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### ► To cite this version:

Gaëlle Uzu, Sophie Sobanska, Yassine Aliouane, Philippe Pradere, Camille Dumat. Study of lead phytoavailability for atmospheric industrial micronic and sub-micronic particles in relation with lead speciation. *Environmental Pollution*, 2009, 157 (4), pp.1178-1185. 10.1016/j.envpol.2008.09.053 . hal-00559688

**HAL Id: hal-00559688**

**<https://hal.science/hal-00559688>**

Submitted on 26 Jan 2011

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1 **Study of lead phytoavailability for atmospheric industrial micronic and**  
2 **submicronic particles in relation with lead speciation.**

3

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11

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15

16 **Capsule**

17 The soil-lettuce lead transfer from atmospheric industrial sub-micronic and micronic  
18 particles depends on particle size.

19

20 **Abstract**

21 Particles from channelled emissions of a battery recycling facility were size-segregated  
22 and investigated to correlate their speciation and morphology with their transfer towards  
23 lettuce. Microculture experiments carried out with various calcareous soils spiked with  
24 micronic and submicronic particles ( $1650 \pm 20 \text{ mgPb.kg}^{-1}$ ) highlighted a greater transfer  
25 in soils mixed with the finest particles. According to XRD and Raman spectroscopy  
26 results, the two fractions presented differences in the amount of minor lead compounds

27 like carbonates, but their speciation was quite similar, in decreasing order of abundance:  
28 PbS, PbSO<sub>4</sub>, PbSO<sub>4</sub>.PbO, α-PbO and Pb<sup>0</sup>. Morphology investigations revealed that  
29 PM<sub>2.5</sub> (i.e. Particulate Matter 2.5 composed of particles suspended in air with  
30 aerodynamic diameters of 2.5 micrometers or less) contained many Pb nano balls and  
31 nano crystals which could influence lead availability. The soil-plant transfer of lead was  
32 mainly influenced by size and was very well estimated by 0.01M CaCl<sub>2</sub> extraction.

33

34 **Keywords:** lead, PM<sub>2.5</sub> and PM<sub>10</sub>, soil-lettuce transfer, phytoavailability.

35

## 36 **1. Introduction**

37 Due to its numerous past and present uses and high persistence, lead is a major  
38 environmental contaminant (Chen et al., 2006). Potentially toxic for living organisms  
39 even at low concentrations, lead constitutes a risk for humans who can absorb it in  
40 various ways (Canfield et al., 2003). In the context of contaminated gardens, elevated  
41 lead intake by humans can be due to the consumption of crop plants grown on soils with  
42 relatively high plant-available metal concentrations, ingestion of contaminated soil,  
43 either accidentally or intentionally (pica), inhalation of soil particles and drinking water  
44 with high soluble concentrations of metals (Alexander et al., 2006). The total quantities  
45 of lead emitted in the environment by industries have decreased sharply in recent  
46 decades (Glorennec et al., 2007) and are strictly controlled in Europe nowadays. Lead  
47 was recently classified as a substance of very high concern in the European REACH law  
48 (Regulation EC 1907/2006 of the European Parliament and of the Council of 18  
49 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction  
50 of Chemicals). However, particles enriched with lead are still generated especially by

51 lead-recycling plants (Batonneau et al., 2004; Ohmsen, 2001) and constitute the main  
52 source of lead pollution for soils (Miquel, 2001; Donisa et al., 2000).

53 According to Zhang et al. (2005), emitted particles present a large granulometric  
54 spectrum in the atmosphere, but during the last decade the proportion of fine particle  
55 matter (PM) increased with the use of more effective filters in industry. Indeed PM<sub>10</sub> are  
56 target species of the World Health Organization (WHO, 2001) and the European Union  
57 Framework Directive on ambient air quality assessment (EU, 1999), due to their  
58 adverse effects on the environment and human health. While micrometric and sub-  
59 micrometric fractions contribute very little to ambient particle mass, they may occur in  
60 substantial number concentrations. Most of the studies dealing with the characterization  
61 of metal-enriched particles in the ambient air provide information on quantitative  
62 measurements for PM<sub>10</sub> fractions (EU directives 96/62 and 99/30) and very few on the  
63 sub-micronic fraction (Lazaridis et al., 2002). The lack of knowledge regarding metal  
64 speciation in the industrial particles results mainly from a lack of analytical tools, both  
65 sensitive and specific to the size of the particles.

66 These fine particles are highly reactive due to their high specific area and can be  
67 transported over long distances in the troposphere (Barrie, 1992). They could therefore  
68 present a greater impact on the biosphere than coarse particles (Fernandez Espinosa,  
69 2005). Ruby et al. (1992) concluded that the bioaccessibility of lead rises strongly in  
70 particles under 2.4 µm size. But, the phytoavailability of lead in industrial particles as a  
71 function of their size and speciation have not been studied yet. In comparison with zinc,  
72 lead generally shows a relatively low mobility in soils (Dumat et al., 2006). It can  
73 however migrate through the soil with dissolved organic matter (Cecchi et al., 2008) or  
74 be mobilized by certain plants (Arshad et al., 2008). Moreover, carried from the air to

75 the soils as fine particles, lead could be released more easily in soil solution  
76 (Komarnicki, 2005).

77 We therefore focused our study on the links between soil-plant transfer of lead,  
78 size and speciation of particles emitted by a lead recycling plant, currently the main  
79 source of atmospheric emissions (Cecchi et al., 2008). The objectives were the  
80 following: (i) the elemental and molecular characterisation of micrometer and  
81 nanometer sized lead-rich particles and (ii) to study the influence of particle  
82 characteristics on lead soil-plant transfer.

83 The physico-chemical characterization of industrial PM<sub>10</sub> and PM<sub>2.5</sub> particles  
84 collected in the plant was investigated using both bulk and micro analysis techniques:  
85 (i) MEB-EDS to determine the morphology and chemistry on the scale of a particle  
86 (Laskin et al., 2006; Choel et al., 2005); (ii) Raman microspectrometry to study particle  
87 speciation (Batonneau et al., 2004; 2006; Falgayrac et al., 2006; Sobanska et al., 2006).  
88 The transfer of lead from particles to the lettuce *Lactuca sativa* a widely grown garden  
89 vegetable was investigated in the laboratory: two different uncontaminated calcareous  
90 soils were spiked with PM<sub>10</sub> and PM<sub>2.5</sub> for soil-plant experiments with a biotest device  
91 that enabled careful study of rhizosphere and roots in addition to the transfer to the  
92 shoots (Chaignon and Hinsinger, 2003). The study was finally completed by CaCl<sub>2</sub>  
93 extraction experiments carried out according to Houba et al. (1996) to estimate lead  
94 phyto-availability.

95 The hypothesis tested throughout all these experiments was that particle  
96 characteristics have a significant influence on lead soil-plant transfer and translocation.

97

## 98 **2. Materials and methods**

99 2.1. Particle sampling and size separation.

100 A secondary lead smelter which currently recycles batteries was chosen as a  
101 representative example of the smelter metal industry to develop a methodology aimed at  
102 the risk assessment of industrial lead particles. The plant of the Chemical Metal  
103 Treatment Company (STCM) is located in the urban area of Toulouse (43°38'12" N,  
104 01°25'34" E). According to the French authorities (DRIRE, 2007), 328 kg of Total  
105 Suspended Particles (TSP) including 31 kg of lead were emitted by this factory in 2007.

106 Three sources of particles corresponding to the three work units involving  
107 different steps in the process are identified in the plant: (i) the battery grinding unit  
108 where battery components are separated under wet conditions (ii) the smelter where lead  
109 pastes are processed in rotary furnaces at 1200°C and finally (iii) the refinery where  
110 lead is purified from unwanted metals or enriched. The same process has been used for  
111 thirty years in the plant. This study focuses on channeled emissions only generated by  
112 the furnace unit, considering the transfer towards the biosphere. The particle collection,  
113 performed three months after complete cleaning of the three work units (March, 12,  
114 2007), is therefore representative of that emission period. Our aim was to characterize  
115 the reactivity of the particles in relation with their previously determined speciation and  
116 size, not to follow one specific parameter over time.

117 1kg of particles was collected in polyethylene bags from the air-sleeve filters of  
118 the furnace, then sealed and transferred in sealed opaque containers for transport to the  
119 laboratory. Samples were passed through a 2-mm stainless steel AFNOR sieve. Process  
120 dust was stored in a cool (4°C) dark place with Merck desiccant.

121 Because 80 % of emitted particles were smaller than 10 µm, PM<sub>2.5</sub> and PM<sub>10</sub> were  
122 size-segregated by artificial resuspension in a Teflon bag (Batonneau et al., 2004;  
123 Young et al. 2002) and collected by impaction onto a PM<sub>10/2.5</sub> Dekati inertial impactor.  
124 The cascade impactor consists of two successive stages with aerodynamic cut-off

125 diameters of 10 and 2.5  $\mu\text{m}$  when it operates at 10 L/min airflow.  $\text{PM}_{10}$  present an  
126 aerodynamic diameter between 2.5 and 10  $\mu\text{m}$ , whereas the  $\text{PM}_{2.5}$  stage collects  
127 particles  $< 2.5\mu\text{m}$ .

128

## 129 2.2. Characterization of particles

130 Elemental total contents of the two size fractions were determined by ICP-OES (IRIS  
131 Intrepid II XDL) after heated digestion with standard acid ( $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HF}$ ,  
132 Suprapur, Merk) in a PTFE vessel. Levels of C, H, S and O were determined after  
133 burning in an elemental analyser with coulometric-catharometric detection and IR.

134 X-ray diffraction patterns of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  were recorded on an INEL  
135 diffractometer equipped with a curved detector CPS 120 and  $\text{Co}(\text{K}\alpha)$  radiation allowing  
136 a  $120^\circ/2\theta$  detection. Crystallized compounds were identified by comparison with the  
137 diffraction patterns of the JCPDS database. The relative abundance of each crystallized  
138 phase detected in samples was qualitatively estimated by using the relative intensity of  
139 the strongest X-ray pattern peaks of each considered phase. It should be noticed that  
140 only crystallized phases with an abundance superior to 5 % in weight can be detected by  
141 XRD.

142 Particles were characterized using complementary microscopy and imaging  
143 techniques to determine elementary and molecular composition, size, morphology and  
144 heterogeneity of the individual lead-rich particles.

145 X-ray elemental mapping and secondary images were obtained using an  
146 Environmental Scanning Electron Microscope (ESEM) working in high-vacuum mode.  
147 The Quanta 200 FEI instrument was equipped with an energy-dispersive X-ray (EDX)  
148 detector. ESEM was operated at 10-25 kV. Particles were dispersed on carbon

149 substrates and analysed without further preparation. Because of the ESEM  
150 configuration, light element detection (C, N, and O) was ambiguous.

151 Raman microspectrometric measurements were carried out with a LabRAM  
152 confocal spectrometer (Jobin Yvon, Horiba Gr, France). The spot size of the laser  
153 focused by a 100×objective (numerical aperture (NA) = 0.90) was estimated to be  $1 \mu\text{m}^2$   
154 in size. A liquid nitrogen-cooled CCD (Jobin-Yvon, 2048 pixels  $\times$  512 pixels) was used  
155 for detection. The Raman backscattering was excited at 632.8 nm provided by an  
156 internal, air-cooled, linearly polarized helium-neon laser. The laser power delivered to  
157 the sample was 8 mW. The microscope stage was XY-motorized and computer-  
158 controlled for point by point scanning with 0.1  $\mu\text{m}$  resolution, 1  $\mu\text{m}$  reproducibility and  
159 90 mm  $\times$  60 mm spatial range. The glass plate with the impacted particles was mounted  
160 on the microscope stage without any further preparation. Data acquisition consisted in  
161 recording many spectra in point-by-point scanning mode with 1  $\mu\text{m}$  as a minimum step,  
162 one accumulation and 30 s spectrum acquisition time. For identification of Raman  
163 spectra the experimental spectra were compared to reference spectra using Spectral  
164 Library Search ID 301 software (Thermo Galactic).

165

### 166 2.3. Measure of soil-plant lead transfer performing microculture experiments

167 Lettuce was chosen because it is a common vegetable widely grown for human  
168 consumption and has recently been used by several authors for metal transfer studies  
169 (Khan et al., 2007; Waisberg et al., 2004; Alexander et al., 2006). Moreover, lettuce is  
170 often used around plants to estimate atmospheric pollution.

171 The biotest presented on figure 1 was first described by Niebes et al. (1993) and  
172 then adapted by Chaignon and Hinsinger (2003). A small PVC cylinder (25 mm inner  
173 diameter) was closed by a polyamide net (900  $\mu\text{m}$  mesh) inserted into a larger cylinder,



174 itself closed by a finer polyamide mesh (30  $\mu\text{m}$ , Fyltis/Nytel, Sefar filtration). A space  
175 of 3 mm was left between the net and the finer mesh, where the roots could develop as a  
176 mat.

177 Commercial lettuce seeds, “Batavia blonde dorée” cultivar, were surface sterilized with  
178 0.9% CaClO for 15 min and rinsed with deionised water. Three seeds were sown in the  
179 container on the surface of the coarser mesh.

180 Lettuces were first grown hydroponically for 21 days to obtain a large flat mass of roots  
181 that fully covered the fine mesh.

182 The devices were placed on top of troughs containing an aerated complete nutrient  
183 solution with the macroelements: 5 mM  $\text{KNO}_3$ , 5 mM  $\text{Ca}(\text{NO}_3)_2$ , 2 mM  $\text{KH}_2\text{PO}_4$  and  
184 1.5 mM  $\text{MgSO}_4$  and oligoelements: 9.11  $\mu\text{M}$   $\text{MnSO}_4$ , 1.53  $\mu\text{M}$   $\text{ZnSO}_4$ , 0.235  $\mu\text{M}$   
185  $\text{CuSO}_4$ , 24.05  $\mu\text{M}$   $\text{H}_3\text{BO}_3$ , 0.1  $\mu\text{M}$   $\text{Na}_2\text{MoO}_4$  and 268.6  $\mu\text{M}$  Fe/EDTA. The height of the  
186 nutrient solution was adjusted daily to keep the fine mesh wet during the whole pre-  
187 culture period. The experiment was conducted in a growth chamber (temperature  $24 \pm$   
188  $0.5$  °C/ $18 \pm 0.5$  °C day/night cycles; photoperiod 16 h under daylight fluorescent lamps  
189 providing  $400 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  [Philips 600W, Eindhoven, Netherlands] and 8 h darkness;  
190 relative humidity 70%).

191 Then, the second step involved an eight-day soil-plant contact period: five replicate  
192 plants for each treatment were transferred onto the various soil samples.

193 Top soils of two calcic cambisol profiles (FAO, 1998) produced by quaternary  
194 alluvial deposits, were sampled. These two calcareous soils (noted soil-1 and soil-2)  
195 with various physicochemical properties (table 1) were chosen because that kind of soil  
196 happens to be observed around several battery recycling plants. Moreover, if the lettuce  
197 species could favor lead transfer, the choice of calcareous soils could reduce it. The  
198 soils differ by texture, soil cultivation, organic matter (OM) and CEC: soil-1 was

199 uncultivated loamy-sandy clay with 2% of OM and soil-2 was sandy-clayey loam under  
200 sunflowers with 1% of OM and a higher CEC.

201 These two soils were spiked with  $PM_{2.5}$  and  $PM_{10}$  up to  $[Pb] = 1650 \pm 20 \text{ mg.kg}^{-1}$ .  
202 60 mg of particles were added per box containing 10 g of soil and were agitated for a  
203 day. Soils were turned over every fifteen days for four months. This long period was  
204 chosen to allow time for natural equilibration of the various sorption mechanisms in the  
205 soil (Alexander et al., 2006). The relatively high total lead soil concentration was  
206 chosen to be representative of a real soil pollution situation observed for atmospheric  
207 fallout from an STCM plant (Cecchi et al., 2008) and we wanted to be sure that enough  
208 lead was available for the plant in soil solution. Surveys of garden soils in several  
209 countries have shown wide ranges of concentrations of heavy metals. For example,  
210 Culbard et al. (1988) found concentrations of up to  $14,100 \text{ mg Pb kg}^{-1}$ . Some soils were  
211 left without crops, to determine the pH possible variation due to soil solution influence.  
212 During the growth, pH was measured daily and nutrient solution level was maintained  
213 constant. pH of nutrient solution was  $5.5 \pm 0.3$  during the hydroponic and soil contact  
214 phases.

215 This biotest device presents two main advantages: (i) the roots are physically separated  
216 from the soil which enables total recovery of the shoots, roots and soil; (ii) the thickness  
217 of the soil layer used enables it to be considered it as rhizosphere soil and provides  
218 enough rhizosphere material to evaluate root-induced changes in metal speciation.

219 Roots and aerial parts were collected and analysed separately after the soil plant  
220 contact period. Biomass was determined before oven-drying at  $80^\circ\text{C}$  for 48H. Lead  
221 bound to the outer root cell walls, called  $[Pb]_{\text{adsorbed}}$ , was determined according to the  
222 method of acidic desorption as described by Ferrand et al. (2006): roots were shaken  
223 end over end with 40mL of 0.001M HCl for 3 min, and then 360  $\mu\text{L}$  of 1 M HCl was

224 added to yield a final concentration of 0.01 M HCl. After shaking for another 5 min, the  
225 suspension was filtered through ashless paper. Then, plant roots and aerial parts were  
226 mineralized separately in a 1:1 mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> at 80°C for 4h. After  
227 filtration, the major and trace element concentrations were determined with an IRIS  
228 Intrepid II XDL ICP-OES. The concentration in roots after mineralization is considered  
229 as uptaken lead ([Pb]<sub>roots</sub>). The accuracy of the acidic digestion and analytical  
230 procedures was verified using the reference material Virginia tobacco leaves, CTA-  
231 VTL-2, ICHTJ.

232

#### 233 2.4. Estimation of lead availability by CaCl<sub>2</sub> extraction experiments

234 For the determination of the phytoavailable fraction, according to Menzies et al.  
235 (2007) neutral salts extractants provide the most useful indication. The 0.01 M CaCl<sub>2</sub>  
236 extraction procedure gives a good indication of lead phytoavailability (Meers et al.,  
237 2007). The CaCl<sub>2</sub> procedure, first described by Houba, et al. (1996), was performed on  
238 the two contaminated soils and particle samples (PM<sub>10</sub> and PM<sub>2.5</sub>). 30 mL of 0.01 M  
239 CaCl<sub>2</sub> solution was mixed with 3 g of soil (1:10 solid solution ratio) in 50ml  
240 polypropylene centrifugation tubes placed on a shaker table (Heidolph promax 1020) at  
241 50 oscillations/min for 2h, 20°C. After extraction, the tubes were centrifuged at 10,000  
242 g for 30 min (Avanti 30 centrifuge Beckman). The supernatant liquid was then filtered  
243 (0.22µm), acidified to 2% with distilled HNO<sub>3</sub> (15M, suprapur 99.9%) and stored at  
244 4°C before analysis. That CaCl<sub>2</sub> extraction procedure was performed on particles,  
245 reference soils, and the two spiked soils before and after culture. Extracted metal  
246 concentrations were determined by an IRIS Intrepid II XDL/ Thermo Electron  
247 Corporation model ICP-AES Calibration used reference materials (ion 915 from  
248 National Water Research Institute, Canada).

249

## 250 2.5. Statistical data treatment

251 The plant absorption and chemical extraction data obtained were subjected to  
252 analysis of variance (ANOVA) with one factor, using the software Statistica, Edition'98  
253 (StatSoft Inc., Tulsa, OK, USA). For each bioassay, mean values with different letters  
254 represent a significant difference ( $p < 0.05$ ) as measured by the LSD Fisher test. Letters  
255 are reported on the figures and tables.

256

257 **3. Results**258 3.1.  $PM_{10}$  and  $PM_{2.5}$  characterization:

259 Elemental concentrations in particles are shown in table 2. All results are given as  
260 the mean of the three replicates for each sample ( $PM_{10}$  and  $PM_{2.5}$ ) and standard  
261 deviations never exceed 7%. No significant difference except for Fe in the total  
262 elemental concentrations was observed in relation with the size of the particle. Major  
263 elements found in the samples were, by mass: Pb (27%), O (15%) and S (7.5%) for both  
264 fractions. High levels of Na (3-4%) were due to the industrial recycling process where  
265 Na is used to lower the melting point of Pb. Several other metals: Cd (2.5%), Zn (0.5%),  
266 Fe (0.1-0.4%) and Sb (0.1%) are also present. The remaining elements to complete to  
267 100% are expected to be chloride and other trace metals.

268 XRD patterns of  $PM_{10}$  and  $PM_{2.5}$  provide identification of major crystallized  
269 species in bulk samples. The results are presented in table 3. Particles are mainly  
270 composed of metallic sulfides, sulfates, oxides and perchlorates. A significant amount  
271 of  $Na_2SO_4$  was found in  $PM_{10}$  samples. Regardless of the size, the major phases  
272 identified were the same and one more Fe species was detected for  $PM_{2.5}$ .

273 The ESEM-EDX analysis provided the morphology and elemental composition of  
274 individual particles in the two size fractions. PM<sub>10</sub> samples exhibited both particles with  
275 a size range between 2 and 10 μm and large aggregates composed of many micron-sized  
276 particles without specific shapes (figure 2). The main elements detected by EDX in  
277 these aggregates were, by order of importance, Pb, S, Cl, Sn, Na, and Fe. The chemical  
278 complexity of aggregates did not allow the detection of minor elements. Elemental  
279 mapping recorded on PM<sub>10</sub> showed the chemical heterogeneity of aggregates. PM<sub>2.5</sub>  
280 samples are composed of fine aggregates of few submicronic particles exhibiting  
281 characteristic features i.e. needles (< 100 nm), nano crystals (< 500 nm), cubes (~300  
282 nm) and balls (~500 nm). Elemental analysis of particles showed that needles mainly  
283 contain Pb and S, nano crystals are composed of Pb, S and Cl while Na and S are  
284 detected in cubic particles. Compared to the PM<sub>10</sub> sample, numerous Pb only-rich  
285 nanoballs were observed in PM<sub>2.5</sub> (figure 2).

286 Raman microspectrometry combines the analytical capability of Raman  
287 spectroscopy to distinguish *in situ* a wide range of chemical substances in aerosols with  
288 the spatial resolution of a confocal optical microscope (~1 μm<sup>3</sup>) which enables  
289 investigation of individual particles. The scanning of a large area of sample (300 μm<sup>2</sup>)  
290 by automated analyses enables the analysis of a huge number of particles. The data  
291 treatment of all the spectra recorded in this area leads to the major and minor  
292 component identification. xPbO.PbSO<sub>4</sub> (x = 1,2,3), PbSO<sub>4</sub>, α-PbO, PbCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>,  
293 and ZnSO<sub>4</sub> were identified in both PM<sub>10</sub> and PM<sub>2.5</sub> samples as major species. The laser-  
294 damaging effect generates complete and irreversible oxidation of PbS to PbSO<sub>4</sub> as  
295 described previously (Batonneau et al., 2000). The Raman mapping of species within  
296 particles exhibits a large heterogeneity of particle composition. A typical Raman image  
297 of PM<sub>2.5</sub> particles is shown in figure 3. A large number of particles are composed of

298 lead sulphate and are agglomerated with other compounds such as sodium sulphate or  
299 carbonates in both PM<sub>10</sub> and PM<sub>2.5</sub> size fractions. The results suggest that no significant  
300 differences in lead speciation are observed in accordance with the particle size.  
301 However, for the minor lead compounds (like carbonates) not exactly quantified by  
302 XRD, differences in percentages between the two size fractions could exist.

303

### 304 3.2. Assessment of the available fraction with CaCl<sub>2</sub> extraction

305 Figure 4A and 4B shows respectively total lead concentrations extracted by CaCl<sub>2</sub>  
306 and percentages of extracted lead with CaCl<sub>2</sub> (relative, with respect to total lead  
307 concentrations in different substrates) for various samples: the single particles, soil-1 and  
308 spiked soil-1 before and after an eight-day exposure of *Lactuca sativa*.

309 Due to high levels of lead in particles (330,000 mg.kg<sup>-1</sup>), maximum lead quantities were  
310 extracted from PM<sub>10</sub> and PM<sub>2.5</sub>. But, in comparison with total lead contents, lead in  
311 uncultivated spiked soils was 0.2% exchangeable, while PM<sub>10-2.5</sub> presented a 0.01%  
312 exchangeability. Reference soils were under ICP-OES limit detection. After culture, a  
313 significantly greater lead quantity was extracted by CaCl<sub>2</sub> for the soil spiked with the  
314 finest PM<sub>2.5</sub> fraction than in PM<sub>10</sub>. A 1 unit pH decrease was measured after plant-soil  
315 contact while the pH values of the control soils (left without crops but with nutrient  
316 solution influence) remained constant. Concerning CaCl<sub>2</sub> extraction, no significant  
317 differences were observed between the two particle sizes in the PM<sub>10-2.5</sub> and spiked soil-  
318 1 before culture; The same trends described above for soil-1 were also observed for soil-  
319 2.

320

### 321 3.3. Influence of lead exposure on plant growth.

322 Fresh biomass data are shown in figure 5. After eight days of soil-plant exposure,  
323 biomasses for aerial parts grown on spiked soils were slightly lower than in the  
324 respective unspiked soils. No significant biomass differences were observed among the  
325 two types of spiking ( $PM_{10-2.5}$ ). In controls, fresh weights were approximately  $18.5 \pm 2.5$   
326 g for aerial parts and  $3.7 \pm 0.7$  g for roots while in spiked soils, weights reached  $12 \pm 4$   
327 g and  $2.5 \pm 1$  g respectively. This slight influence of lead on plant biomass could be due  
328 to lead toxicity (Sharma & Dubey, 2005) or water status (Parys et al., 1998).

329

#### 330 3.4. Absorption and adsorption of lead in the lettuce

331 Figure 6 presents results of lead transfer from soil to the various compartments of  
332 the plant (roots and shoots) and the distribution between adsorption (noted  $[Pb]_{adsorbed}$ )  
333 and absorption for roots ( $[Pb]_{roots}$ ) respectively described in the materials and method  
334 section as lead only adsorbed at the root surface and lead truly taken up by the plant.  
335 Measurements on the reference samples (Tobacco leaf VTL-2) validated the assay: the  
336 concentration found was  $21.4 \pm 1.1$  mg.kg<sup>-1</sup>, for a certified value of  $22.1 \pm 1.2$  mg.kg<sup>-1</sup>.  
337 Several trends were observed dealing with the influence of the particle type, soil type  
338 and lead location. For both soils, a significant increase of lead adsorption on roots,  
339 absorption and translocation throughout the shoots was observed, when the finest  
340 particles were added in comparison with the  $PM_{10}$ . Global uptakes ( $[Pb]_{adsorbed} +$   
341  $[Pb]_{roots} + [Pb]_{shoots}$ ) were greater for soil 1 than for soil 2. The main lead fraction was  
342 adsorbed on root membranes where concentrations were up to  $985 \pm 147$ .kg<sup>-1</sup> for  $PM_{10}$   
343 contaminated soils and up to  $1281 \pm 195$  mg.kg<sup>-1</sup> for  $PM_{2.5}$  contaminated soils. The soils  
344 spiked with  $PM_{10}$  allowed a lead uptake of  $230 \pm 24$  mg.kg<sup>-1</sup> by roots and a translocation  
345 to aerial parts of  $7.7 \pm 2.7$  mg.kg<sup>-1</sup>. While in the  $PM_{2.5}$  spiked soils, root and shoot  
346 concentrations reached  $275 \pm 40$  mg.kg<sup>-1</sup> and  $12.19 \pm 3$  mg.kg<sup>-1</sup> respectively.

347

348 **4. Discussion**349 (1) Influence of particle size on soil-plant transfer and lead translocation.

350        Whatever the soil, for a given total lead concentration (1650 mg Pb.kg<sup>-1</sup> soil),  
351 higher lead soil-plant transfer and translocation were observed for the finest particles.  
352 Roots exposed to PM<sub>2.5</sub> spiked soils allowed a 20% greater lead uptake and a 30%  
353 increase in adsorbed lead. Shoots presented a 60% increase in translocated lead in PM<sub>10</sub>  
354 spiked soils. For the first time in industrial particles, the transfer of lead to the soil  
355 solution and its translocation throughout the plant is reported to increase as the particle  
356 size decreases.

357        Douay et al. (2006), measuring lead concentrations in lettuces in urban gardens  
358 (1572 mg Pb.kg<sup>-1</sup>) observed a shoot concentration of 5 mg Pb.kg<sup>-1</sup> DW. The soil to plant  
359 metal transfer measured in this study (for one week of lead exposure) was relatively  
360 high in comparison with previously reported data in publications dealing with  
361 vegetables (BAPPET, 2007), probably because of particle size, but also due to  
362 numerous factors that influence the soil-plant transfer of metals (Kabata-Pendias, 2004;  
363 Dumat et al., 2001 & 2006; Costa & Morel, 1993; Oliver et al., 1994).

364        Root transfer factors (TF-roots) and shoot transfer factors (TF-shoots) were  
365 calculated as ratios between [Pb]<sub>roots</sub>, [Pb]<sub>shoots</sub> with [Pb]<sub>soil</sub>. TFr ranged from 0.10 to  
366 0.17 and TFs were between 0.005 and 0.007 (table 4). These relatively low values  
367 illustrate the known low mobility and availability of lead and are comparable to Khan et  
368 al.'s results (2008) reporting 0.15 for TFr and 0.07 for TFs. As transfer factors for  
369 vegetables decrease with increasing levels of lead in the soil (Zheng et al., 2007; Wang  
370 et al., 2006), we therefore expected a greater influence of particle size on transfer with a  
371 lower total lead concentration in soil.



372 According to Sobanska et al. (1999), lead smelter emissions contain PbS, PbSO<sub>4</sub>,  
373 PbSO<sub>4</sub>.PbO, Pb, α-PbO compounds and numerous nano balls were observed for PM<sub>2.5</sub>.  
374 Dumat et al. (2001) and Cecchi et al. (2008) working on soils polluted by lead produced  
375 by industrial atmospheric fallout from smelters, concluded that lead chemical speciation  
376 strongly influences its bioavailability. The sequence of solubility constants from the  
377 CHESS data base for the lead is the following: PbCO<sub>3</sub> > PbSO<sub>4</sub> > PbO > Pb<sup>0</sup>. In water  
378 media and equilibrium conditions, lead carbonate and sulphate will be much more labile  
379 than PbO or Pb<sup>0</sup> species. However, according to Birkefeld et al. (2006 & 2007) which  
380 used an in-situ method to study dissolution and phase transformation of lead particles  
381 from a smelter in different soils, the sequence of solubility is strongly dependent on soil  
382 characteristics (like texture, pH, lime amount...). They observed that PbO was rapidly  
383 covered by lead-hydroxy carbonates (hydrocerussite) in some soils while in other it was  
384 relatively stable. Moreover, according to the general review of Ruby et al. (1992),  
385 release of lead in the soil solution depends on particle size, speciation and soil  
386 geochemistry. In soil solution, ligands like fulvic acids or low weight organic acids  
387 excreted by roots can displace the equilibrium (Ferrand et al., 2006). Finally, as no  
388 significant difference among speciation forms was noticed between PM<sub>10</sub> and PM<sub>2.5</sub>, all  
389 changes observed in reactivity were attributed to size differences.

390 Whatever the particle size, greater lead absorption by lettuce was observed for  
391 soil-1 than for soil-2. In comparison with soil-2, soil-1 has more clay, its CEC is higher  
392 and its level of lime is lower (see Table 1). According to Twining et al. (2004), we  
393 could expect that lead transfer would be higher for soil-2. However, several hypotheses  
394 can explain the results observed: (i) the higher amount of carbonates present in the soil-  
395 2 could reduce lead absorption (Birkefeld et al., 2006 & 2007); (ii) the complex  
396 influence of soil organic matter on the transfer of metals (Yin et al., 2002; Inaba &

397 Takenaka, 2005); (iii) for the total lead concentration studied, the relatively high  
398 quantity of lead could be available in the soil solution (due to high solubility of the fine  
399 particles) reducing the influence of soil characteristics.

400 Total lead in the roots ( $[Pb]_{\text{roots}} + [Pb]_{\text{adsorbed}}$ ) reached 1500 mgPb/ kg dry weight.  
401 Lead in roots was predominantly adsorbed onto the cell walls, 80 % of the total lead in  
402 roots, and depends on the nature of the particles used for exposure: the uptake was  
403 greater for PM<sub>2.5</sub> than PM<sub>10</sub>. According to Seregin et al. (2004), Pb<sup>2+</sup> binds to the  
404 carboxy groups at the root surface reducing the translocation rate of lead (Pendergrass et  
405 al., 2006; Piechalak et al., 2002). To illustrate this phenomenon, the translocation  
406 factors or shoot/root ratios calculated indicate the ability of plants to transport metals  
407 from the roots toward the aerial parts (Ferrand et al., 2006): they ranged between 0.03  
408 and 0.04 (table 4). But considering the lower biomasses in roots than in shoots, we can  
409 also reason with lead quantities. Whatever the type of soil or spiking, the total lead  
410 quantity in shoots ( $Pb_{\text{shoots}} \times \text{dry weight}$ ) between 0.003 and 0.007 mg Pb translocated  
411 which represents up to 33% (PM<sub>2.5</sub>) of the total lead uptake. This percentage is not  
412 negligible with respect to risks concerning consumption of vegetables.

413

#### 414 (2) Behaviour of lead in the rhizosphere and assessment of lead availability

415 Relatively high lead transfer was observed for the lettuce cultivated on the two  
416 alkaline spiked calcareous soils. PM<sub>10-2.5</sub> can therefore release lead in particular in the  
417 rhizosphere of *Lactuca sativa*. The lead availability estimated by the CaCl<sub>2</sub> procedure  
418 was greater for soils spiked with the finest particles and for both soils it increased after  
419 soil-plant contact:  $[Pb]_{\text{CaCl}_2}$  in spiked soil with PM<sub>2.5</sub> >  $[Pb]_{\text{CaCl}_2}$  in spiked soil with  
420 PM<sub>10</sub>. Under the root activity influence, the CaCl<sub>2</sub> lead extracted from polluted soils  
421 increased and a one-unit pH decrease in soil was measured. Lin et al. (2004) and Kidd

422 and Monterroso (2005) also observed that exchangeable lead was much higher in the  
423 rhizosphere than in the bulk soil. Producing exudates, plants can modify metal  
424 speciation and behaviour in the rhizosphere (Lin et al., 2004; Laperche, 1997; Welch,  
425 1995). This phenomenon has been particularly observed for calcareous soil by  
426 Chaignon and Hinsinger (2003). As pH influences metal solubility and transfer (Wang  
427 et al., 2006), the rhizosphere acidification could have displaced the equilibrium towards  
428 bicarbonates, which are less stable than carbonates (Sauvé et al., 1998). An effect of soil  
429 on particle solubility was also observed: particles present a  $\text{CaCl}_2$  exchangeability ten  
430 times lower than in spiked soil. Quantities extracted for particles were only up to 1.5%  
431 of the solution extraction. Mixed with soil for four months, particle solubility could  
432 therefore have changed.

433 In order to estimate the transfer of lead from polluted soils towards lettuce,  
434 relationships were sought between: lead mobilised by  $\text{CaCl}_2$  extraction performed on  
435 soils before culture and lead concentrations in lettuce (shoots and roots). Equations were  
436 obtained from 6 parameters (2 soils; uncontaminated, spiked with  $\text{PM}_{10}$  or  $\text{PM}_{2.5}$ ), and  
437 every condition was studied by 5 replicates finally involving 30 observations.  
438 Significant correlations were observed between lead concentrations in shoots (Equation  
439 1 below, with  $r^2 = 0.8$ ) or in roots (Equation 2 below, with  $r^2 = 0.9$ ) and lead extracted  
440 by  $\text{CaCl}_2$ .

441 Equation 1:  $[\text{Pb}]_{\text{shoots}} = 2.11 \times [\text{Pb}]_{\text{CaCl}_2} + 2.13$   $r^2 = 0.797$   $p < 0.01$   $n = 30$

442 Equation 2:  $[\text{Pb}]_{\text{roots}} = 35.02 \times [\text{Pb}]_{\text{CaCl}_2} + 4.24$   $r^2 = 0.915$   $p < 0.005$   $n = 30$

443 Both for  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , the  $\text{CaCl}_2$  chemical extraction was therefore a good indicator  
444 of soil-plant transfer. As previously shown by Pueyo et al. (2004), the  $0.01 \text{ mol l}^{-1}$   
445  $\text{CaCl}_2$  extraction procedure seems to be a suitable method for the determination of  
446 phytoavailable lead. This test simplifies the matrix and could avoid *in vivo* tests.

447

**448 Conclusions and perspectives**

449 A significant size influence was found for soil-plant lead transfer and translocation  
450 throughout the lettuce when micronic and nanometric industrial particles were  
451 compared: roots exposed to PM<sub>2.5</sub> spiked soils allowed a 20% greater lead uptake and a  
452 30% increase in adsorbed lead. Shoots presented a 60% increase in translocated lead in  
453 PM<sub>10</sub> spiked soils. Our results highlight that source characteristics strongly influence  
454 metal transfer: total metal soil concentration is insufficient to estimate the risk induced  
455 by soils polluted by metals. Lead speciation was quite similar in PM<sub>10</sub> and PM<sub>2.5</sub>  
456 particles i.e. PbS, PbO.PbSO<sub>4</sub>, PbO, PbCO<sub>3</sub> and Pb<sup>0</sup>, were predominant however  
457 differences could exist for minor lead components. Moreover, the high amount of Pb-  
458 rich nano balls and nano crystals much more dispersed for PM<sub>2.5</sub> could influence the  
459 lead transfer in the rhizosphere acidified by plant root activity. Lead concentrations in the  
460 edible part of lettuces were very well estimated by 0.01M CaCl<sub>2</sub> extraction.

461 In order to check the generality of the size influence of industrial particles on soil-  
462 plant transfer, further experiments could be performed on other vegetables and various  
463 soils testing aging effects. Moreover, the study of other metals and metalloids measured  
464 in the particles will be performed.

465

**466 Acknowledgements**

467 ADEME, the French Agency for Environment and Energy as well as the STCM, are  
468 gratefully acknowledged for their financial support and technical help. This research  
469 project was supported by the National CNRS CYTRIX-EC2CO program. We thank Dr  
470 J. Silvestre from ENSAT for cropping advice, P. Recourt from *Laboratoire*  
471 *Geosystèmes*, UMR CNRS 8157, University of Lille for ESEM-EDX measurements and

472 J. Laureyns from LASIR UMR CNRS 8516, for Raman Microspectrometry assistance.  
473 Finally, Dr P. Winterton from UPS is acknowledged for English review.

474

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**Figure legends**

674

675 **Figure 1**

676 Microculture device.

677

678 **Figure 2**679 ESEM images of PM<sub>2.5</sub> (A) and PM<sub>10</sub> (B).

680

681 **Figure 3**

682 Raman image of PM<sub>2.5</sub> particles after a smoothing procedure. Blue 4PbO.PbSO<sub>4</sub>, pink  
683 PbO.PbSO<sub>4</sub>, red Na<sub>2</sub>SO<sub>4</sub> and green substrate.

684

685 **Figure 4**

686 Total contents (A) and relative contents (B) of lead extracted with CaCl<sub>2</sub> on particles  
687 (white), spiked soils with lead particles of different size before (grey) and after (black) a  
688 seven-days exposure of *Lactuca sativa*, n=5.

689

690 **Figure 5**

691 Plant biomass data for aerial parts (black) and roots (grey). The error bars indicate the  
692 standard deviation while different letters show significant differences (p<0.05) as  
693 measured by an LSD fisher test (one-factor ANOVA ).

694

695 **Figure 6**

696 Lead concentrations in different plant compartments: A: adsorbed onto roots, B: root  
697 uptake and C: translocated in shoots.

698

699 **Table 1**

700 Physico-chemical characteristics of the two soils used for micro-culture experiments.

	<b>unit</b>	<b>Soil-1</b>	<b>Soil-2</b>
<b>pH</b>		8.3	8.4
<b>CEC</b>	cmol+/kg	19.9	8.9
<b>Clay</b>	(g.kg <sup>-1</sup> )	405	195
<b>Silt</b>		261	390
<b>Sand</b>		334	415
<b>C/N</b>		9.15	8.9
<b>MO</b>	(g.kg <sup>-1</sup> )	18.8	12.5
<b>Total carbonates</b>	(g.kg <sup>-1</sup> )	36.8	98
<b>P<sub>2</sub>O<sub>5</sub> Joret Hebert</b>	(g.kg <sup>-1</sup> )	0.28	0.215
<b>Cd (HF extraction)</b>	(mg.kg <sup>-1</sup> )	0.22	0.175
<b>Pb (HF)</b>		35.5	21
<b>Zn (HF)</b>		101	48
<b>Cu (HF)</b>		28.5	31

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705 **Table 2**

706 Total elemental analysis of particles.

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	<b>Contents (mg.kg<sup>-1</sup>) ± 7%</b>												
<b>Sample</b>	<b>Al</b>	<b>As</b>	<b>Cd</b>	<b>Cu</b>	<b>Fe</b>	<b>O</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Sb</b>	<b>Zn</b>	<b>S</b>	<b>C</b>
<b>PM<sub>2.5</sub></b>	10	867	25243	480	1395	149300	31691	41	272834	1266	5194	78100	12100
<b>PM<sub>10</sub></b>	52	841	23139	617	4010	150000	39697	97	267353	1361	5372	74300	11500

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710 **Table 3**711 Determination of main chemical speciation of lead in the PM<sub>10</sub> and PM<sub>2.5</sub> particles by712 X-Ray Powder Diffraction Analysis <sup>a</sup>

Sample	Cristallized compound	Estimated % of phases
PM <sub>10</sub>	<b>PbS</b> ,	55
	<b>PbO.PbSO<sub>4</sub></b> , <b>PbSO<sub>4</sub></b> , Pb(ClO <sub>4</sub> ) <sub>2</sub> , Pb,	25
	<b>Na<sub>2</sub>SO<sub>4</sub></b>	10
	CdS, Cd(ClO <sub>4</sub> ) <sub>2</sub> , ZnO, ZnSO <sub>4</sub>	10
PM <sub>2,5</sub>	<b>PbS</b> ,	55
	<b>PbO.PbSO<sub>4</sub></b> , <b>PbSO<sub>4</sub></b> , Pb(ClO <sub>4</sub> ) <sub>2</sub> , Pb,	25
	<b>Na<sub>2</sub>SO<sub>4</sub></b>	10
	CdS, Cd(ClO <sub>4</sub> ) <sub>2</sub> , ZnO, ZnSO <sub>4</sub> , FeS <sub>2</sub>	10

713

714 <sup>a</sup>The major compounds are written in bold

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718

719 **Table 4**

720 Transfer factors in roots (TFr) and shoots (TFs) and translocation ratios.

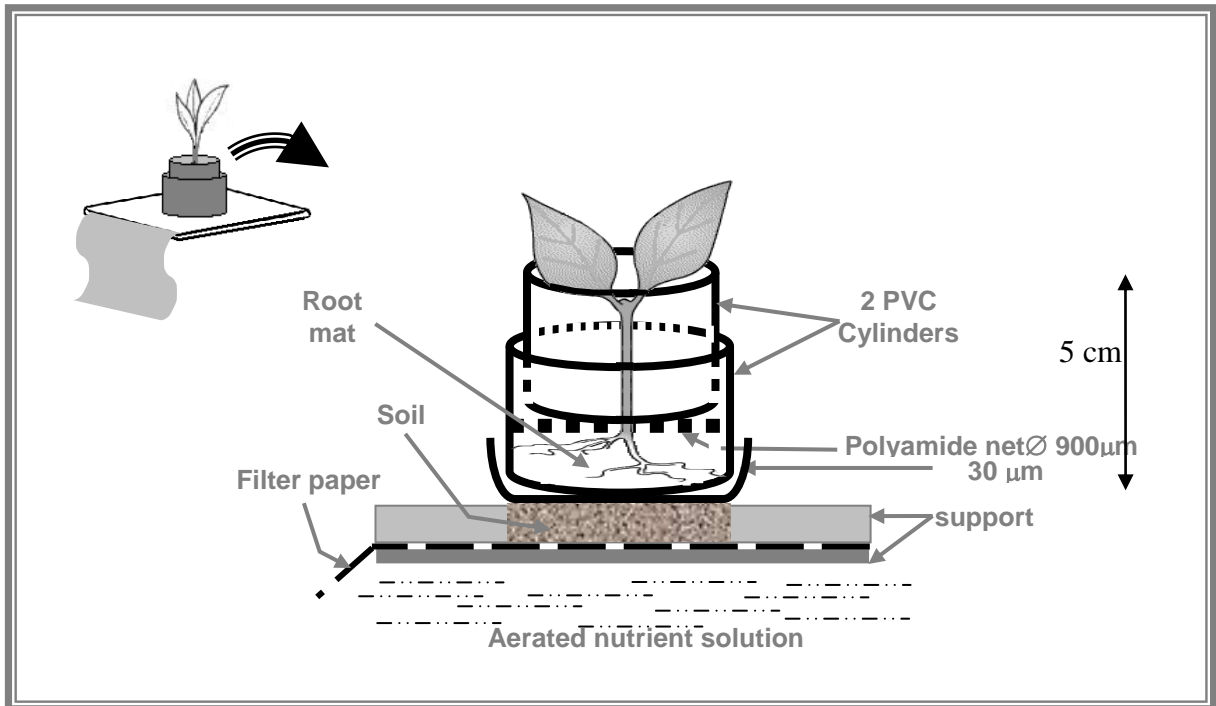
<b>Soil</b>	<b>TFs</b>	<b>TFr</b>	<b>Translocation</b>
<b>S1 + PM<sub>10</sub></b>	0.005	0.14	0.03
<b>S1 + PM<sub>2.5</sub></b>	0.007	0.17	0.04
<b>S1</b>	0.081	0.26	0.31
<b>S2 + PM<sub>10</sub></b>	0.004	0.10	0.04
<b>S2 + PM<sub>2.5</sub></b>	0.005	0.15	0.03
<b>S2</b>	0.01	0.44	0.18

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**Figure 1**

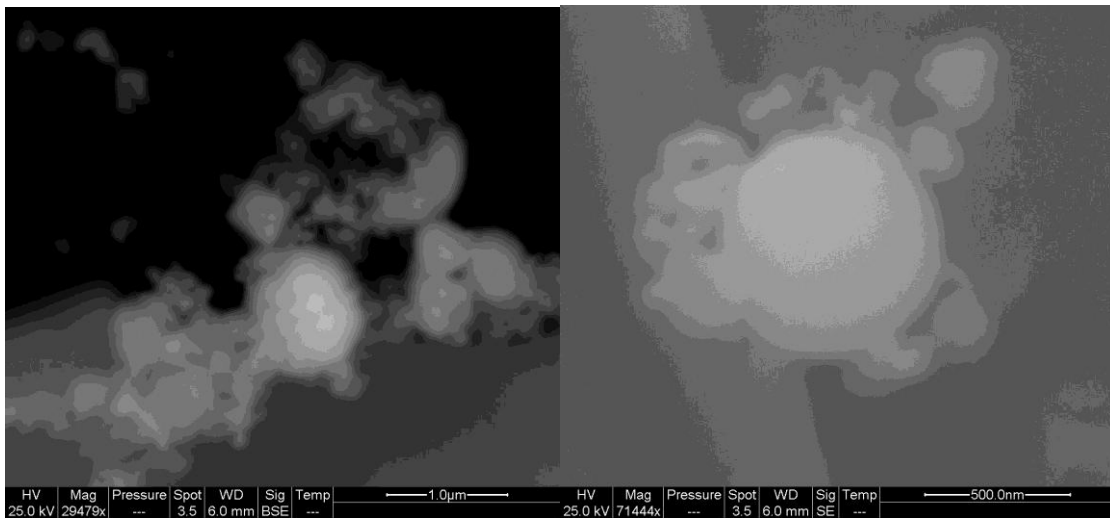


749

**Figure 2**

750

**(A)**

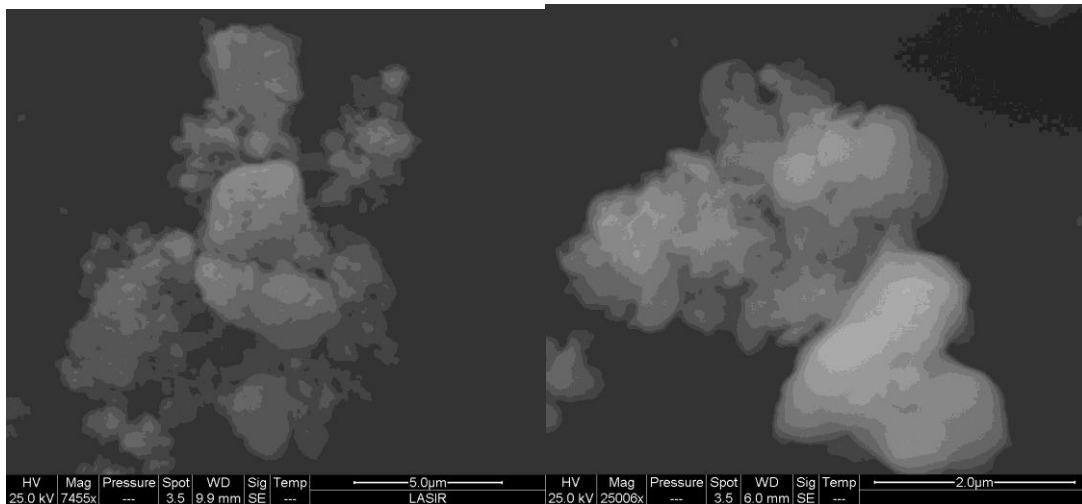


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**(B)**



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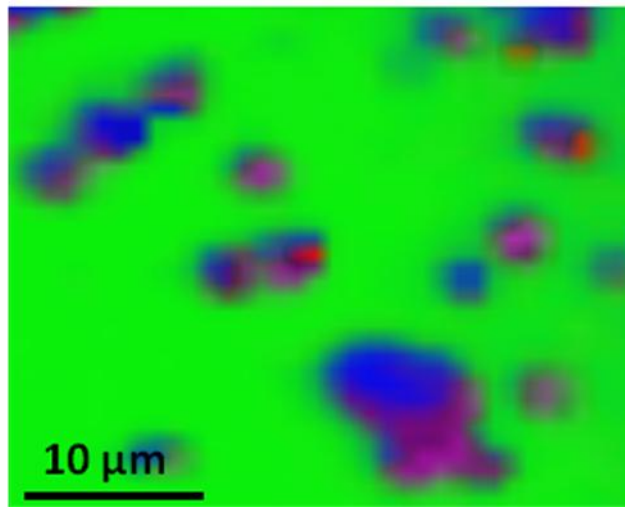
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**Figure 3**



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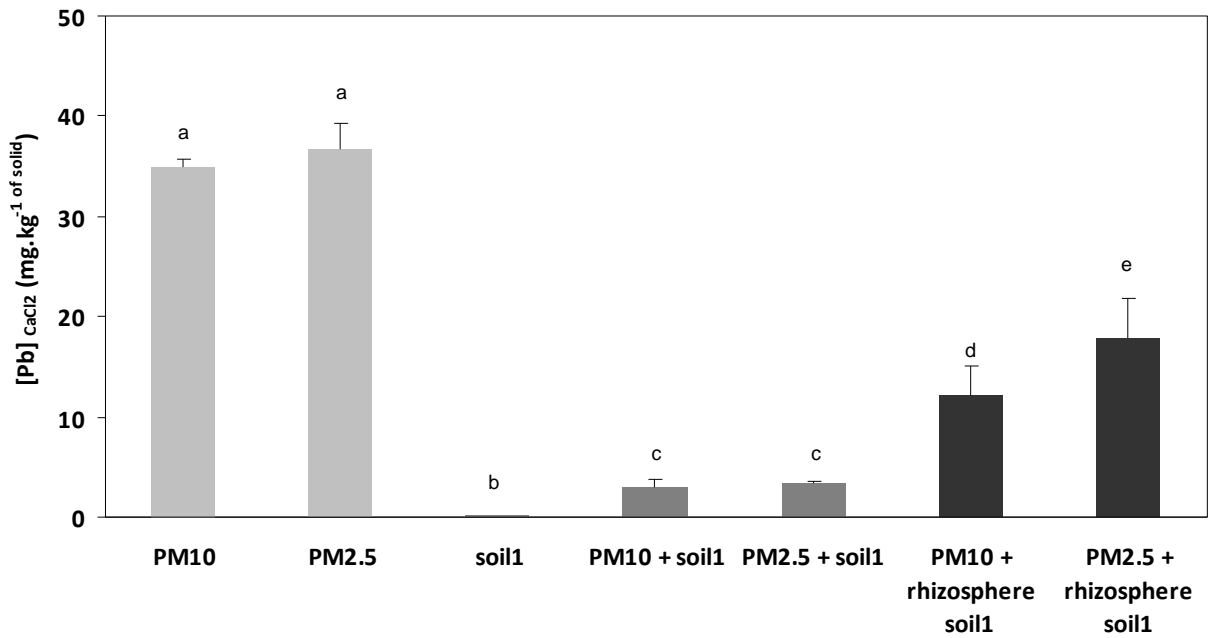
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764

**Figure 4**

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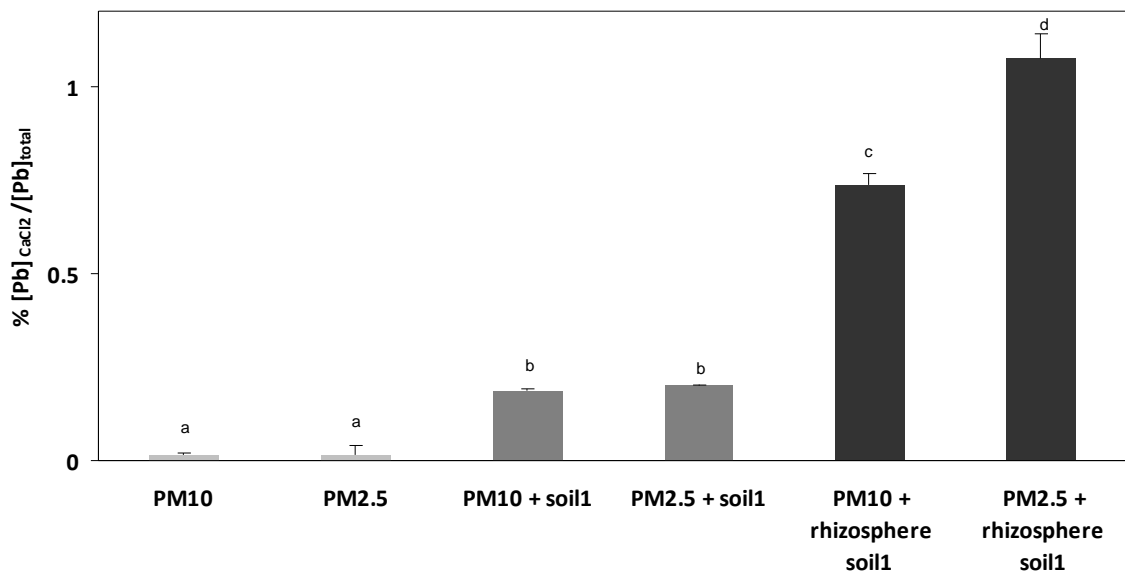
(A)



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(B)



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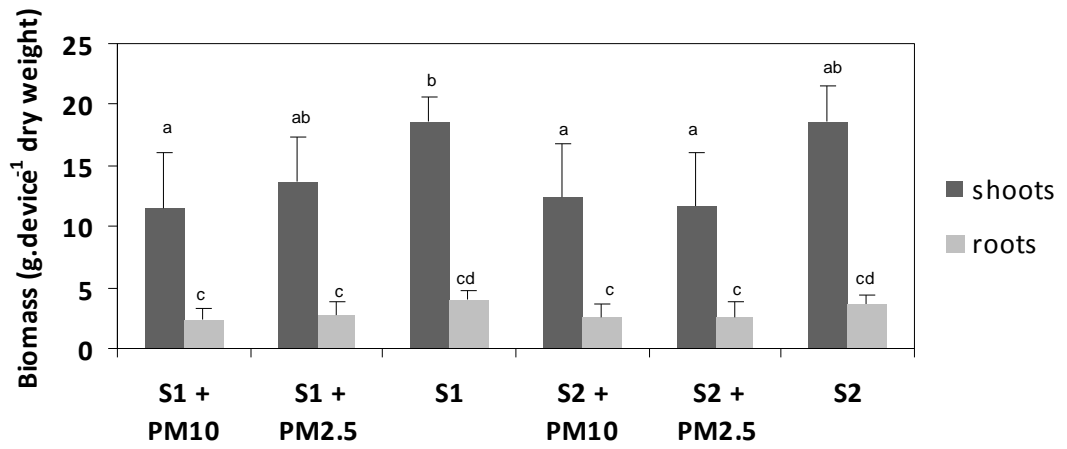
**Figure 5**

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**Figure 6**

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(A)

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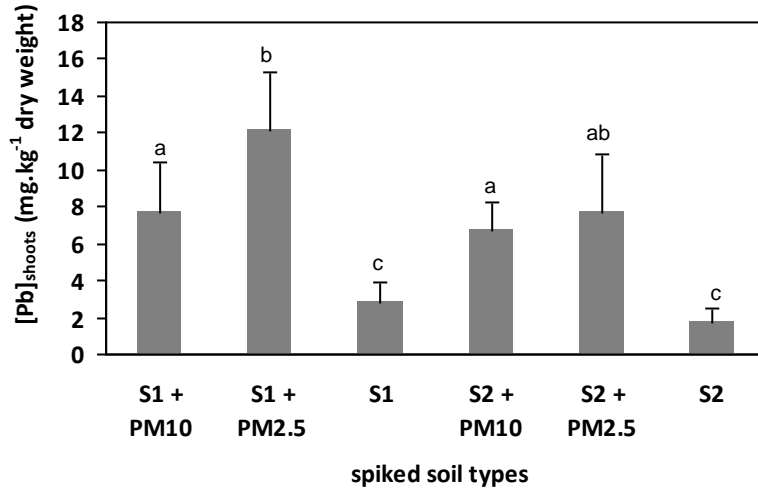
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(B)

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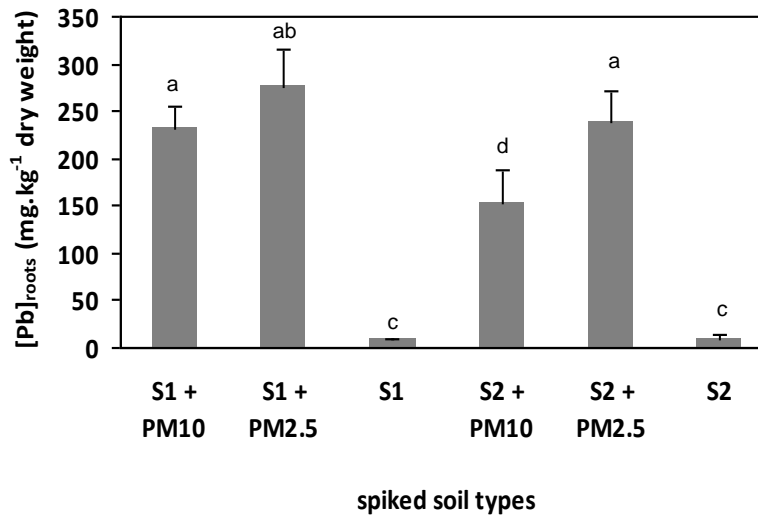
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(C)

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