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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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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, PbSO₄, PbSO₄.PbO, α-PbO and Pb⁰. Morphology investigations revealed that
29 PM_{2.5} (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 CaCl₂ extraction.

33

34 **Keywords:** lead, PM_{2.5} and PM₁₀, 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 PM₁₀ 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 PM₁₀ 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 PM₁₀ and PM_{2.5} 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 PM₁₀ and PM_{2.5} 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 CaCl₂
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_{2.5} and PM₁₀ 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_{10/2.5} Dekati inertial impactor.
124 The cascade impactor consists of two successive stages with aerodynamic cut-off

125 diameters of 10 and 2.5 μm when it operates at 10 L/min airflow. PM_{10} present an
126 aerodynamic diameter between 2.5 and 10 μm , 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 (HNO_3 , HCl and 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 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 μm resolution, 1 μm 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 μm 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 μm mesh) inserted into a larger cylinder,

174 itself closed by a finer polyamide mesh (30 μm , 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 KNO_3 , 5 mM $\text{Ca}(\text{NO}_3)_2$, 2 mM KH_2PO_4 and
184 1.5 mM MgSO_4 and oligoelements: 9.11 μM MnSO_4 , 1.53 μM ZnSO_4 , 0.235 μM
185 CuSO_4 , 24.05 μM H_3BO_3 , 0.1 μM Na_2MoO_4 and 268.6 μM 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 $^\circ\text{C}/18 \pm 0.5$ $^\circ\text{C}$ 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 ± 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°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 μL 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 HNO₃ and H₂O₂ 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]_{roots}). 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 CaCl₂ 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 CaCl₂
236 extraction procedure gives a good indication of lead phytoavailability (Meers et al.,
237 2007). The CaCl₂ procedure, first described by Houba, et al. (1996), was performed on
238 the two contaminated soils and particle samples (PM₁₀ and PM_{2.5}). 30 mL of 0.01 M
239 CaCl₂ 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 HNO₃ (15M, suprapur 99.9%) and stored at
244 4°C before analysis. That CaCl₂ 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. PM₁₀ 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 PM₁₀ showed the chemical heterogeneity of aggregates. PM_{2.5}
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 PM₁₀ sample, numerous Pb only-rich
285 nanoballs were observed in PM_{2.5} (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^3) which enables
289 investigation of individual particles. The scanning of a large area of sample (300 μm^2)
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. $x\text{PbO}\cdot\text{PbSO}_4$ ($x = 1,2,3$), PbSO_4 , $\alpha\text{-PbO}$, PbCO_3 , Na_2SO_4 ,
293 and ZnSO_4 were identified in both PM₁₀ and PM_{2.5} samples as major species. The laser-
294 damaging effect generates complete and irreversible oxidation of PbS to PbSO_4 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_{2.5} 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 PM₁₀ and PM_{2.5} 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 CaCl₂ extraction

305 Figure 4A and 4B shows respectively total lead concentrations extracted by CaCl₂
306 and percentages of extracted lead with CaCl₂ (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⁻¹), maximum lead quantities were
310 extracted from PM₁₀ and PM_{2.5}. But, in comparison with total lead contents, lead in
311 uncultivated spiked soils was 0.2% exchangeable, while PM_{10-2.5} 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 CaCl₂ for the soil spiked with the
314 finest PM_{2.5} fraction than in PM₁₀. 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 CaCl₂ extraction, no significant
317 differences were observed between the two particle sizes in the PM_{10-2.5} 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 ± 2.5
326 g for aerial parts and 3.7 ± 0.7 g for roots while in spiked soils, weights reached 12 ± 4
327 g and 2.5 ± 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 ± 1.1 mg.kg⁻¹, for a certified value of 22.1 ± 1.2 mg.kg⁻¹.
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 ± 147 .kg⁻¹ for PM_{10}
343 contaminated soils and up to 1281 ± 195 mg.kg⁻¹ for $PM_{2.5}$ contaminated soils. The soils
344 spiked with PM_{10} allowed a lead uptake of 230 ± 24 mg.kg⁻¹ by roots and a translocation
345 to aerial parts of 7.7 ± 2.7 mg.kg⁻¹. While in the $PM_{2.5}$ spiked soils, root and shoot
346 concentrations reached 275 ± 40 mg.kg⁻¹ and 12.19 ± 3 mg.kg⁻¹ 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⁻¹ soil),
351 higher lead soil-plant transfer and translocation were observed for the finest particles.
352 Roots exposed to PM_{2.5} 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 PM₁₀
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⁻¹) observed a shoot concentration of 5 mg Pb.kg⁻¹ 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]_{roots}, [Pb]_{shoots} with [Pb]_{soil}. 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, PbSO₄,
373 PbSO₄.PbO, Pb, α-PbO compounds and numerous nano balls were observed for PM_{2.5}.
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: PbCO₃ > PbSO₄ > PbO > Pb⁰. In water
378 media and equilibrium conditions, lead carbonate and sulphate will be much more labile
379 than PbO or Pb⁰ 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 PM₁₀ and PM_{2.5}, 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_{2.5} than PM₁₀. According to Seregin et al. (2004), Pb²⁺ 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_{2.5}) 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_{10-2.5} can therefore release lead in particular in the
417 rhizosphere of *Lactuca sativa*. The lead availability estimated by the CaCl₂ 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_{2.5} > $[Pb]_{\text{CaCl}_2}$ in spiked soil with
420 PM₁₀. Under the root activity influence, the CaCl₂ 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 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 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 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 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 PM_{10} and $\text{PM}_{2.5}$, the 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 mol l^{-1}
445 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_{2.5} 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 PM₁₀ 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 PM₁₀ and PM_{2.5}
456 particles i.e. PbS, PbO.PbSO₄, PbO, PbCO₃ and Pb⁰, 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_{2.5} 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 CaCl₂ 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

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474

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670

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672

673

Figure legends

674

675 **Figure 1**

676 Microculture device.

677

678 **Figure 2**679 ESEM images of PM_{2.5} (A) and PM₁₀ (B).

680

681 **Figure 3**

682 Raman image of PM_{2.5} particles after a smoothing procedure. Blue 4PbO.PbSO₄, pink
683 PbO.PbSO₄, red Na₂SO₄ and green substrate.

684

685 **Figure 4**

686 Total contents (A) and relative contents (B) of lead extracted with CaCl₂ 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.

| | unit | Soil-1 | Soil-2 |
|--|------------------------|---------------|---------------|
| pH | | 8.3 | 8.4 |
| CEC | cmol+/kg | 19.9 | 8.9 |
| Clay | (g.kg ⁻¹) | 405 | 195 |
| Silt | | 261 | 390 |
| Sand | | 334 | 415 |
| C/N | | 9.15 | 8.9 |
| MO | (g.kg ⁻¹) | 18.8 | 12.5 |
| Total carbonates | (g.kg ⁻¹) | 36.8 | 98 |
| P₂O₅ Joret Hebert | (g.kg ⁻¹) | 0.28 | 0.215 |
| Cd (HF extraction) | (mg.kg ⁻¹) | 0.22 | 0.175 |
| Pb (HF) | | 35.5 | 21 |
| Zn (HF) | | 101 | 48 |
| Cu (HF) | | 28.5 | 31 |

701

702

703

704

705 **Table 2**

706 Total elemental analysis of particles.

| | Contents (mg.kg⁻¹) ± 7% | | | | | | | | | | | | |
|-------------------------|---|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|----------|----------|
| Sample | Al | As | Cd | Cu | Fe | O | Na | Ni | Pb | Sb | Zn | S | C |
| PM_{2.5} | 10 | 867 | 25243 | 480 | 1395 | 149300 | 31691 | 41 | 272834 | 1266 | 5194 | 78100 | 12100 |
| PM₁₀ | 52 | 841 | 23139 | 617 | 4010 | 150000 | 39697 | 97 | 267353 | 1361 | 5372 | 74300 | 11500 |

707

708

709

710 **Table 3**711 Determination of main chemical speciation of lead in the PM₁₀ and PM_{2.5} particles by712 X-Ray Powder Diffraction Analysis ^a

| Sample | Cristallized compound | Estimated % of phases |
|-------------------|--|-----------------------|
| PM ₁₀ | PbS , | 55 |
| | PbO.PbSO₄ , PbSO₄ , Pb(ClO ₄) ₂ , Pb, | 25 |
| | Na₂SO₄ | 10 |
| | CdS, Cd(ClO ₄) ₂ , ZnO, ZnSO ₄ | 10 |
| PM _{2.5} | PbS , | 55 |
| | PbO.PbSO₄ , PbSO₄ , Pb(ClO ₄) ₂ , Pb, | 25 |
| | Na₂SO₄ | 10 |
| | CdS, Cd(ClO ₄) ₂ , ZnO, ZnSO ₄ , FeS ₂ | 10 |

713

714 ^aThe major compounds are written in bold

715

716

717

718

719 **Table 4**

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

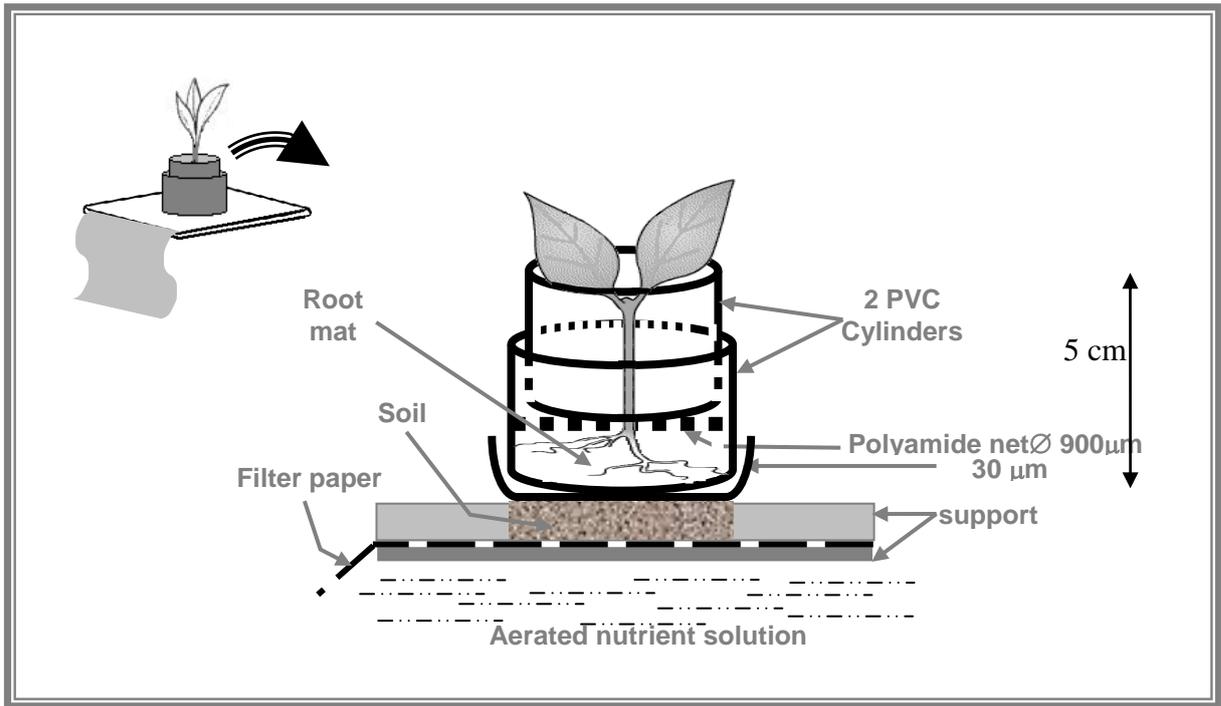
| Soil | TFs | TFr | Translocation |
|------------------------------|------------|------------|----------------------|
| S1 + PM₁₀ | 0.005 | 0.14 | 0.03 |
| S1 + PM_{2.5} | 0.007 | 0.17 | 0.04 |
| S1 | 0.081 | 0.26 | 0.31 |
| S2 + PM₁₀ | 0.004 | 0.10 | 0.04 |
| S2 + PM_{2.5} | 0.005 | 0.15 | 0.03 |
| S2 | 0.01 | 0.44 | 0.18 |

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Figure 1

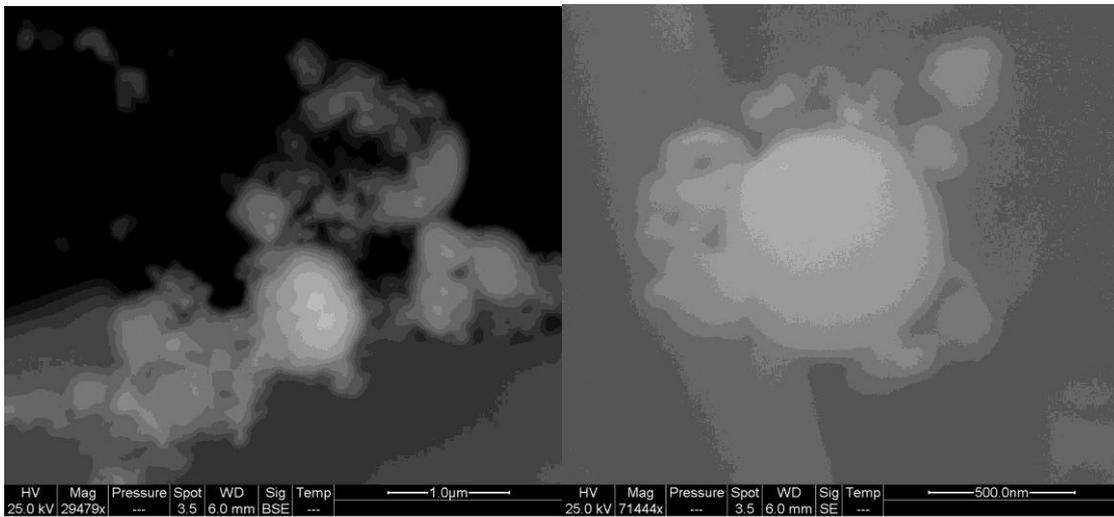


749

Figure 2

750

(A)

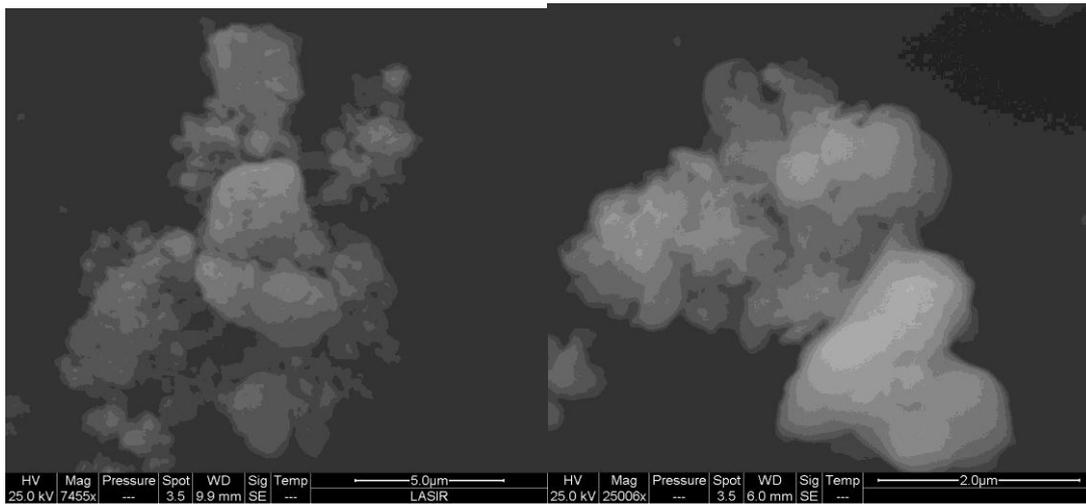


751

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(B)



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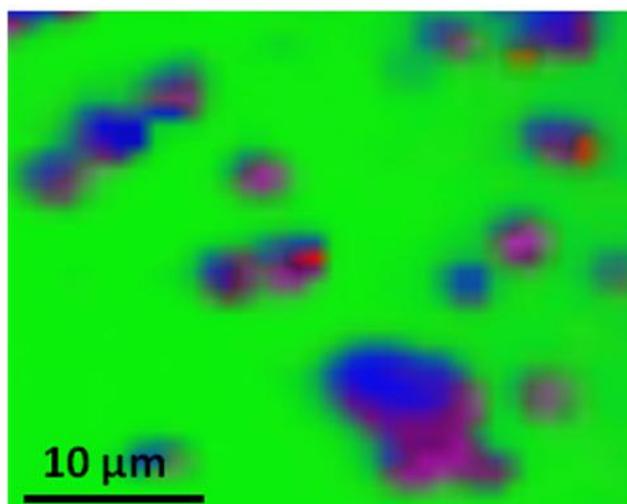
758

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Figure 3



762

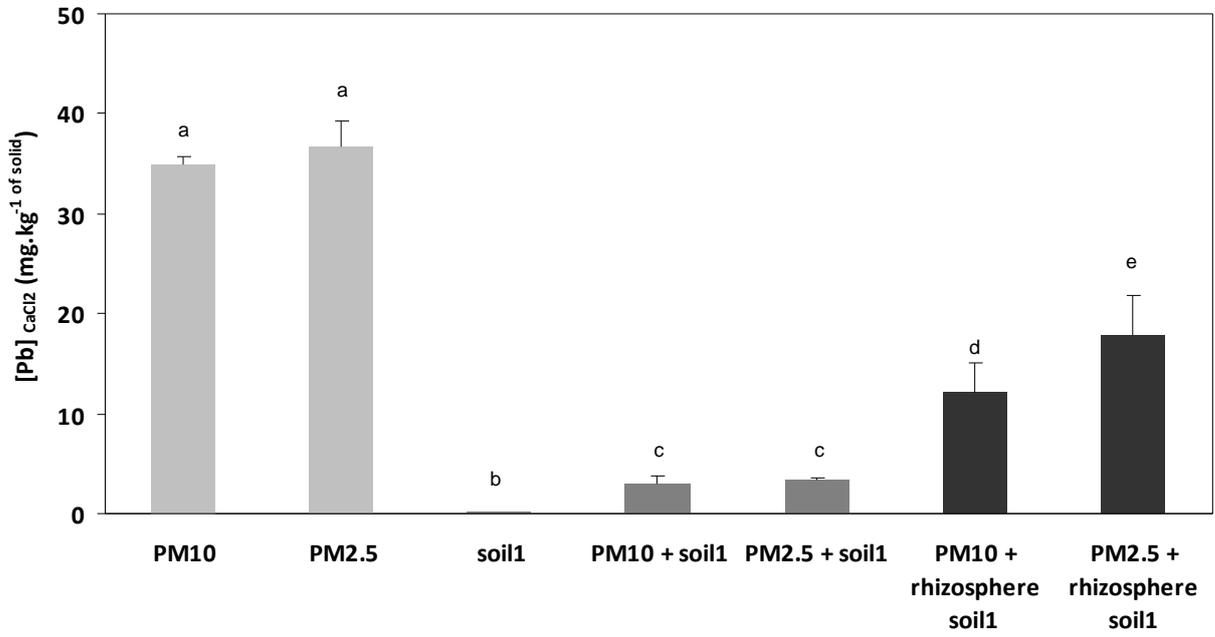
763

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Figure 4

765

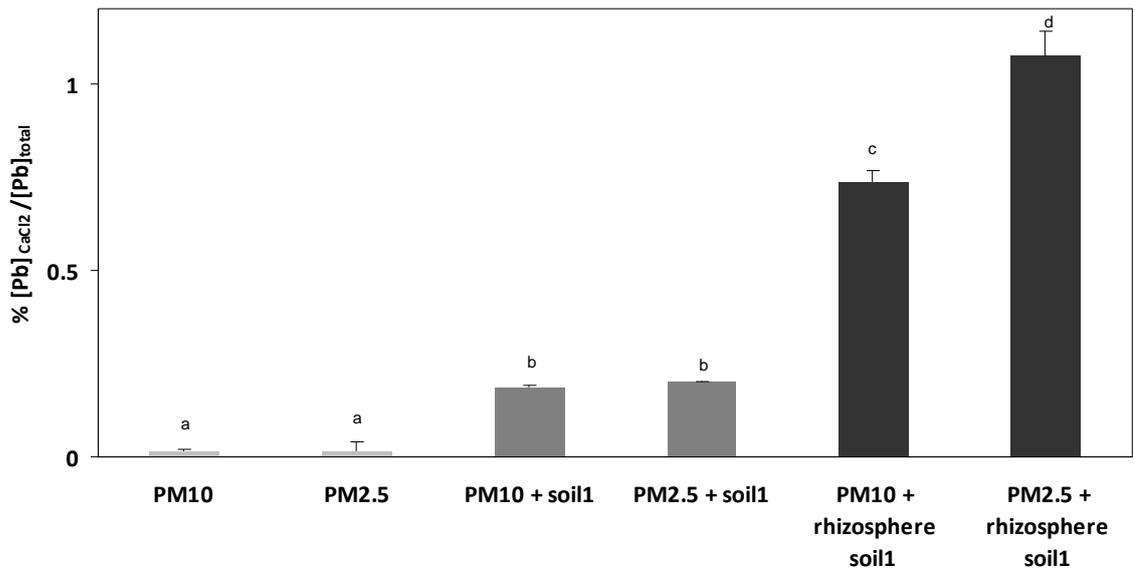
(A)



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767

(B)



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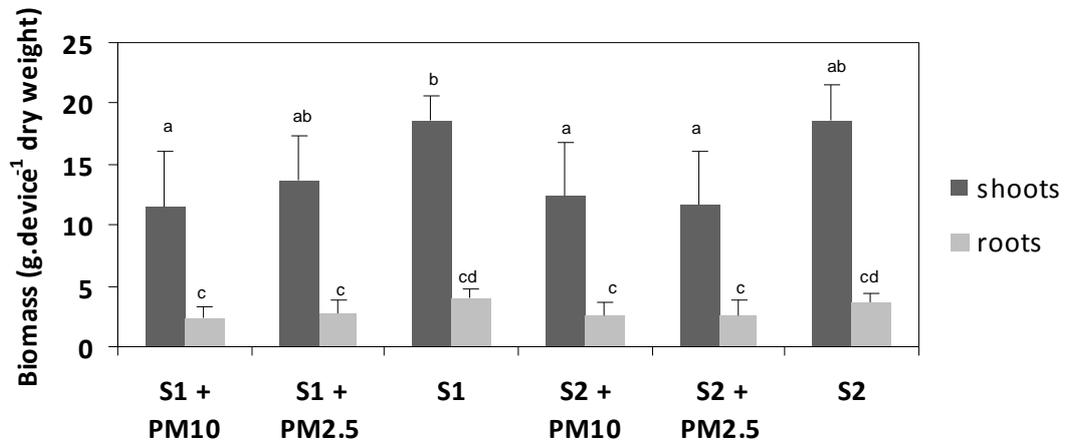
Figure 5

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Figure 6

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(A)

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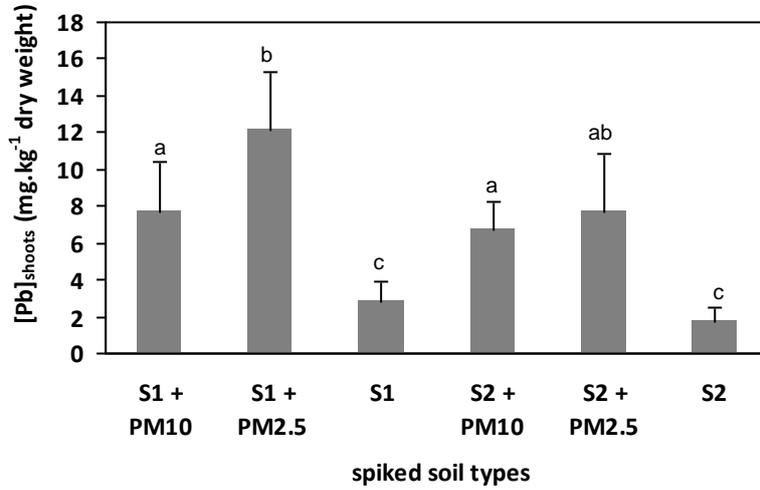
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786

(B)

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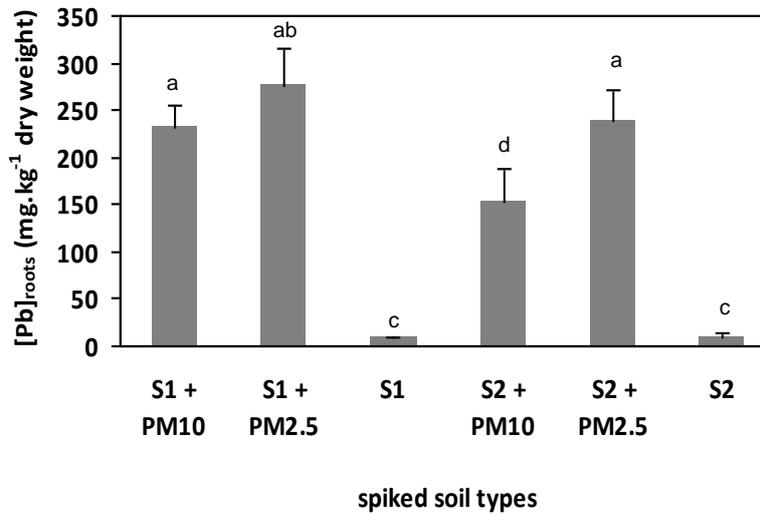
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(C)

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