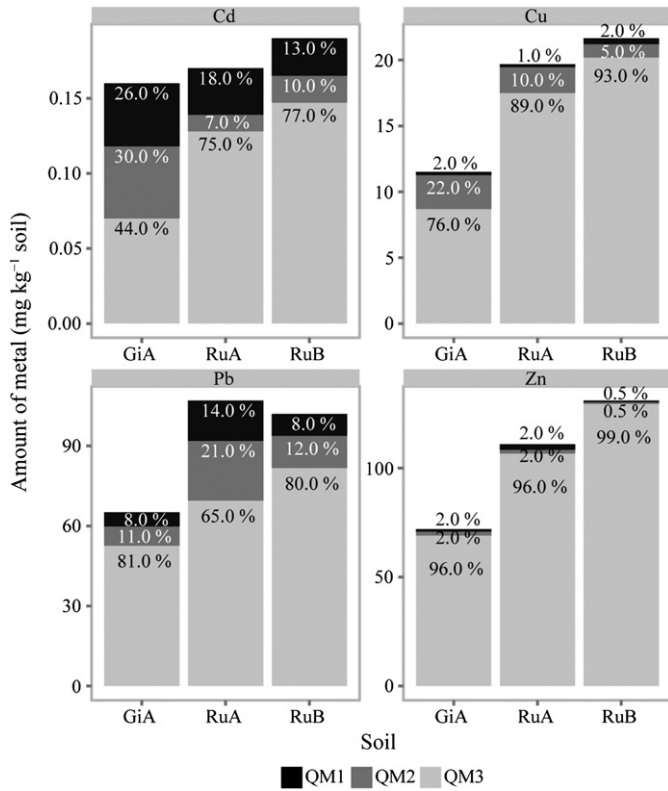
Extracted metal amount per soil weight unit versus time exhibits the expected pattern: first, rapid extraction, followed by a slower increase, which may reach a plateau at the end of the experiment (Fig. 4). Interestingly, similar results are obtained for both replicates, whatever the horizon or metal studied (most of the time  $\pm 10\%$  maximum, see Figs. 4 and 5). Although pH values remained stable throughout the experiment, the final 1440-min points often lay outside the trends defined by the other time points and were therefore not included in further



**Fig. 4.** Amount of metal extracted vs. time. Each point shows the mean value for the three AAS measurements. Crosses show mean value for kinetic extraction duplicates. Dashed grey lines represent best fitted models.







**Fig. 6.** Distribution of Cd, Cu, Pb and Zn expressed as  $Q_{M1}$ ,  $Q_{M2}$  and  $Q_{M3}$  (in  $\text{mg kg}^{-1}$  soil) for each soil studied. The corresponding fractions  $F_{M1}$ ,  $F_{M2}$ , and  $F_{M3}$  (in %) are also indicated.

treatments. The fraction of metal extracted at the end of the experiment was always less than 60%, and often below 25%, of total metal concentrations (Fig. 6).

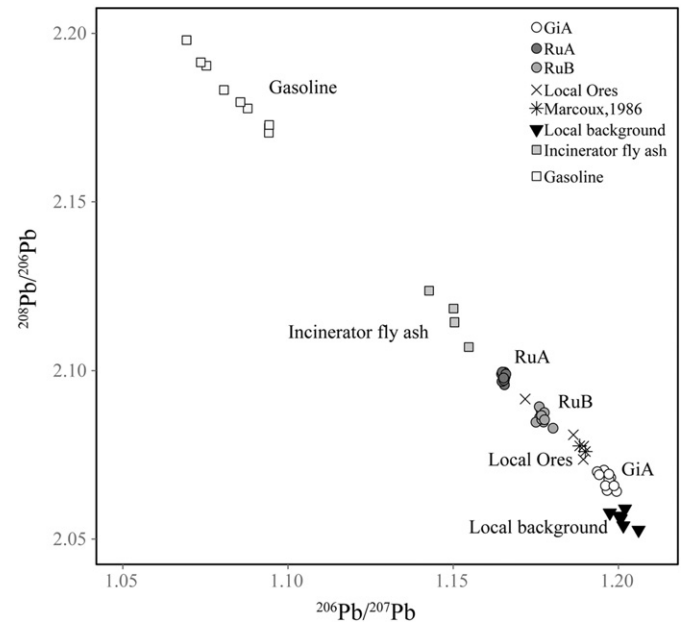
### 3.2.3. Stable lead isotopes

Each soil horizon is clearly different in terms of lead isotopic composition, as measured in soil extracts (Fig. 7): La Ruchette, A horizon ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.165\text{--}1.166$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.096\text{--}2.100$ ); La Ruchette, B horizon ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.175\text{--}1.180$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.085\text{--}2.089$ ); Gien-sur-Cure, A horizon ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.194\text{--}1.199$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.064\text{--}2.070$ ). These data are shown in a  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{206}\text{Pb}/^{207}\text{Pb}$  diagram, together with main potential lead sources: French leaded gasoline before lead was banned and incinerator fly ash (Monna et al., 1997), local galena ores (Marcoux, 1986 and present study), local geological background assessed from deep, non-contaminated forest soil horizons (Lévêque et al., 2002) and a pre-anthropogenic peat sequence (Monna et al., 2004). It is worth noticing that no temporal evolution in terms of lead isotopic composition was observed during the extraction experiment (Fig. 8).

## 4. Discussion

### 4.1. Spatial distribution of metals

It is not surprising to see higher trace-metal levels and greater spatial heterogeneity at La Ruchette, because mining took place at that site, but not at Gien-sur-Cure (Fig. 3). Although known to have been mined at least for iron, La Ruchette has also been recognised as a naturally rich polymetallic district (Gourault et al., 2012). An iron ore



**Fig. 7.**  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in soil-horizon kinetic solutions (circles). Stars correspond to local ores reported in Marcoux (1986). Crosses represent some galena discovered during soil sampling and measured by HR-ICP-MS (Camizuli, unpublished data). Other potential sources: local background (Lévêque et al., 2002; Monna et al., 2004), incinerator fly ash and leaded gasoline (Monna et al., 1997) are also plotted for comparison.

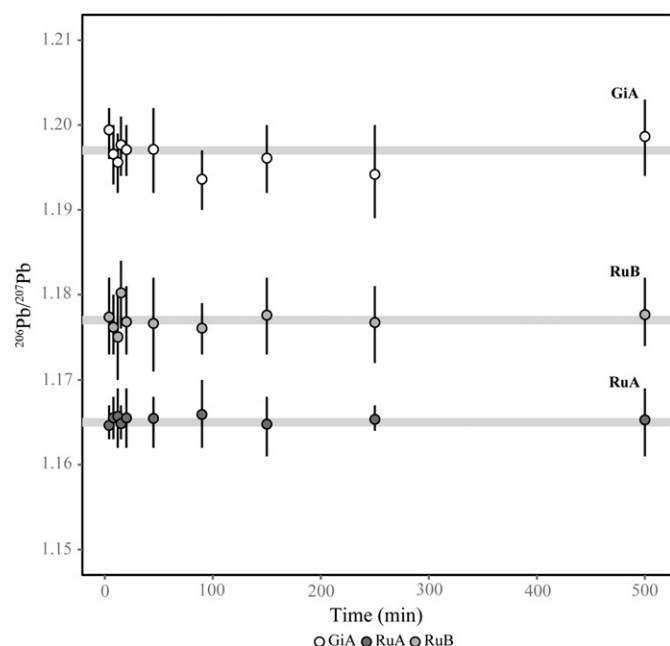
collected in the south of the grid (Fig. 3) yielded high TM contents reaching  $\sim 100 \text{ mg kg}^{-1}$  Pb,  $\sim 1000 \text{ mg kg}^{-1}$  Cu, and  $750 \text{ mg kg}^{-1}$  Zn (Camizuli, unpublished data). It should nonetheless be noticed that high TM contents do not perfectly match mining works, perhaps because zones of past mining or metallurgy remain undiscovered, either in the study area or close by.

### 4.2. Kinetic modelling

Whatever the metal and corresponding soil horizon,  $A_M(t)$  clearly defines two linear segments with different and non-null intercepts and slopes (Fig. 5), demonstrating that the model described in Eq. 2 is suitable. This two first-order reactions model was statistically validated whatever the soil and metal studied. The  $R^2$  values were higher than 0.92 (Table 4), and regression estimates were significantly non-null ( $p < 0.05$ , Fig. 4). Note that tests performed using a third exponential term and including the 1440-min point were not significant.

For this model, the  $\lambda_{M1}$  values for the A horizons studied (i.e. GiA and RuA) are close (Table 4). Whatever the metal, the  $\lambda_{M1}$  values are always smaller in the RuA horizon:  $0.12\text{--}0.15 \text{ min}^{-1}$  than in the RuB horizon:  $0.24\text{--}0.54 \text{ min}^{-1}$ . In other words, the labile pool in RuB is removed faster than that of the overlying horizon, RuA. This suggests a fundamental difference in the nature of the groups rendering the metals as supported by the soil properties. RuA has the highest clay and organic matter contents, and most metals are probably held by the oxides or organically bound (Table 2). The differences in exchangeable cation pools also highlight the different nature of the implicated groups. The trend, from the highest to the lowest  $\lambda_{M1}$  values, generally found in the literature (i.e.  $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$ , Wasay et al., 2007), is more or less observed here as Cd extracts faster:  $\text{Cd} > \text{Zn} \sim \text{Cu} \sim \text{Pb}$  at GiA and at RuB, while no difference can be noticed in RuA. For all samples, Cd presents the highest fraction associated to the fast leaching reaction ( $F_{M1}$ ) demonstrating the high availability of this element. Cd and Zn are generally bound to the exchangeable fraction, unlike Pb and Cu, which are usually

**Fig. 5.** Rate of metal extraction vs. time. Removal rates were calculated using the amount of metal extracted. Crosses show mean value for kinetic extraction duplicates. Dashed grey lines represent best fitted models.



**Fig. 8.** Time variation of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in soil-horizon kinetic solutions (circles). Error bars are given at 95% confidence level. Grey line represents the mean  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios for each profile.

bound to organic matter or oxides (Manouchehri et al., 2011; Labanowski et al., 2008; Gandois et al., 2010; Santos et al., 2010). The  $\lambda_{M2}$  values, which range from  $10^{-3}$  to  $2 \cdot 10^{-2} \text{ min}^{-1}$ , are about 1 to 2 orders of magnitude smaller than the corresponding  $\lambda_{M1}$  values. These values are compatible with results from previously published studies performed under similar chemical conditions, but focusing on different types of material: coastal sediments (Abi-Ghanem et al., 2009; Fangueiro et al., 2005) and agricultural soils (Bermond et al., 2005; Labanowski et al., 2008; Santos et al., 2010).

For Cd, Pb and Zn, the “labile” and “less labile” pools (i.e.  $Q_{M1}$  and  $Q_{M2}$ ) are similar for all soil horizons (Table 4). However, for Cu,  $Q_{M2}$  is significantly higher than  $Q_{M1}$  ( $Q_{M2}/Q_{M1} \sim 2\text{--}10$ , Table 4). For all metals, the amount of non-extractable metal ( $Q_{M3}$ ) is much higher than  $Q_{M1}$  or  $Q_{M2}$  alone, and is also higher than  $Q_{M1} + Q_{M2}$ , except for Cd in the A horizon at Gien-sur-Cure (GiA). At La Ruchette (RuA and RuB), while total concentrations ( $Q_{\text{tot}}$ ) are similar in both soil horizons, the amount of

non-extractable metal in the A horizon ( $Q_{M3}$ ) is always less than that in the underlying B horizon (Fig. 6); this is particularly true for lead.

Although EDTA is known to be a powerful reagent for trace-element extraction (Bermond et al., 1998), in this study, it is the residual, non-extractable fraction ( $F_{M3}$ ) which always predominates, varying from 44% to 77% for Cd, 76% to 93% for Cu, and 65% to 80% for Pb (Fig. 6). Even more surprisingly, the highest residual fractions were found for Zn (96–99%), which is supposed to be a rather mobile metal (Citeau et al., 2003; Fernandez et al., 2010; Sun et al., 2001). In a study of agricultural soils, contaminated more recently, residual fractions ( $F_{M3}$ ) ranged from 40% to 55% for Zn and Cu, and from 10% to 15% for Pb and Cd (Labanowski et al., 2008). In the forest soils studied here, the lower proportion of metals extracted can be explained by various complementary processes. Generally, the fraction most easily extracted by reagents is thought to be mainly of anthropogenic origin, because its binding association with soil constituents is often lower than for metals of natural origin. In view of the acid soil conditions (pH  $\sim$  4.5) here, these atmospherically deposited metals, mainly of anthropogenic origin, may have partly percolated over time, in a dissolved form, through the soil profile to depths below the horizons studied (Ettler et al., 2012; Gandois et al., 2010; Hernandez et al., 2003; van Oort et al., 2009). The cation-exchange capacity of the soils in this study indicates that the soil matrix is not available for exchange with the soil solution. Aluminium takes up a large amount of charge in the CEC (Table 2) and hence prevents the fixation of other elements like divalent ions (Pb, Cd, Cu, Zn). Consequently, the predominant metal pool today corresponds to a metal fraction strongly bound to soil particles. Besides, the contamination is mostly ancient, and organic matter is present at high levels in these forest soils. These conditions may have prevented metal leaching due to the formation of stable organo-metallic complexes over time, as previously suggested by Labanowski et al. (2007). Moreover, to some extent, TMs may migrate to depth when associated to particulate organic matter (POM) or iron colloids (Citeau et al., 2003; van Oort et al., 2006).

Stable lead isotopes might help to understand better the origin of the lead forming the two pools. The lead isotope signatures of the soil-horizon kinetic solutions are incompatible with leaded gasoline sold before Pb was phased out ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.067\text{--}1.094$  in 1995; Fig. 7), and too radiogenic to be mainly affected by modern industrial sources, previously estimated on fly ash from incinerators ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.142\text{--}1.155$ ). The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.165\text{--}1.166$ ) for the A horizon kinetic solution from La Ruchette are below the values for the small number of measurements available for local Pb ores ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.172\text{--}1.189$ ).

**Table 4**  
Kinetic parameters:  $\lambda_i$  and amounts,  $Q_{Mi}$ , of metal extracted with EDTA per kg of soil defined by the two-first-order reactions model (together with associated standard deviation),  $R^2$  values, total metal concentrations:  $Q_{\text{tot}}$ , amount of metal non-extracted:  $Q_{M3}$ , and proportion of metals in each  $Q_{Mi}$  pool:  $F_{Mi}$ , sd stands for standard deviation of regression estimates.

	$\lambda_{M1}$ ( $\text{min}^{-1}$ )	sd	$\lambda_{M2}$ ( $\text{min}^{-1}$ )	sd	$Q_{M1}$ ( $\text{mg kg}^{-1}$ )	sd	$Q_{M2}$ ( $\text{mg kg}^{-1}$ )	sd	$R^2$	$Q_{\text{tot}}$ ( $\text{mg kg}^{-1}$ )	$Q_{M3}$ ( $\text{mg kg}^{-1}$ )	$Q_{M2}/Q_{M1}$	$F_{M1}$ (%)	$F_{M2}$ (%)	$F_{M3}$ (%)
<b>Cd</b>															
GiA	0.349	0.096	0.021	0.003	0.042	0.003	0.048	0.003	0.970	0.16	0.07	1.14	26	30	44
RuA	0.126	0.019	0.009	0.004	0.031	0.003	0.011	0.004	0.924	0.17	0.13	0.35	18	7	75
RuB	0.543	0.086	0.008	0.001	0.025	0.001	0.018	0.001	0.973	0.19	0.15	0.72	13	10	77
<b>Cu</b>															
GiA	0.140	0.025	0.0022	0.0002	0.246	0.016	2.57	0.12	0.998	11.5	8.7	10.4	2	22	76
RuA	0.142	0.035	0.0044	0.0002	0.218	0.024	1.96	0.04	0.998	19.7	17.5	8.99	1	10	89
RuB	0.237	0.031	0.0049	0.0004	0.448	0.018	1.01	0.03	0.993	21.7	20.2	2.25	2	5	93
<b>Pb</b>															
GiA	0.150	0.013	0.0065	0.0005	5.3	0.2	7.2	0.5	0.995	65.1	52.6	1.36	8	11	81
RuA	0.118	0.008	0.0055	0.0004	15.1	0.5	22.4	0.6	0.997	107	69.2	1.48	14	21	65
RuB	0.288	0.032	0.0063	0.0005	8.2	0.2	12.1	0.4	0.990	102	81.5	1.48	8	12	80
<b>Zn</b>															
GiA	0.121	0.012	0.0016	0.0008	1.11	0.04	1.8	0.6	0.979	72	69.1	1.62	2	2	96
RuA	0.148	0.013	0.0064	0.0012	2.6	0.1	1.7	0.1	0.984	111	107	0.65	2	2	96
RuB	0.347	0.033	0.0053	0.0006	0.74	0.02	0.75	0.04	0.987	131	130	1.01	0.5	0.5	99

However, the study of atmospheric deposition archived in a peat sequence sampled at Port-des-Lamberts, located only 7 km from the mining site of La Ruchette (Fig. 1), described ancient anthropogenic inputs related to local mining and metallurgy, characterised by isotopic  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios ranging from 1.160 to 1.180 (Monna et al., 2004). At La Ruchette, sampling was undertaken in a relatively elevated zone, avoiding mining works, so that any anthropogenic input must be of atmospheric origin, and not from liquid urban waste. As a result, lead isotopic compositions measured in the A horizon of La Ruchette are driven (i) mainly by local mining/metallurgy, with  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios probably ranging from 1.160 to 1.180, (ii) diffuse and minor human-derived modern inputs characterised by faintly radiogenic signatures (e.g. leaded gasoline), and (iii) lead naturally present in soils, with high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of ~1.20–1.21. The anthropogenic lead present in the B horizon (RuB) must have slowly migrated downwards from the A horizon. The anthropogenic contribution is nonetheless below that of the RuA horizon. As a result, lead isotopic signatures are more radiogenic in RuB ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.175\text{--}1.180$ ) than in RuA ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.165\text{--}1.166$ ). At Gien-sur-Cure, far from any local mining works, lead is predominantly of natural origin, as shown by  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios between 1.194 and 1.199, close to the background signature level ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.20\text{--}1.21$ ; Fig. 7).

These findings indicate that each of the soil horizons contains lead from many different sources in various proportions. It would have been tempting to consider a “labile” pool mainly composed of lead of anthropogenic origin, because this type of lead is known to be less strongly bound than the natural lead present in the lattice network of minerals (Erel et al., 1997; Steinmann and Stille, 1997; Teutsch et al., 2001). One possible hypothesis could be that after the first “labile” pool has been rapidly extracted ( $\lambda_{M1} \gg \lambda_{M2}$ ), natural lead would predominate in the “less labile” second pool, resulting in more radiogenic values over time, during the experiment. In our case, this pattern does not apply because no such temporal evolution of lead isotopic ratios was observed (Fig. 8). The kinetic extraction of trace metals from soils provides no information as to their origin, except by demonstrating a blend of sources. The two pools identified probably correspond to metals trapped by different kinds of particles.

## 5. Conclusion

For both the non-contaminated soil horizon and the profile of the soil affected by historical mining, at least since Prehistory, kinetic extractions of metals were successfully modelled by a two first-order reactions model. All metals studied here exhibit approximately the same kinetic behaviour. In mining contexts, more metals are extracted from the topsoil than from the underlying horizon, although total concentrations are similar. The B horizon of La Ruchette presents notably higher  $\lambda_{M1}$  values for all metals than the A horizon, highlighting a more rapid kinetic extraction of the first pool. The “labile” and “less labile” pools of Cu, Pb, Zn, and Cd represent only a small fraction of the total metal content in soil (assessed by total digestion). Two hypotheses are therefore proposed: (i) binding to soil particles, possibly as organo-metallic complexes, is strong, more particularly in the B horizon or, (ii) past anthropogenic inputs have been partly leached through the soil profiles because of the acidic soil pH. These two processes are not mutually exclusive. Stable lead isotopes do not allow the origins of the lead present in the two pools of a given soil horizon to be differentiated. Both pools in the same soil horizon will have the same isotopic composition, resulting from a blend of sources, yet they will present different kinetic behaviours. However, each soil horizon will have a different isotopic composition, because of its contamination history, and the intrinsic parameters controlled by post-depositional processes. Traces of past mining and metallurgy may persist in soils long after such activities have ceased. However, at least in the forest soils studied here, the low TM lability shown through kinetic extractions suggests that trace metals should not represent a threat for biota. Results only concern two specific soils, one of them sampled in an area presenting a high geochemical spatial

heterogeneity. This study should not therefore be viewed as a work allowing the fate of metals to be understood at the scale of the Morvan, but as an exploratory study to evaluate the interest of combining kinetic extraction in soil horizons and lead isotopic measurements in a past mining context. It should also be mentioned that such an approach is costly and time consuming, so that it cannot be routinely employed. However, it clearly demonstrates the pertinence of integrating archaeological knowledge into the environmental sciences. Historical mining sites like those investigated here can be used as powerful proxies to model the impacts of present-day societies on the surrounding environment and to forecast the long-term fate of metals in soils.

## Conflict of interest

The authors declare no conflict of interest.

## Acknowledgements

We are grateful to the FEDER, the Regional Council of Burgundy, the University of Burgundy, and Bibracte for funds. The Morvan Regional Nature Park is thanked for constant support. The French Ministry of Research is thanked for the Ph.D. grant of Estelle Camizuli. We wish also to thank Claude Gourault and Gilles Hamm for their invaluable assistance during sampling. We are grateful to the four anonymous reviewers whose judicious comments have greatly improved the manuscript.

## References

- Abi-Ghanem C, Bermond A, Besançon S, Nakhlé K, Khalaf G. Cd and Pb extractability with EDTA in sediments of three contrasted sites of the Lebanese coast. *Leban Sci J* 2009;10:33.
- AFNOR. Evaluation de la Qualité des Sols. Recueil Normes et Réglementation, 1: Méthodes d'Analyse Chimique. Paris: Association française de normalisation; 2004.
- Aleksander-Kwaterczak U, Helios-Rybicka E. Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of South Poland. *J Soils Sediments* 2008;9:13–22.
- Bade R, Oh S, Sik Shin W. Assessment of metal bioavailability in smelter-contaminated soil before and after lime amendment. *Ecotoxicol Environ Saf* 2012;80:299–307.
- Bermond A. Limits of sequential extraction procedures re-examined with emphasis on the role of  $\text{H}^+$  ion reactivity. *Anal Chim Acta* 2001;445:79–88.
- Bermond A, Yousfi I, Ghestem J-P. Kinetic approach to the chemical speciation of trace metals in soils. *Analyst* 1998;123:785–9.
- Bermond A, Varrault G, Sappin-Didier V, Mench M. A kinetic approach to predict soil trace metal bioavailability: preliminary results. *Plant Soil* 2005;275:21–9.
- Brunori C, Creminisi C, D'Annibale L, Massanisso P, Pinto V. A kinetic study of trace element leachability from abandoned-mine-polluted soil treated with SS-MSW compost and red mud. Comparison with results from sequential extraction. *Anal Bioanal Chem* 2005;381(7):1347–54.
- Cauuet B, Bouscaillet M. Sondage d'une mine à la Pâturage des Grangerands. In: Guichard V, editor. *Rapp. Annu. Act. Sci. Bibracte. Centre Archéologique Européen de Bibracte. Glux-en-Glenne*; 2006. p. 129–61.
- Chopin EIB, Alloway BJ. Trace element partitioning and soil particle characterisation around mining and smelting areas at Tharsis, Riotinto and Huelva, SW Spain. *Sci Total Environ* 2007;373(2–3):488–500.
- Citeau L, Lamy I, van Oort F, Elsass F. Colloidal facilitated transfer of metals in soils under different land use. *Colloids Surf A* 2003;217:11–9.
- Cloquet C, Carignan J, Libourel G, Sterckeman T, Perdrix E. Tracing source pollution in soils using cadmium and lead isotopes. *Environ Sci Technol* 2006;40:2525–30.
- Delaville M. Notes sur les gisements de minerais de fer de Champ-Robert et d'Arleuf (Morvan). *Bull Soc Geol Fr* 1858;15:726–8.
- Delfour J. Géologie et gîtologie du Morvan. *Le Règne minéral-Hors-Série XIII*. ; 20079–15.
- Douay F, Pruvot C, Waterlot C, Fritsch C, Fourrier H, Loriette A, et al. Contamination of woody habitat soils around a former lead smelter in the North of France. *Sci Total Environ* 2009;407:5564–77.
- Dunn CE, Balma RG, Spirito WA. Geochemistry of marine sediments from the Strait of Georgia, British Columbia. *Geol Surv Can* 1996:41. [Report No.: open file 3052].
- Erel Y, Patterson CC. Leakage of industrial lead into the hydrocycle. *Geochim Cosmochim Acta* 1994;58:3289–96.
- Erel Y, Veron A, Halicz L. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. *Geochim Cosmochim Acta* 1997;61:4495–505.
- Ettler V, Mihaljevič M, Komarek M. ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. *Anal Bioanal Chem* 2004;378:311–7.
- Ettler V, Vaněk A, Mihaljevič M, Bezdička P. Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. *Chemosphere* 2005;58:1449–59.
- Ettler V, Mihaljevič M, Šebek O, Matys Grygar T, Klementová M. Experimental in situ transformation of Pb smelter fly ash in acidic soils. *Environ Sci Technol* 2012;46:10539–48.

- Fangueiro D, Bermond A, Santos E, Carapuça H, Duarte A. Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA extraction: search for optimal experimental conditions. *Anal Chim Acta* 2002;459:245–56.
- Fangueiro D, Bermond A, Santos E, Carapuça H, Duarte A. Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information. *Talanta* 2005;66:844–57.
- Fernandez C, Labanowski J, Jongmans T, Bermond A, Cambier P, Lamy I, et al. Fate of airborne metal pollution in soils as related to agricultural management: 2. Assessing the role of biological activity in micro-scale Zn and Pb distributions in A, B and C horizons. *Eur J Soil Sci* 2010;61:514–24.
- Fonseca B, Pazos M, Figueiredo H, Tavares S, Sanromán MA. Desorption kinetics of phenanthrene and lead from historically contaminated soil. *Chem Eng J* 2011;167:84–90.
- France. Arrêté interministériel du 8 janvier 1998 relatif à l'épandage des boues issues du traitement des eaux usées; 1998. [NOR ATEE9760538A].
- Galf Navarro EM, Villanueva Tagle ME, Larrea Marín MT, Pomares Alfonso MS. Comparison of USEPA 3050B and ISO 14869-1: 2001 digestion methods for sediment analysis by using FAAS and ICP-OES quantification techniques. *Quim Nova* 2011;34(8):1443–9.
- Gandois L, Probst A, Dumat C. Modelling trace metal extractability and solubility in French forest soils by using soil properties. *Eur J Soil Sci* 2010;61:271–86.
- Gismera MJ, Laca J, da Silva P. Study of metal fractionation in river sediments. A comparison between kinetic and sequential extraction procedures. *Environ Pollut* 2004;127(2):175–82.
- Gleyzes C, Tellier S, Astruc M. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trends Anal Chem* 2002;21:451–67.
- Gourault C. Les anciennes mines du Haut Morvan. Méthode d'inventaire, essai de caractérisation. Master degree dissertation. Dijon: Université de Bourgogne; 2009.
- Gourault C, Peraud W, Camizuli E, Guillaumet J-P, Hamm G, Monna F, et al. Minéralogie de la mine du Prabis (Villapourçon, Nièvre, France). *Bourgogne Nature*; 2012:93–116.
- Gutzman DW, Langford CH. Kinetic study of the speciation of copper (II) bound to a hydrous ferric oxide. *Environ Sci Technol* 1993;27:1388–93.
- Hernandez L, Probst A, Probst JL, Ulrich E. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci Total Environ* 2003;312:195–219.
- Hudson-Edwards KA, Macklin MG, Miller JR, Lechler PJ. Sources, distribution and storage of heavy metals in the Rio Pilcomayo Bolivia. *J Geochem Explor* 2001;72:229–50.
- IUSS Working Group WRB. World reference base for soil resources 2006, first update 2007. *World Soil Resources Reports* 103; 2006. [Rome].
- Izquierdo M, Tye AM, Chenery SR. Sources, lability and solubility of Pb in alluvial soils of the River Trent catchment, U.K. *Sci Total Environ* 2012;433:110–22.
- Jalali M, Tabar SS. Kinetic extractions of nickel and lead from some contaminated calcareous soils. *Soil Sediment Contam Int J* 2013;22:56–71.
- Jouffroy-Bapicot I, Pulido M, Baron S, Galop D, Monna F, Lavoie M, et al. Environmental impact of early palaeometallurgy: pollen and geochemical analysis. *Veg Hist Archaeobot* 2007;16:251–8.
- Kabata-Pendias A. Trace elements in soils and plants. 4th ed. Boca Raton, FL: CRC Press, Taylor & Francis Group; 2011.
- Kochem Mallmann FJ, Rheinheimer dos Santos D, Cambier P, Labanowski J, Lamy I, Santana MA, et al. Using a two site-reactive model for simulating one century changes of Zn and Pb concentration profiles in soils affected by metallurgical fallout. *Environ Pollut* 2012;162:294–302.
- Komárek M, Ettler V, Chrástný V, Mihaljevič M. Lead isotopes in environmental sciences: a review. *Environ Int* 2008;34:562–77.
- Kylander ME, Cortizas AM, Rauch S, Weiss DJ. Lead penetration and leaching in a complex temperate soil profile. *Environ Sci Technol* 2008;42:3177–84.
- Forel B. La métallurgie des alliages à base de cuivre en Bourgogne et en France orientale à l'âge du bronze. Dissertation in Archaeology. Dijon: Université de Bourgogne; 2009.
- Labanowski J, Sebastia J, Foy E, Jongmans T, Lamy I, van Oort F. Fate of metal-associated POM in a soil under arable land use contaminated by metallurgical fallout in northern France. *Environ Pollut* 2007;149:59–69.
- Labanowski J, Monna F, Bermond A, Cambier P, Fernandez C, Lamy I, et al. Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate. *Environ Pollut* 2008;152:693–701.
- Leleyter L, Rousseau C, Biree L, Baraud F. Comparison of EDTA, HCl and sequential extraction procedures, for selected metals (Cu, Mn, Pb, Zn), in soils, riverine and marine sediments. *J Geochem Explor* 2012;116–117:51–9.
- Lévêque J, Philippe S, Baize D, Monna F, Haack U. Chapitre 22: Utilisation des isotopes stables pour la détermination de l'origine (géogène ou industrielle) du plomb. In: Baize D, editor. Les éléments traces métalliques dans les sols. Paris: INRA Editions; 2002. p. 375–91.
- Lo IMC, Yang XY. EDTA extraction of heavy metals from different soil fractions and synthetic soils. *Water Air Soil Pollut* 1999;109:219–36.
- Macklin MG, Hudson-Edwards KA, Dawson EJ. The significance of pollution from historic metal mining in the Pennine orefields on river sediment contaminant fluxes to North Sea. *Sci Total Environ* 1997;194/195:391–7.
- Manouchehri N, Bermond A. EDTA in soil science: a review of its application in soil trace metal studies. *TAET* 2009;3:1–15.
- Manouchehri N, Besançon S, Bermond A. Major and trace metal extraction from soil by EDTA: equilibrium and kinetic studies. *Anal Chim Acta* 2006;559:105–12.
- Manouchehri N, Besançon S, Bermond A. Kinetic characterizing of soil trace metal availability using Soil/EDTA/Chelex mixture. *Chemosphere* 2011;83(7):997–1004.
- Marcoux E. Isotopes du plomb et paragenèses métalliques, traceurs de l'histoire des gîtes minéraux: illustration des concepts de source, d'héritage et de régionalisme dans les gîtes français. Documents — BRGM N°117Orléans: Ed. du Bureau de recherches géologiques et minières; 1986.
- Monna F, Lancelot J, Croudace IW, Cundy AB, Lewis JT. Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: implications for Pb pollution sources in urban areas. *Environ Sci Technol* 1997;31:2277–86.
- Monna F, Loizeau J-L, Thomas BA, Guéguen C, Favarger P-Y. Pb and Sr isotope measurements by inductively coupled plasma-mass spectrometer: efficient time management for precision improvement. *Spectrochim Acta Part B* 1998;53:1317–33.
- Monna F, Loizeau JL, Thomas B, Guéguen C, Favarger PY, Losno R, et al. Noise identification and sampling frequency determination for precise Pb isotopic measurements by quadrupole-based inductively coupled plasma mass spectrometry. *Analisis* 2000;28:750–7.
- Monna F, Petit C, Guillaumet J-P, Jouffroy-Bapicot I, Blanchot C, Dominik J, et al. History and environmental impact of mining activity in Celtic Aeduan territory recorded in a peat bog (Morvan, France). *Environ Sci Technol* 2004;38:665–73.
- Monna F, Camizuli E, Nedjai R, Cattin F, Petit C, Guillaumet J-P, et al. Tracking archaeological/historical mines using prospectivity mapping. *J Archaeol Sci* 2013n. [submitted for publication].
- Nirel PMV, Morel FMM. Pitfalls of sequential extractions. *Water Res* 1990;24:1055–6.
- Pajak M, Jasik M. Heavy metal (Zn, Pb, Cd) concentration in soil and moss (*Pleurozium schreberii*) in the Brynica district, southern Poland. *iForest* 2011;4:176.
- Pinheiro J, Bates D, DebRoy S, Sarkar D, The R Development Core Team. nlme: linear and nonlinear mixed effects models; 2013.
- Pyatt FB, Gilmore G, Grattan JP, Hunt CO, McLaren S. An imperial legacy? An exploration of the environmental impact of ancient metal mining and smelting in southern Jordan. *J Archaeol Sci* 2000;27:771–8.
- Quantum GIS Development Team. Quantum GIS geographic information system. Open source geospatial foundation project. <http://qgis.osgeo.org>, 2010.
- R Development Core Team. R: a language and environment for statistical computing. Vienne: R Foundation for Statistical Computing; 2008.
- Reimann C, Smith DB, Woodruff LG, Flem B. Pb-concentrations and Pb-isotope ratios in soils collected along an east–west transect across the United States. *Appl Geochem* 2011;26:1623–31.
- Reimann C, Flem B, Fabian K, Birke M, Ladenberger A, Négrel P, et al. Lead and lead isotopes in agricultural soils of Europe — the continental perspective. *Appl Geochem* 2012;27:532–42.
- Santos S, Costa CAE, Duarte AC, Scherer HW, Schneider RJ, Esteves VI, et al. Influence of different organic amendments on the potential availability of metals from soil: a study on metal fractionation and extraction kinetics by EDTA. *Chemosphere* 2010;78:389–96.
- Semlali RM, van Oort F, Denaix L, Loubet M. Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. *Environ Sci Technol* 2001;35(21):4180–8.
- Steinmann M, Stille P. Rare earth element behavior and Pb, Sr, Nd isotope systematics in a heavy metal contaminated soil. *Appl Geochem* 1997;12:607–23.
- Sun B, Zhao F, Lombi E, McGrath S. Leaching of heavy metals from contaminated soils using EDTA. *Environ Pollut* 2001;113:111–20.
- Tamas C-G. Caractérisation minéralogique des mines anciennes du Morvan. Post-doctoral report. Dijon: Université de Bourgogne; 2004.
- Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 1979;51:844–51.
- Teutsch N, Erel Y, Halicz L, Banin A. Distribution of natural and anthropogenic lead in Mediterranean soils. *Geochim Cosmochim Acta* 2001;65:2853–64.
- Ure AM, Quevauviller P, Muntau H, Griepink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int J Environ Anal Chem* 1993;51:135–51.
- van Oort F, Jongmans AG, Citeau L, Lamy I, Chevallier P. Microscale Zn and Pb distribution patterns in subsurface soil horizons: an indication for metal transport dynamics. *Eur J Soil Sci* 2006;57:154–66.
- van Oort F, Thiry M, Jongmans T, Bourennane H, Cambier P, Lamy I, et al. Pollutions métalliques: distributions hétérogènes du Zn, Pb, Cd et Cu et relations avec l'usage des sols. In: Philippe Cambier, Schwartz C, van Oort F, editors. Contaminations métalliques des agrosystèmes et écosystèmes péri-industriels. Versailles: Editions Quae; 2009. p. 16–44.
- Wasay SA, Barrington S, Tokunagal S, Prasher S. Kinetics of heavy metal desorption from three soils using citric acid, tartaric acid, and EDTA. *J Environ Eng Sci* 2007;6(6):611–22.
- Wickham H. Ggplot2: elegant graphics for data analysis. (Use R!). New York: Springer; 2009.
- Yu J, Klarup D. Extraction kinetics of copper, zinc, iron, and manganese from contaminated sediment using disodium ethylenediaminetetraacetate. *Water Air Soil Pollut* 1994;75:205–25.