Influence of metal process micronic and submicronic particles on vegetables quality and ecosystems.

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Abstract
Impact of atmospheric process particles enriched with metals (PM) on various vegetables was studied. Foliar metal interception was measured and calculated. Soil-plant transfer and phyto-toxicity were also studied. Influence of species and washing procedure on metal burning was observed. High correlation was obtained between measured and simulated lead plant uptake values. Ageing effect in polluted soils was highlighted with stabilisation or mobilization of metals in function of contact duration between soils and PM.

Key words: atmospheric fallouts, metal micronics and submicronic particles, Microtox, modelling, plants

Introduction
Micro and nano particulate matters (PM) are emitted in the environment by industrial activities. Carried from the air as fine particles, metals could become toxic for terrestrial ecosystem including plants and microbial communities (Doshi et al., 2008). Moreover, they involve risks for human health (Perrone et al., 2010). This study focused on a secondary smelter that recycles batteries releasing fine lead enriched particles in the atmosphere (Uzu et al., 2009 & 2010). The specific composition of these particles, as a mix of several metals, makes them chemically complex and different from the traditionally manufactured particles that are often monometallic synthetic models. The aim of the study was to investigate (i) metal uptake by various cultivated plants (lettuce, parsley and rey-grass) by measuring metal concentrations and their localisation in shoots, (ii) foliar interception modelling in lettuce (iii) the ecotoxicity of process PM by using two standardised tests (germination and Microtox).

Materials and methods
A secondary lead-recycling plant: STCM (Chemical Metal Treatment Company) was chosen as the experimental area for studying and modelling foliar interception of industrial atmospheric fallouts. The factory is located in the urban area of Toulouse, France (43°38'12'' N, 01°25'34'' E).
Particle characterisation: Laser granulometric analyses using a Malvern Mastersizer S had shown that emissions PM have a majority of fine particles (91 % are less than 10 µm). Their elemental total contents were determined by ICP-OES after heated digestion. Main metal contents in factory emissions were Cd, Sb, As, Cu, Zn and Pb at respectively 2.7, 1.8, 0.09, 0.09, 0.7 and 33.4 % (Uzu et al., 2011).
Metal concentration and interception modelling: various cultivated plants lettuce (*Lactuca sativa*) and parsley (*Petroselinum crispum*), vegetables currently cultivated in kitchen gardens with high foliar surfaces and short life-cycle; and rye-grass (*Lolium perenne L.*) main plant eaten by animals, were cultivated in pots containing each 4 kg of uncontaminated soil in the smelter courtyard under atmospheric fallouts for one month. Controls were kept under a non polluted atmosphere. A geotextile membrane was placed on the soil to protect it against atmospheric fallouts.
Industrial atmospheric fallouts in the smelter courtyard were measured using plastic Owen gauges. Climate variations: precipitations (mm), temperatures (°C) and hours of sunshine were recorded every day by a meteorological station. Five plants of each species were harvested every 2 weeks (every week for lettuce that is used for modelling); their shoots were cut, washed according to human or animal exposure scenario and dried. After acid mineralisation, samples were digested and analysed by ICP-OES and ICP-MS. Modelling was performed using the model described by Muller et al. (1993) adapted by Bonnard and Quiot (2009).
Standardised tests: For germination assay and Microtox test, three soils (with different properties) were amended with metallic particles from the smelter emissions up to three different concentrations in lead: [Pb] = 825 ± 15 mg kg^{-1} (C1) ; [Pb] = 1650 ± 20 mg kg^{-1} (C2) and 2475 ± 20 mg kg^{-1} (C3). Germination test and growth assays were carried out as described in the AFNOR X31-201 (AFNOR, 1982) and ISO11269-2 standard recommendations with modifications for PM studies as described by Lin and Xing (2007). The normalised Microtox test (AFNOR T 90-320, AFNOR, 1991 and ISO 11348, ISO, 2009) is used to determine the potential toxicity of liquid or solid samples on marine bacteria *Vibrio fischeri*, and by extension, toxicity on soil microbial activity. It measures the decrease in light emitted by the bioluminescent bacteria. Toxicity is reported as effective concentration EC50 (Barrena et al., 2009).

Results and Discussion

Metal concentrations in plants showed an accumulation of PM in shoots. Pb was the most accumulated metal. After 4 weeks, [Pb] raised: 122 ± 5.5 mg kg^{-1} dry weight (DW) of lettuce shoots (above the UE limit concentration in leave vegetables), 299 ± 33 mg kg^{-1} DW of parsley shoots and 700 ± 28 mg kg^{-1} DW of rye-grass shoots (not washed),

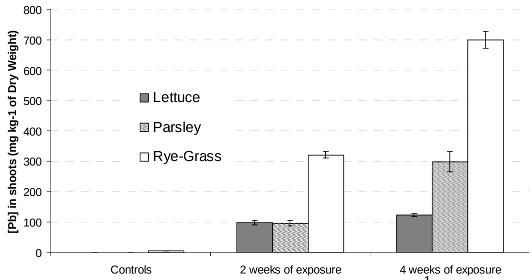
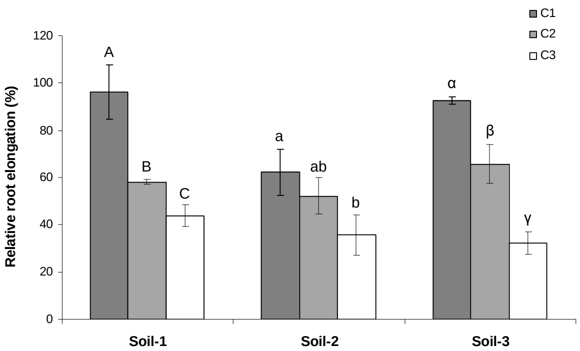


Figure 1: Lead concentrations (in mg kg^{-1} of dry weight ± SD) in lettuce, parsley and rye-grass after 2 and 4 weeks of exposure, compared to controls.

These differences in Pb accumulation could be explained by realistic washing methods (done by consumers) and plant accumulation capacity (due to their morphology and anatomy). Same results have been collected for other metals by ICP-MS (results not shown).

Comparison between modelling and experimental results (performed on lettuce) shows that our model is efficient to predict Pb concentration values in shoots (geometric mean = 1).

Ecotoxicity results show that metallic particles have a toxic effect on seedling growth (Figure 2), but lettuce germination was not affected (Lin and Xing, 2007).



Soil properties modify the amplitude of ecotoxicity.

Figure 2: Influence of PM concentration and soil properties on root growing

As reported by Strigul et al. (2009), PM influence bacteria metabolism (EC_{50} = 68.69 and 13.08 mg L^{-1} after respectively 5 and 15 min of contact), Figure 3.

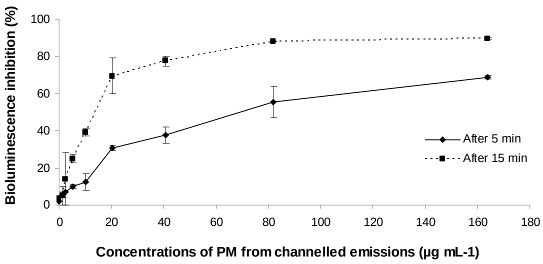


Figure 3: Effect of PM concentrations on bioluminescence inhibition for *Vibrio fisheri*.

Then, for our original experiment using process particles, results on toxicity to *Vibrio fisheri* bacteria move on the same way than phytotoxicity results.

Conclusions

Process atmospheric PM enriched with metals induced diffuse pollution in ecosystems. Metal deposition can constitute a risk for animals and humans who can absorb it in various ways such as plant ingestion. Thus, atmospheric pollution must be studied and controlled in the context of environmental and sanitary risk assessment.

References

AFNOR X31-201, 1982. Soil Quality – Test for the inhibition of seed germination by means of a substance. Paris, France.

AFNOR T90-320, 1991. Détermination de l'inhibition de la luminescence de *P. phosphoreum*. Paris, France.

R., Barrena, E., Casals, J., Colón, X., Font, A., Sánchez, V., Puntes. 2009. Evaluation of the ecotoxicity of model nanoparticles. Chemosphere 75: 850-857.

Doshi, R., B., Washington, C., Christodoulatos, Wazne, O'Connor, G. 2008. Nano-aluminium: Transport through sand columns and environmental effects on plant and soil communities. Environ. Res. 106 : 296-303.

ISO 11348, 2009. Qualité de l'eau - Détermination de l'effet inhibiteur d'échantillons d'eau sur la luminescence de Vibrio fischeri (Essai de bactéries luminescentes) – Paris, France.

Lin, D., B., Xing. 2007. Phytotoxicity of nanoparticles : Inhibition of seed germination and root growth. Environ. Poll. 150: 243-250.

Perrone, M.G., M., Gualtieri, L., Ferrero, C., Lo Porto, R., Udisti, E., Bolzacchini, M., Camatini. 2010. Seasonal variations in chemical composition and in vitro biological effects of fine PM from Milan. Chemosphere 78, 1368-1377.

Strigul, N., L., Vaccari, C., Galdun, M., Wazne, X., Liu, X., K., Jasinkiewicz. 2009. Acute toxicity of boron, titanium dioxide, and aluminum nanoparticles to *Daphnia magna* and *Vibrio fischeri*. Desalination 248: 771–782.

Uzu, G., S., Sobanska, S., P., Pradere, C., Dumat, C. 2009. Study of lead phytoavailability for atmospheric industrial micronic and sub-micronic particles in relation with lead speciation. Environ. Poll. 157: 1178-1185.

Uzu, G., S., Sobanska, G., Sarret, M., Munoz, C., Dumat. 2010. Foliar lead uptake by lettuce exposed to atmospheric fallouts. Environ. Sci. Technol. 44: 1036-1042.

Uzu, G., S., Sobanska, G., Sarret, J.J., Sauvain, P.Pradère, C., Dumat, 2011. Characterization of lead-recycling facility emissions at various workplaces: major insights for sanitary risks assessment. J. Haz. Mat. 186: 1018-1027.