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1 **Lead distribution in soils impacted by a secondary lead smelter:**
2 **experimental and modelling approaches**

3
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42 **Abstract**

43 Smelting activities are one of the most common sources of trace elements in the environment.
44 The aim of this study was to determine the lead distribution in upper horizons (0-5 and 5-
45 10 cm) of acidic soils in the vicinity of a lead-acid battery recycling plant in northern France.
46 The combination of chemical methods (sequential extractions), physical methods (Raman
47 microspectroscopy and scanning electron microscopy with an energy dispersive spectrometer)
48 and multi-surface complexation modelling enabled an assessment of the behaviour of Pb.
49 Regardless of the studied soil, none of the Pb-bearing phases commonly identified in similarly
50 polluted environments (e.g., anglesite) were observed. Lead was mainly associated with
51 organic matter and manganese oxides. The association of Pb with these soil constituents can
52 be interpreted as evidence of Pb redistribution in the studied soils following smelter particle
53 deposition.

54

55 Keywords: lead, polluted soils, soil organic matter, manganese oxides.

56 **1 Introduction**

57 The speciation and the lability of trace elements (TE) in soils allow the assessment of their
58 potential mobility and ecotoxicological effects in the environment (Sparks, 2003). Organic
59 matter (OM), clays and metal hydroxides (Al, Fe and Mn) have large and reactive surface
60 areas, making them good scavengers of TE in soils and soil solutions (Hooda, 2010).

61 Many techniques are available to identify or quantify the relative contributions of the phases
62 involved in Pb retention in soil. For instance, chemical extractions, such as single and
63 sequential extractions (SE), are commonly used to assess the contribution of each adsorptive
64 surface throughout the soil. Many SE procedures exist, and most comprise between 3 and 8
65 steps to separate different geochemical forms, e.g., exchangeable, acid-soluble, reducible,
66 oxidizable or residual (Tessier et al., 1979; Gleyzes et al., 2002; Rao et al., 2008; Laveuf et
67 al., 2009). Isotopic dilution can be another method to quantify the exchangeable pools of
68 metals in soil (Atkinson et al., 2011; Marzouk et al., 2013). Physical methods, such as
69 scanning electron microscopy coupled with energy dispersive spectrometer (SEM-EDS),
70 Raman microspectroscopy (RMS) and X-ray absorption spectroscopy (XAS), can also be
71 used to fully characterize the TE species in natural systems (Morin et al., 1999; Sobanska et
72 al., 1999; Uzu et al., 2011). Modelling is another approach to determine the TE distribution in
73 the soil. The use of multi-surface complexation models can predict adsorption and ion
74 exchange for various soil constituents (Weng et al., 2001; Cancès et al., 2003; Dijkstra et al.,
75 2004; Pourret et al., 2015; Ren et al., 2015).

76 Smelting activities are one of the most common sources of TE in the environment
77 (Fernandez-Turiel et al., 2001; Liénard et al., 2014; Ettler, 2016). In the particular case of
78 lead-acid battery recycling, different stages of the process, such as crushing, fusion, reduction
79 and refining, are responsible for emissions of various metals and compounds. Metallic lead
80 (Pb^0), anglesite ($PbSO_4$), lead oxide (PbO) and cerussite ($PbCO_3$) are the predominant species
81 found in the vicinity of lead smelters (Sobanska et al., 1999; Ettler et al., 2005; Ettler et al.,
82 2008; Uzu et al., 2011; Schreck et al., 2012). Particles from primary Pb smelters are
83 composed of relatively insoluble phases (such as $PbSO_4$, $PbSO_4 \cdot PbO$, and PbS), while

84 particulates from secondary Pb smelters are composed of much more soluble phases (such as
85 caracolite, $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$, and potassium lead chloride, KPb_2Cl_5) (Ettler et al., 2012; Ettler,
86 2016). Several studies have already addressed the transformation of these Pb-bearing phases
87 in fly ash using batch experiments (Bataillard et al., 2003; Ettler et al., 2005, Ettler et al.,
88 2008, Ettler et al., 2009, Vitkova et al., 2009) or in field conditions using polyamide
89 experimental bags (Ettler et al., 2012). However, very few studies have examined the
90 redistribution of Pb in smelter-impacted soils (e.g., Morin et al., 1999, Ettler et al., 2005).
91 The objective of the present study was to determine the Pb distribution in the upper horizons
92 of contaminated acidic soils located in the vicinity of a secondary lead smelter. An original
93 approach combining chemical methods (sequential extractions), physical methods (RMS and
94 SEM-EDS) and multi-surface complexation modelling was used to identify Pb phases and to
95 assess the contributions of major reactive components (organic matter, clays, iron and
96 manganese hydroxides) in soils. This approach provides a better understanding and prediction
97 of the behaviour of Pb in smelter-impacted soils.

98 **2 Materials and methods**

99 **Soil sampling and characterization**

100 Three heavily contaminated soils were sampled near a secondary lead smelter in northern
101 France (Figure A1; further details on the study area are available in Schneider et al., 2016a).
102 Two of the soils are luvisols cambisols (IUSS Working Group WRB, 2014) and developed on
103 Quaternary loam (S1 and S2). The third soil (S3) is a hydromorphic gleysol (IUSS Working
104 Group WRB, 2014) developed on altered upper Cambrian black shales. In this work, only the
105 surficial horizons (A horizon) presenting the highest lead levels were studied. After the litter
106 was removed, two soils samples (0-5 cm: top (T); 5-10 cm: bottom (B)) were collected
107 independently. The six soil samples were stored in polyethylene bags and brought to the
108 laboratory.

109 The soils were air-dried and sieved through 2 mm mesh. A fraction of the samples was finely
110 crushed for total organic carbon (TOC; NF ISO 14235 (AFNOR, 1998)), total metal content
111 and XRD measurements. The total soil metal contents (Pb, Mn and Fe) were determined by
112 inductively coupled plasma mass spectroscopy (ICP-MS) following tri-acid digestion (HNO_3 -
113 HClO_4 -HF). The soil pH was determined in a mixture of 1:2.5 soil:water (w/v) according to
114 the French standard X 31-103 (AFNOR, 1988). The cation exchange capacity (CEC) was
115 determined by the ammonium acetate saturation method according to the French standard NF-
116 X 31-130 (AFNOR, 1999). Finally, the clay, silt and sand contents were determined by the
117 pipette method following the French standard NF-X 31-107 (AFNOR, 2003).

118

119 **Sequential Extraction**

120 To estimate the chemical partitioning of Pb in the six soil samples, an SE procedure
121 comprising eight steps, adapted from Laveuf et al. (2009), was used (Table 1). The extractions
122 were made in triplicate on 1 g of sieved (2 mm), air-dried soil in polypropylene tubes. After
123 each extraction step, the tubes were centrifuged at 3000 g for 20 min. The supernatants were
124 filtered (0.2 μm) and stored at 4°C prior to analysis. The residues were washed with 10 mL of
125 ultrapure water (Milli-Q, 18.2 m Ω). A blank experiment was run at the same time as each

126 extraction procedure. Because of the very high TOC contents in the soil samples, the 4th step
127 of the SE was repeated three times. All the supernatants were acidified with ultrapure HNO₃
128 before analysis via inductively coupled plasma atomic emission spectroscopy (ICP-AES).

129

130 **X-ray diffraction**

131 Bulk soil samples of the three topsoils (S1T, S2T and S3T) were wet-sieved at 500, 200, 50
132 and 20 μm in deionized water, without preliminary treatments. The remaining fractions
133 (< 20 μm) were further fractionated by sedimentation in deionized water according to Stokes
134 law. The particle-size fractions obtained were < 2, 2-20, 20-50, 50-200, 200-500 and 500-
135 2000 μm.

136 The mineralogical compositions of the fine fraction (< 2 μm) of the three topsoil samples
137 were determined by X-ray powder diffraction analysis. A Bruker AXS D8 diffractometer
138 using Cu-Kα radiation and operating in step scan mode between 3 and 70° 2θ with 0.04° 2θ
139 steps and a counting time of 10 s per step was used. The identification and quantification of
140 mineral phases was performed using Diffrac Eva software and the ICDD Database (2003).

141

142 **Scanning electron microscope with an energy dispersive spectrometer**

143 The morphology and elemental distribution of the Pb-enriched areas of the three topsoil
144 samples (S1T, S2T and S3T) were investigated with a Hitachi TM-1000 and a Hitachi S3400
145 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS).
146 The bulk soil samples and size fractions with high Pb contents (determined with a field
147 portable X-ray fluorescence instrument, data not shown) were directly mounted on a stub or
148 embedded in GEOFIX epoxy resin and prepared as thin sections for microscopic
149 observations.

150

151 **Raman microspectroscopy**

152 The RMS technique was used to provide molecular characterization of Pb-host phases in the
153 three topsoil samples. RMS measurements were carried out using a LabRAM HR Evolution
154 confocal Raman microspectrometer (Horiba, Jobin Yvon) equipped with a 785 nm
155 wavelength laser beam, with an energy of 8 mW at the sample surface, a back illuminated
156 liquid-nitrogen-cooled charge-coupled device (CCD) detector (1024×512 pixels) and a
157 microscope objective (Olympus BX40; 100×, 0.8 NA) in the backscattering mode. A video
158 camera provided an optical view of the samples. The spot size of the laser focused by the
159 objective at the surface of sample was estimated to be of the order of 1 μm² in the XY plane.
160 Measurements were focused on metal-enriched areas previously observed by SEM-EDS after
161 a careful relocation. For identification of molecular species, the experimental spectra (Raman
162 band positions and relative intensities) were compared with reference spectra of pure
163 (anglesite, cerussite and Pb oxides) and synthetic compounds. Goethite (α-FeOOH) and
164 ferrihydrite were synthesized according to Schwertmann and Cornell (2000) and hydrous
165 manganese oxides (HMO) were synthesized according to Gadde and Laitinen (1974).
166 Adsorption of Pb(II) on synthetic goethite, ferrihydrite and HMO was achieved following the
167 method described by Xu et al. (2006). This procedure yielded HMO and ferrihydrite samples
168 with 5 wt % of Pb and goethite samples with 2 wt % of Pb. The total amount of metal

169 adsorbed was calculated from a mass balance by subtracting the final aqueous concentration
170 from the initial one after filtration at 0.2 μm .

171

172 **Donnan Membrane Technique and dissolved organic carbon fractionation**

173 The total and free concentrations of Pb, as well as the dissolved organic carbon (DOC) in the
174 soil solution, were measured in the six soil samples following a soil-column Donnan
175 membrane technique (SC-DMT; Temminghoff et al., 2000) with $2.10^{-3} \text{ mol.L}^{-1} \text{ Ca(NO}_3)_2$ as
176 background electrolyte at a soil:solution ratio of 80 g.L^{-1} (Schneider et al., 2016b). According
177 to the batch technique of Van Zomeren and Comans (2007), dissolved organic matter (DOM)
178 was fractionated into humic acids (HA), fulvic acids (FA), hydrophilic acids (Hy), and
179 hydrophobic neutral organic matter (HON) (more details are given in Schneider et al., 2016b).
180 In this study, the reactive DOM was assumed to be the measured FA fraction. This fraction
181 represents between 21.1% and 27.3% of the total DOM (Schneider et al., 2016b).

182

183 **Multi-surface complexation modelling**

184 In this study, a multi-surface complexation model was used to describe the metal partitioning
185 in the six soil samples. Different sub-models were used to describe metal adsorption on
186 organic and inorganic surfaces. All the calculations were made with ECOSAT (Keizer and
187 Van Riemsdijk, 1999).

188 An ion exchange model was used to calculate TE adsorption on clays according to the
189 Gaines-Thomas convention (Appelo and Postma, 1996).

190 The binding of metal to amorphous iron oxides (amor-Fe) was estimated with the two-site
191 surface complexation diffuse-double layer (DDL) model using generic parameters from
192 Dzombak and Morel (1990). The amounts of amor-Fe were estimated with the Fe proportions
193 extracted with the 5th fraction of the SE (F5: bound to amorphous iron oxides; Table 1). The
194 amor-Fe was assumed to be ferrihydrite, with a molecular weight of 481 g.mol^{-1} and a
195 specific surface area of $600 \text{ m}^2.\text{g}^{-1}$ (Dzombak and Morel, 1990). The amount of crystalline
196 iron oxides (cry-Fe) was estimated with the 6th fraction of the SE (F6: bound to crystalline
197 iron oxides; Table 1) and was assumed to be goethite, with a molecular weight of 88.9 g.mol^{-1}
198 and a specific surface area of $50 \text{ m}^2.\text{g}^{-1}$ (Weng et al., 2001). The modelled proportions of Pb
199 associated with goethite using the CD-MUSIC model and the generic parameters from the
200 literature (Hiemstra and Van Riemsdijk, 1996; Ponthieu et al. 2006) were negligible as they
201 represented less than 0.1% of the total Pb content of the soil. For this reason, the cry-Fe was
202 not taken into account in the following results and discussion.

203 Metal binding to hydrous manganese oxides (HMO) was described by the 2-pK diffuse layer
204 model with a molecular weight of 119 g.mol^{-1} and a specific area of $746 \text{ m}^2.\text{g}^{-1}$ using generic
205 parameters from Tonkin et al. (2004). The amount of HMO was estimated with the proportion
206 of Mn extracted in the 3rd step of the SE (F3: bound to manganese oxides; Table 1).

207 Finally, metal binding to the dissolved organic matter (DOM) and soil organic matter (SOM)
208 was described with the non-ideal competitive adsorption Donnan model (NICA-Donnan;
209 Kinniburgh et al., 1999). The reactive DOM was assumed to be fulvic acids (Schneider et al.,
210 2016b), and the reactive SOM was assumed to be humic acids (Weng et al., 2001; Ren et al.,
211 2015). The reactive content of DOM, i.e., the fulvic acids fraction, was measured according to
212 the batch technique of Van Zomeren and Comans (2007).

213 The reactive content of SOM was calculated following Weng et al. (2001). SOM and clays
214 are the main constituents that contribute to the soil CEC. The clay content ($< 2 \mu\text{m}$) was used
215 as an estimate of the clay minerals content in the soil. To calculate the contribution of clay
216 minerals to the soil CEC, average CEC values (an average CEC for each clay mineral
217 identified by XRD) were used: 0.25, 0.09, 0.3 and 0.25 mol.kg^{-1} for muscovite, kaolinite,
218 chlorite and illite, respectively (Sparks, 2003). The CEC due to SOM was then obtained by
219 subtracting the clay-related CEC from the measured soil CEC. Finally, the site densities of
220 HA, as defined by Milne et al. (2003), were used to estimate the proportion of reactive SOM
221 as HA.

222 Based on a large collection of data, Milne et al. (2003) derived “generic” parameters for the
223 NICA-Donnan model to describe proton and metal ions binding to FA and HA. These generic
224 parameters have succeeded in producing reasonable predictions over a wide range of
225 environmental conditions for metal ions such as Cd and Cu but are more controversial for Pb
226 (Weng et al., 2001; Cancès et al., 2003; Bonten et al., 2008). Xiong et al. (2013) defined new
227 generic parameters to describe proton and Pb binding to FA and HA. In this study, we
228 compared the Pb distribution modelling using the parameters from Milne et al. (2003) with
229 that obtained using the parameters from Xiong et al. (2013) (Table A1).

230 Model inputs were (i) soil solution pH; measured FA; free Cd, Cu, Pb and Zn activities; and
231 Ca, NO_3 , Na and Cl concentrations in the soil solutions (as measured with SC-DMT; Table
232 A2), and (ii) the concentrations of reactive sorption surfaces in the soil samples.

233 **3 Results**

234 The soil physicochemical properties are presented in Table 2. Their mineral compositions and
235 their reactive sorption surfaces are listed in Table 3. The six soil samples are acidic, with pH
236 values between 4.3 and 4.6. The S1 and S2 soil samples exhibit moderate SOM contents
237 (between 9.4 and 20.6%), while the S3 soil samples show very high SOM contents (49.8% in
238 S3T and 47.9% in S3B). The soil CEC ranges from 14.7 to $61.9 \text{ cmol.kg}^{-1}$ and is significantly
239 correlated with the SOM contents ($R^2 = 0.998$, $p < 0.001$). The six soil samples are heavily
240 contaminated with Pb, with contents ranging from 881 to 9034 mg.kg^{-1} . The Pb content is
241 higher in the S1 and S2 topsoil samples than in the deeper samples, whereas the content
242 increases slightly with depth in S3.

243

244 **Geochemical partitioning of Pb**

245 The exchangeable (F1) and acid-soluble (F2) fractions of Pb represent between 32.5% and
246 49.7% of the total Pb content in the soil samples (Figure 1). The proportion of Pb extracted
247 with the exchangeable fraction (F1) is higher for S1 and S2 (between 1.3% and 2% of the
248 total Pb) than for S3 (0.5% of the total Pb). The acid-soluble fraction is the most important in
249 S1 and S2 (between 37% and 48%), whereas Pb is mainly released in the easily oxidisable
250 fraction (F4) in S3 (48% for S3 and 14-27% for S1 and S2; Table A3). These results suggest
251 that Pb is mainly associated with organic matter in S3 and are consistent with the high SOM
252 values in these two soil samples (Table 2).

253 The fraction of Pb bound to manganese oxides (F3) in S1 and S2 ranges from 14% to 20%,
254 while it only ranges from 2.4% to 3.5% in S3. However, the highest proportions of

255 manganese oxides occur in S2 (S2T: 51% and S2B: 27%) and S3 (S3T: 43%), which have the
256 highest total Mn contents (Table 2 and Table A3).

257 For all soil samples, the proportion of Pb bound to amorphous iron oxides (F5; between 5.7%
258 and 11%) is always higher than that bound to crystalline iron oxides (F6; between 1.3% and
259 3.8%). The total Fe contents are slightly higher for the S3 soil samples (Table 2), but the
260 proportions of iron corresponding to amorphous and crystalline iron oxides are similar in the
261 6 soil samples (Table A3).

262 Finally, the oxidisable fraction (F7) is negligible (< 0.3% of total Pb), and the residual
263 fraction (F8) ranges from 3% to 14% of the total Pb.

264

265 **Chemical associations of Pb at the micrometre scale**

266 In the six soil samples, no Pb-bearing minerals could be identified by XRD. Although PbSO₄,
267 PbCO₃, KPb₂Cl₅ and Na₃Pb₂(SO₄)₃Cl are known to be the major particulate phases directly
268 rejected by a secondary lead smelter (Ettler, 2016), these Pb-rich phases were not observed.

269 The selected soil samples were imaged and analysed by SEM-EDS to better constrain the Pb
270 distribution within the host phases and the chemical associations between Pb and other
271 elements at the microscopic scale. Although soils are very complex and heterogeneous at this
272 scale, the main observed elemental association is Pb-Mn. In all the studied soil samples, Pb-
273 rich areas systematically correspond to Mn-rich areas. Elemental maps of a topsoil thin
274 section indicate that Pb is mainly concentrated in Mn-rich heterogeneous aggregates (Figure
275 2). In this sample, Pb also seems to be partially associated with Fe. However, in the three
276 studied soils, this association was rarely observed, and the main association was Pb-Mn.
277 These Pb-Mn-rich phases are present in soil aggregates (Figure 3b) or at the surface of plant
278 debris (Figures 3a and 3c). Manganese-rich precipitates on needle litter colonized by fungi
279 have already been observed in previous studies (Blanchette, 1984; Keiluweit et al., 2015).

280 To determine the exact nature of these phases identified by SEM-EDS, Pb-rich areas of the
281 three topsoils (0-5 cm) were analysed by RMS and compared with reference samples (Figure
282 3). The Raman spectra of all the observed areas are very similar, which indicates that the rich-
283 Pb phases are the same regardless of the studied soil sample. The Raman spectra are mainly
284 characterized by a large Raman band at 640 cm⁻¹, and they agree well with the typical Raman
285 spectra of synthesized amorphous manganese oxide with adsorbed Pb (Figure 3). Notably, no
286 other Pb compounds, such as PbSO₄, PbCO₃ or PbO, which are typical compounds found in
287 soils in the vicinity of secondary Pb smelters, were identified by RMS.

288 All these observations at the micrometre scale clearly suggest that the Pb association with
289 manganese oxides occurs in the soils of the studied site. However, diffuse forms of Pb in the
290 soil matrix, for instance, in association with organic matter as suggested by the sequential
291 extraction results, are difficult to identify by RMS and SEM-EDS. To overcome this
292 limitation, a modelling approach was undertaken.

293

294 **Modelling of Pb distribution**

295 The free Pb activity in the soil solutions was used as model input data to estimate the content
296 of Pb in the soil solution and in the soil, as well as its partitioning among the different reactive
297 phases in the 6 soil samples. The calculated total Pb concentrations in the soil solution are
298 very close to the total Pb concentrations measured in the soil solution, regardless of the

299 parameters used to describe Pb-FA interactions in the generic NICA-Donnan model (from
300 Milne et al., 2003 or Xiong et al., 2013). The speciation of Pb in the soil solution is not
301 detailed here, as it is fully discussed in Schneider et al. (2016b).

302 For the six soil samples, the calculated proportions of reactive SOM as HA (between 18.5 and
303 22.1% of the total SOM content) are consistent with previous results obtained by Weng et al.
304 (2001; 16-46%) and Ren et al. (2015; 7-55%).

305 The modelling results obtained with the generic NICA-Donnan parameters from Milne et al.
306 (2003) and from Xiong et al. (2013) were compared (Table A1, Table 4). The model
307 calculations indicated that soil organic matter is the main sorbent of Pb in soils. The Pb
308 associated with SOM represents between 72% and 97% and between 87% and 99% of the
309 total Pb, according to the parameters of Milne et al. (2003) and Xiong et al. (2013),
310 respectively (Table 4). The only difference when using the two set of parameters for the
311 NICA-Donnan model concerns the Pb content associated with SOM (HA) and therefore the
312 total Pb content in the soil. Indeed, the amount of Pb associated with clays, HFO and HMO
313 did not change (Table 4). Using the parameters of Xiong et al. (2013), the quantity of Pb
314 associated with HA is more important than when the parameters of Milne et al. (2003) are
315 used, with a consequential increase in the total Pb content associated with the soil solid phases
316 (between 2.1 and 2.7 times more). Consequently, the proportion of Pb-HMO interactions is
317 larger using the parameters of Milne et al. (2003) than the parameters of Xiong et al. (2013)
318 and represents up to 25% and 12% of total Pb, respectively. The proportion of the nonspecific
319 adsorption on clay surfaces is small and represents between 1.1% and 5.3% with the
320 parameters of Milne et al. (2003) and between 0.5% and 2.2% with the parameters of Xiong
321 et al. (2013). Finally, less than 1% of adsorbed Pb is attributed to HFO.

322 **4 Discussion**

323 **Influence of model parameters on total Pb content prediction**

324 The total Pb contents modelled with the free Pb activities as input data were lower than the
325 measured total Pb contents in the soil. It is well known that the total metal content is not
326 active in adsorption processes (Weng et al. 2001; Ren et al. 2015), yet the multi-surface
327 complexation models are only able to describe the geochemically reactive metal contents. In
328 most modelling studies, 0.43 M HNO₃ is used to estimate the TE contents that the model
329 calculation is able to distribute between the different solid phases in the soil (Weng et al.,
330 2001; Dijkstra et al., 2004; Ren et al., 2015). Other extractants, such as EDTA buffered at a
331 pH of 4.65, have also been used (Bonten et al., 2008; Pourret et al., 2015). In this study, the
332 geochemically reactive Pb content is assumed to be the sum of the Pb extracted in the first six
333 SE fractions (F1 to F6). The multi-surface complexation model should be able to describe the
334 processes involved in the retention of Pb extract with these six fractions.

335 Because soil organic matter is the major sorbent of Pb in the studied soils, the choice of the
336 NICA-Donnan generic parameters has an important impact on the total modelled Pb content.
337 When the NICA-Donnan parameters are taken from Milne et al. (2003), the total modelled Pb
338 contents are substantially lower than those modelled with the parameters from Xiong et al.
339 (2013) (Table 4). Xiong et al. (2013) defined higher affinity constants for Pb in the two
340 reactive sites of HA than Milne et al. (2003), which explains the discrepancy (Table A1).

341 Regardless of the modelled lead distribution, the Xiong et al. (2013) parameters seem more
342 appropriate than the Milne et al. (2003) parameters for estimating the total Pb content
343 distributed amongst the different solid phases of the soil measured with the first six SE
344 fractions. The use of the Xiong et al. (2013) parameters allows a satisfactory description of
345 the geochemically reactive Pb content (between 55% and 122% of the measured Pb in the F1
346 to F6 fractions), considering that the modelling input data are the free Pb activities measured
347 in the soil solution.

348 The model predicted a major association between Pb and organic matter, while the SE and the
349 spectroscopic data indicated the importance of HMO and, to a lesser extent, HFO in the Pb
350 partitioning in the soils. A possible explanation of this difference could be that the reactivities
351 of HMO and/or HFO were underestimated by the modelling.

352

353 **Role of clays**

354 The interactions of Pb with clay minerals have been evidenced by the modelling, even if they
355 represent less than 6% of the geochemically reactive Pb. The adsorption of Pb on the clay
356 minerals is described with an ion exchange model, which only considers weak associations.
357 This Pb fraction should therefore be comprised in the exchangeable fraction (F1) of the SE.
358 To compare the predicted weakly bound Pb with the F1 results, several modelled fractions of
359 Pb have to be considered: total Pb in the soil solution, Pb adsorbed on clays, and Pb
360 electrostatically bound to HA and oxides. The sum of all these modelled fractions is higher
361 than the measured Pb exchangeable fraction. However, when only the sum of the modelled
362 total soil solution Pb and Pb adsorbed on clays is considered, a good agreement is observed
363 with the measured Pb exchangeable fraction (with a slope of 0.90 and a R^2 of 0.91), although
364 Pb electrostatically bound to HA and to oxides was not considered. An explanation could be
365 (i) an overestimation of the Pb-clay fraction estimated with the ion exchange model or (ii) an
366 extraction of Pb electrostatically bound to HA and oxides during the acid-soluble step of the
367 SE (F2; Gleyzes et al., 2002).

368

369 **Role of soil organic matter and manganese oxides**

370 The major particulate phases emitted by secondary lead smelters are known to be caracolite
371 ($\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$), lead chloride (PbCl_2) and potassium lead chloride (KPb_2Cl_5) (Ettler, 2016).
372 Several studies have shown that most of these phases are highly soluble, especially in acidic
373 conditions, and anglesite (PbSO_4) and lead sulfite (PbSO_3) are formed as their main final and
374 stable alteration products (Ettler et al., 2005; Ettler et al., 2008; Vitkova et al., 2009).
375 However, few studies have dealt with the identification and transformation of these phases in
376 soils and little is known about the fate of Pb that is not trapped by the precipitation of
377 secondary phases. In this work, Pb-bearing crystalline phases were not observed. Although
378 this result does not rule out the possible occurrence of small amounts of crystalline Pb phases
379 (e.g., anglesite), it suggests that Pb is mainly present as non-crystalline Pb-bearing species
380 and/or that the proportion of crystalline phases is below the detection limit of XRD.

381 In all the studied soils, despite different soil types and levels of contamination, Pb is mainly
382 associated with organic matter and manganese oxides. The very large proportion of Pb
383 associated with SOM is consistent with previous studies in which SOM was the most
384 important sorption surface for Pb in soils (Lofts and Tipping, 1998; Morin et al., 1999; Weng

385 et al., 2001; Bataillard et al., 2003). The large modelled proportions of Pb bound to SOM are
386 not coherent with the SE results in which Pb is more distributed between several fractions and
387 a large part is extracted during the acid-soluble step. This discrepancy could be explained by a
388 lack of selectivity during the acid-soluble step with a non-negligible portion of the Pb
389 specifically bound to the surface of clays, Fe/Mn oxides and organic matter likely extracted
390 during this second step of the SE (Gleyzes et al., 2002; Young et al., 2006).

391 The modelling and the SE results indicated a non-negligible fraction of Pb associated with
392 manganese oxides. These results are consistent with SEM-EDS and RMS observations, which
393 highlighted the presence of Pb-manganese oxides associations. The modelled and measured
394 proportions of Pb associated with manganese oxides are similar in the S2 soil samples, which
395 present the highest proportions of manganese oxides (Table 3). Significant proportions of
396 manganese oxides are also observed in the S3 soil samples, and the lower (measured and
397 modelled) fraction of Pb bound to manganese oxides is explained by the very high organic
398 matter content. The manganese oxide contents in the S1 soil samples are lower than those in
399 S2 and S3, explaining the lower proportions calculated by the model. However, the measured
400 proportions of Pb bound to HMO (F3 of SE, Table A3) in S1 are similar to that measured in
401 S2. This result could be explained by a lack of selectivity of the SE or, more hypothetically,
402 by a different reactivity of the manganese oxides of the S1 soil samples (Nelson et al., 1999).
403 Nonetheless, our results suggest that manganese oxides contribute significantly to Pb
404 distribution in acidic impacted soils. The importance of manganese oxides in Pb distribution
405 in soils has already been studied (e.g., Fan et al., 2005; Xu et al., 2006) and directly evidenced
406 by X-ray absorption spectroscopy in the surface horizons of wooded soils (Morin et al.,
407 1999). Some studies also reported the role of iron oxides in Pb retention in soil (Ettler et al.,
408 2005). In this study, these mineral phases are not significantly involved in Pb distribution
409 (i.e., less than 1%). Even if manganese oxides are present at much lower concentrations than
410 amorphous iron oxides in the studied soil samples (Table 3), their reactivity is higher (Table
411 4). The adsorption of Pb on manganese oxide minerals starts at very low pH values (pH < 3;
412 Gadde and Laitinen, 1974; Smith, 1999; Fan et al., 2005). At pH values similar to those in the
413 studied soil (pH values of 4 to 5), the adsorption of Pb on other oxides (Fe and Al) is always
414 lower because of their higher pH_{zpc} . Michalkova et al. (2014) and Ettler et al. (2015) recently
415 demonstrated that amorphous manganese oxides (AMO) can be used as an amendment in Pb
416 smelter-polluted agricultural soils to decrease the labile fraction of Pb. They showed that
417 these mineral phases were very efficient at acidic pH values of 4-5. Moreover, several studies
418 have also found that biotic manganese oxides are more reactive than abiotic manganese
419 oxides (Nelson et al., 1999; Saratovsky et al., 2006; Miyata et al., 2007). Nelson et al. (1999)
420 noted that Pb adsorption on biogenic manganese oxide was two to five times greater than the
421 Pb adsorption on a chemically precipitated abiotic manganese oxide. The characterization of
422 biotic manganese oxides is however difficult without additional techniques, such as
423 transmission electron microscopy (TEM) and extended X-ray absorption fine structure (Kim
424 et al., 2003).

425 **5 Conclusion**

426 By combining experimental and modelling approaches, this study emphasizes the role of
427 SOM, and, to a lesser degree, of manganese oxides in the scavenging of Pb in heavily
428 impacted soils. Although crystalline Pb phases are frequently cited as important Pb-bearing
429 phases emitted by lead smelters, none were observed in the acidic soils of this study. The
430 association of Pb with organic matter and manganese oxides can be interpreted as evidence of
431 Pb redistribution in the studied soils after smelter particles deposition. The affinity of Pb with
432 these phases is already known, but direct evidence of the Pb association with manganese
433 oxides in soils has rarely been highlighted. Further studies are needed to clarify the exact
434 nature (abiotic or biotic) of the manganese oxides in order to better model their reactivities
435 and interactions with Pb in the soil.

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438
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612 isotopic dilution. *Soil Use and Management* 21: 450-458.

613

614 **Figure captions**

615 Figure 1: Pb distribution between the eight fractions defined by the sequential extraction
616 scheme.

617

618 Figure 2: Backscattered electron image of a thin section of the S2T soil sample and
619 corresponding elemental maps obtained by EDS. The EDS concentration unit is arbitrary.

620

621 Figure 3: SEM images (backscattered electrons; left), EDS (top) and Raman (bottom) spectra
622 recorded on a fir needle (a) and a soil aggregate (b) from S2T and on a leaf fragment from
623 S1T (c). The Raman spectra of the synthetic manganese oxide with and without 5% adsorbed
624 Pb are also displayed. The white squares correspond to the areas where the EDS and RMS
625 spectra were acquired.

626

627 **Tables**

628

629 Table 1: Sequential extraction procedure adapted from Laveuf et al. (2009).

Soil fraction	Extractant	Volume (mL)	Conditions
F1: Exchangeable	0.1M NaNO ₃	10	20°C, 2 hours, end-over-end shaking
F2: Acid-soluble	1M CH ₃ COONa, pH 5.5 (CH ₃ COOH 99-100%)	20	20°C, 6 hours, end-over-end shaking
F3: Bound to Mn oxides	0.1M NH ₂ OH.HCl/ 0.1M HCl, pH 2	20	2 times: 20°C, 30 minutes, end-over-end shaking
F4: Easily oxidisable fraction	0.1M Na ₄ P ₂ O ₇ , pH 10	10	3 times: 20°C, 90 minutes, end-over-end shaking
F5: Bound to amorphous Fe oxides	0.25M NH ₂ OH.HCl/ 0.25M HCl, pH 1.5.	20	2 times: 60°C, 2 hours, end-over-end shaking
F6: Bound to crystalline Fe oxides	1M NH ₂ OH.HCl/ CH ₃ COOH 25%, pH 1.	30	2 times: 90°C, 3 hours and 1 hour and half, end-over-end shaking
F7: Oxidisable fraction (sulphurs)	750mg KClO ₃ in 5 mL 12M HCl and 10 mL 12M HCl 4M HNO ₃	15 10	20°C, 30 minutes, end-over-end shaking 90°C, 20 minutes, end-over-end shaking
F8: Residual	HF-HClO ₄ -HNO ₃ .	-	-

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Table 2: Soil samples characteristics. The SOM is assumed to be 2 times the TOC.

	<u>pH</u>	<u>Pb</u>	<u>Mn</u>	<u>Fe</u>	<u>Clay</u>	<u>Silt</u>	<u>Sand</u>	<u>SOM</u>	<u>CEC</u>
	water	mg.kg ⁻¹			%			%	cmol.kg ⁻¹
S1T	4.3	3555	267	18333	21.9	63.3	14.8	17.8	22.5
S1B	4.6	1034	260	19800	20.6	65.5	13.9	10.4	14.7
S2T	4.4	9034	1163	19725	26.1	57.6	16.3	20.6	26.6
S2B	4.5	881	647	19000	22.1	62.3	15.6	9.4	15.4
S3T	4.4	6167	678	26033	49.9	42.0	8.1	49.8	61.9
S3B	4.6	7495	267	27733	45.1	43.8	11.1	47.9	60.4

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Table 3: Concentrations of reactive sorption surfaces in the soil samples.

Sample	Mineral phases XRD	Clay charge mol.kg ⁻¹	Calculated HA g.kg ⁻¹	Clay g.kg ⁻¹	Amor-Fe g.kg ⁻¹	Cry-Fe g.kg ⁻¹	Mn oxides g.kg ⁻¹
S1T	Quartz 29%; Muscovite 28%; Kaolinite 18%;	0.15	33.6	219	1.81	5.32	0.02
S1B	Chlorite 8%; Illite 17%.	0.15	20.3	206	2.25	5.22	0.04
S2T	Quartz 24%; Muscovite 32%; Kaolinite 20%;	0.16	39.3	261	2.56	5.84	1.29
S2B	Chlorite 5%; Illite 18%.	0.16	20.8	221	2.43	4.93	0.38
S3T	Quartz 14%; Muscovite 34%; Kaolinite 18%;	0.19	92.2	499	2.42	5.86	0.63
S3B	Chlorite 3%; Illite 30%.	0.19	91.2	451	3.38	5.80	0.11

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Table 4: Modelling of Pb partitioning between the reactive soil solid phases for the 6 soil samples using the generic parameters of Milne et al. (2003) and Xiong et al. (2013). The results are expressed in mg.kg⁻¹ and % of total modelled Pb.

	Milne et al. (2003)				
	Pb-Tot	Pb-HA	Pb-HMO	Pb-HFO	Pb-Clay
	mg.kg ⁻¹				
S1T	682	638 (93.5%)	5.9 (0.9%)	2.3 (0.3%)	35.9 (5.3%)
S1B	331	299 (90.3%)	12.5 (3.8%)	2.1 (0.6%)	17.5 (5.3%)
S2T	1982	1488 (75.1%)	427 (21.5%)	8.8 (0.4%)	57.7 (2.9%)
S2B	442	316 (71.6%)	110 (24.8%)	2.5 (0.6%)	13.2 (3.0%)
S3T	1488	1287 (86.5%)	183 (12.3%)	2.5 (0.2%)	16.3 (1.1%)
S3B	2035	1968 (96.7%)	32.9 (1.6%)	6.8 (0.3%)	27.2 (1.3%)
	Xiong et al. (2013)				
	Pb-Tot	Pb-HA	Pb-HMO	Pb-HFO	Pb-Clay
	mg.kg ⁻¹				
S1T	1790	1746 (97.5%)	5.9 (0.3%)	2.3 (0.1%)	35.9 (2.0%)
S1B	808	776 (96.0%)	12.5 (1.5%)	2.1 (0.3%)	17.5 (2.2%)
S2T	4767	4274 (89.7%)	427 (8.9%)	8.8 (0.2%)	57.7 (1.2%)
S2B	936	810 (86.6%)	110 (11.7%)	2.5 (0.3%)	13.2 (1.4%)
S3T	3379	3178 (94.0%)	183 (5.4%)	2.5 (0.1%)	16.3 (0.5%)
S3B	5468	5401 (98.8%)	32.9 (0.6%)	6.8 (0.1%)	27.2 (0.5%)

643

Figure 1
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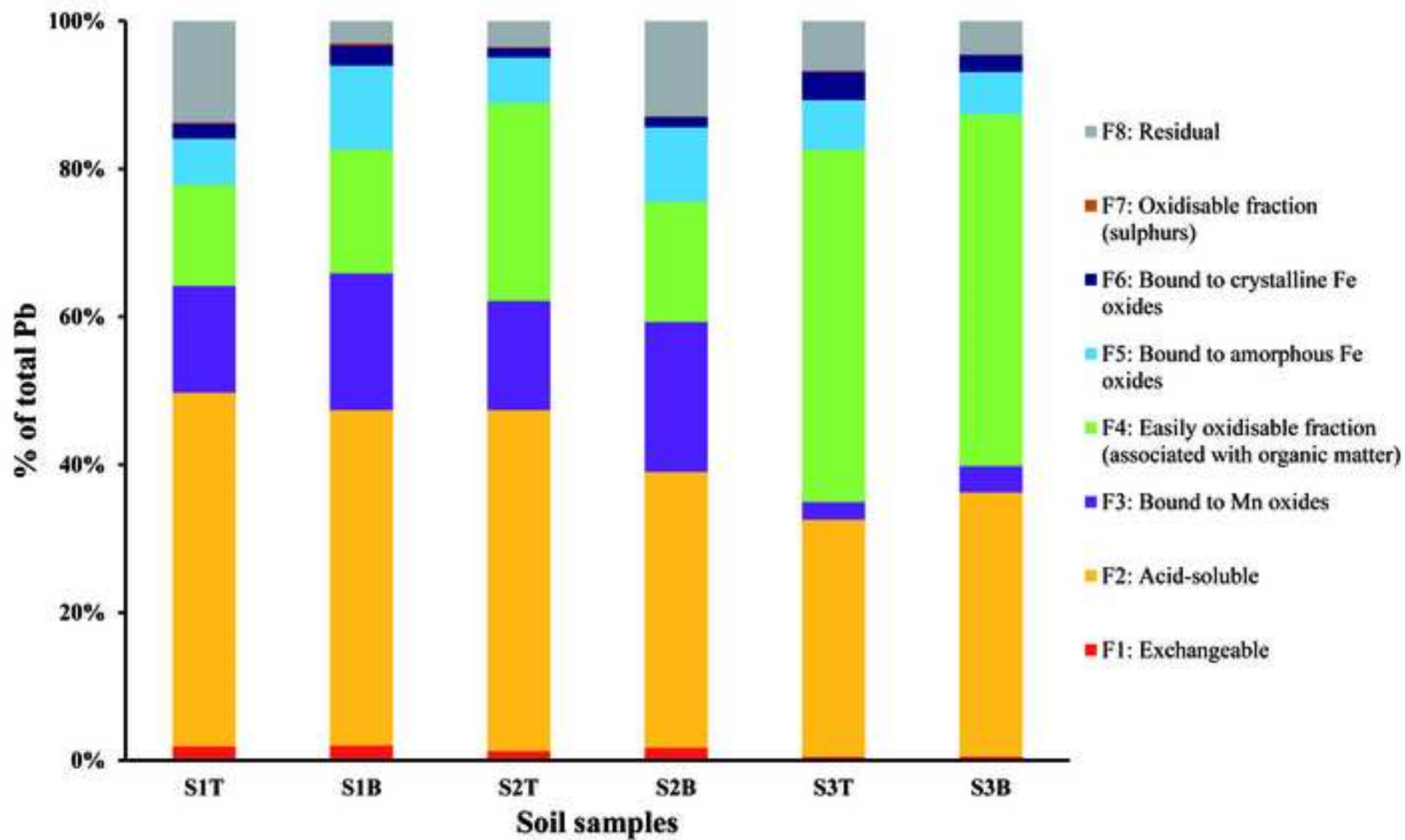


Figure 2
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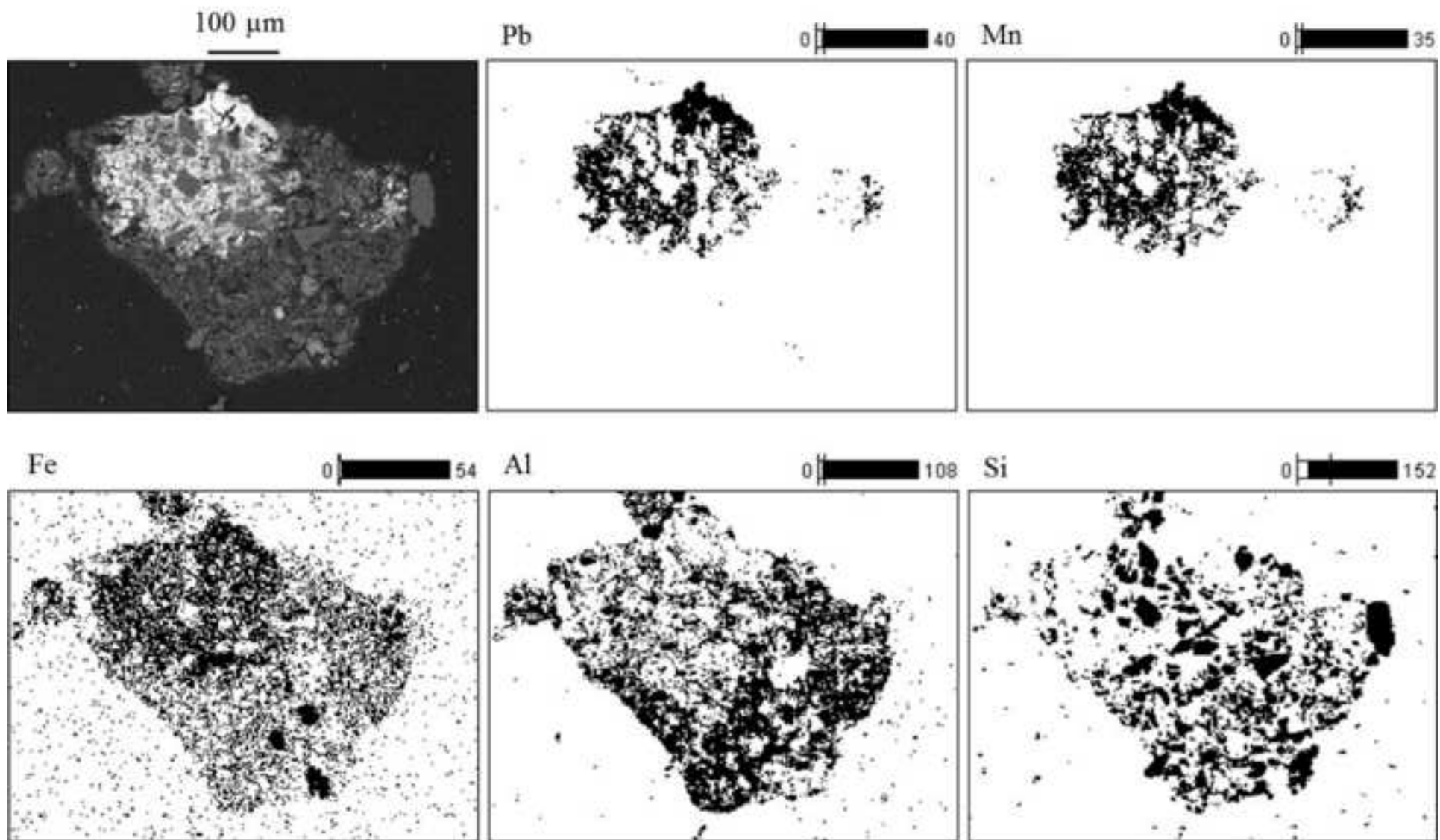
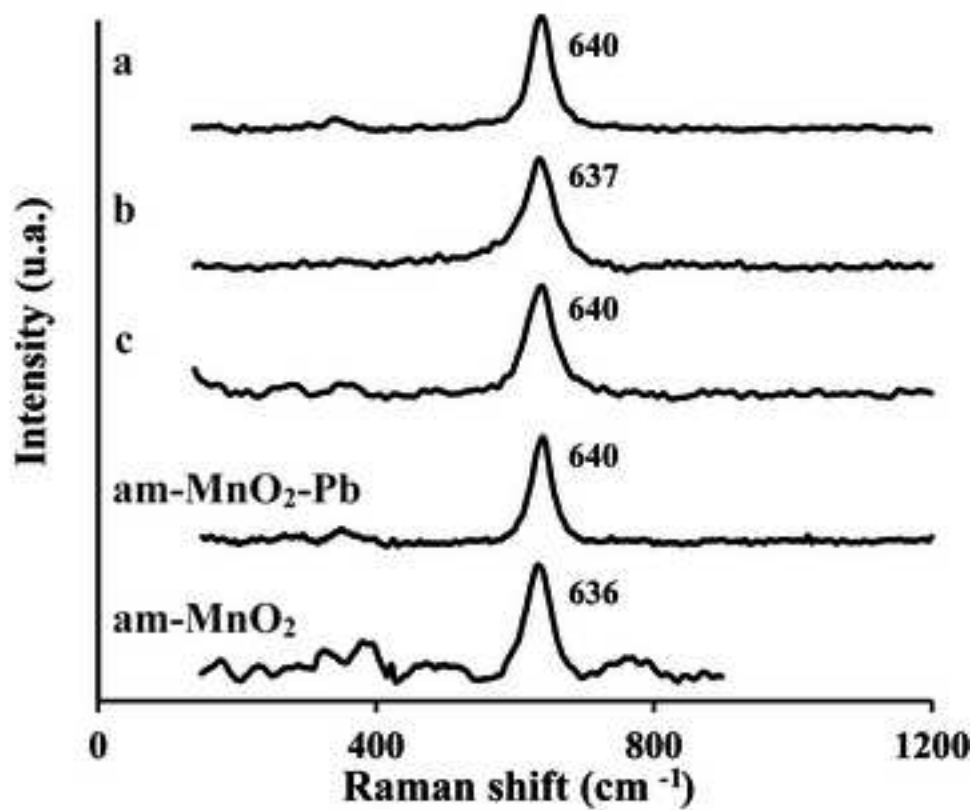
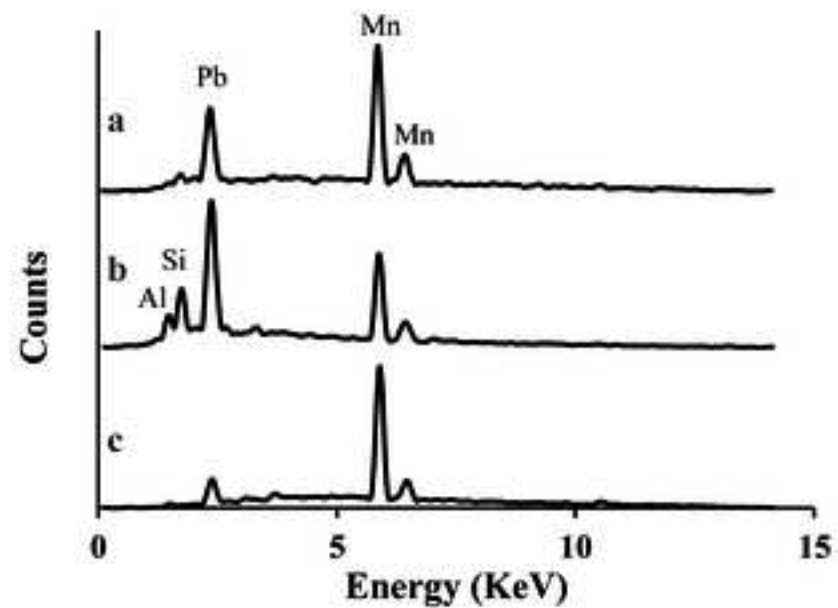
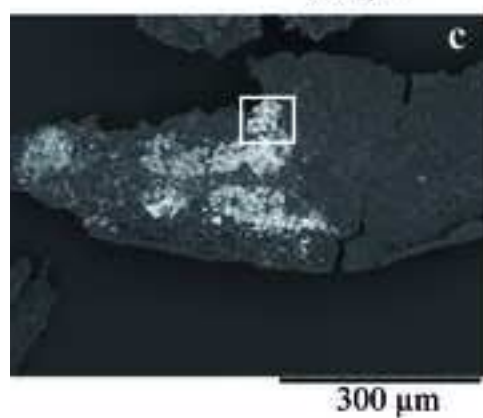
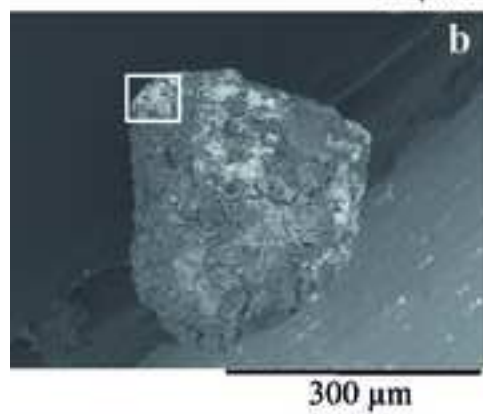
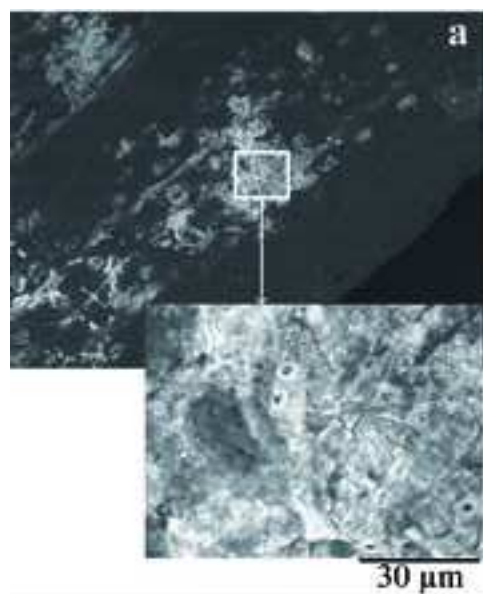


Figure 3
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