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Toxicity in lead salt spiked soils to plants, invertebrates and microbial processes: Unraveling effects of acidification, salt stress and ageing reactions

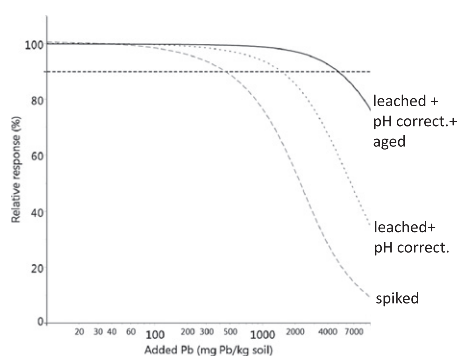
Erik Smolders [a,*], Koen Oorts [b], Sofie Peeters [a], Roman Lanno [c], Karlien Cheyns [d]

[a] *Division Soil and Water Management, K.U.Leuven, Kasteelpark Arenberg 20, B-3001 Leuven, Belgium*
[b] *ARCHE consulting, PJ Van Benedenstraat 4, box 203, B-3000 Leuven, Belgium*
[c] *Department of Evolution, Ecology, and Organismal Biology, Ohio State University; 318 W. 12th Ave, Columbus, OH, USA*
[d] *Veterinary and Agrochemical Research Centre (CODA-CERVA), Leuvensesteenweg 17, B-3080 Tervuren, Belgium*

HIGHLIGHTS

- Lead toxicty in spiked, unleached soils is primarily confounded by salinity stress.
- Toxcity of lead (Pb)to soil organisms in fully aged soils is only found above 1000 mg Pb/kg soil.
- Earthworms are more sensitive to lead (Pb) than plants or microbial processes.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate and effects of toxic trace metals in soil freshly spiked soluble metal salts do not mimic those of metals in the field. This study was set up to test the magnitude of effects of salinity, acidification, and ageing on toxicity of lead (Pb) to plants, invertebrates and soil microbial processes. Three soils were spiked with Pb^{2+} salts up to a concentration of 8000 mg Pb/kg and were tested either after spiking, after soil leaching followed by pH correction, or after a 5-year outdoor ageing period with free drainage followed by pH correction. Soil solution ionic strength exceeded 150 mmol/L in soils tested directly after spiking and this decreased partially after leaching and returned back to background values after 5-year outdoor equilibration. Chronic toxicity to two plants, two invertebrates, and three microbial endpoints was consistently found in all spiked soils that were not leached. This toxicity significantly decreased or became absent after 5 years of ageing in 19 of the 20 toxicity tests by a factor 8 (median factor; range: 1.4–>50), measured by the factor increase of total soil Pb dose required to induce 10% inhibition. The toxicity of Pb in leached soils was intermediate between the other two treatments. The lowest detectable chronic thresholds (EC10) in aged soils ranged 350–5300 mg Pb/kg. Correlation analysis, including data of Pb^{2+} speciation in soil solution, suggests that reduced ionic strength rather than acidification or true ageing is the main factor explaining the soil treatment effects after spiking. It is suggested that future toxicity studies should test fine PbO powder as a relevant source for Pb in soils to exclude the confounding salt effects.

* Corresponding author at: Laboratory for Soil and Water Management, K.U.Leuven, Kasteelpark Arenberg 20, B-3001 Leuven, Belgium.
E-mail address: erik.smolders@ees.kuleuven.be (E. Smolders).

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1. Introduction

Lead (Pb) is probably the first metal extracted from its ores by man and its widespread use since Roman times led to extensive environmental soil pollution (Steinnes, 2013). The human health effects are well documented but effects on soil-dwelling organisms due to soil Pb contamination have been surprisingly difficult to identify in the field. For example, in soils sampled at shooting ranges with total soil Pb concentrations up to 2400 mg Pb/kg, toxic effects to the springtail *Folsomia candida* or to the enchytraeid *Enchytraeus crypticus* were more related to the acid soil pH than to elevated soil Pb (Luo et al., 2014a; Luo et al., 2014b). Lead occurs as the Pb^{2+} ion that has the greatest binding strength in soil among the most commonly studied toxic metals Cd, Cu, Co, Zn, Ni, and Pb (Degryse et al., 2009) and the strong immobilisation of Pb^{2+} is perhaps explaining the relatively low toxicity to organisms exposed to soil Pb via the soil solution.

There is a reasonably large set of Pb toxicity data from laboratory studies conducted using soils freshly spiked with Pb^{2+} salts. Such laboratory data suggest that Pb toxicity occurs near the natural soil background range of Pb (2–200 mg Pb/kg). No Observed Effect Concentrations (NOECs) or 10% effect concentrations (EC10) can be found as low as 50 or 100 mg/kg (added Pb) for barley and oat (Aery and Jagetiya, 1997; Khan and Frankland, 1984) 129 mg/kg for earthworms (Bengtsson et al., 1986) and 150 to 200 mg/kg for soil microbial respiration and N-mineralization (Chang and Broadbent, 1982; Doelman and Haanstra, 1984). The toxicity in soils freshly spiked with soluble metal salts overestimate toxicity in corresponding field-contaminated soils due to lack of sufficient equilibration time in the spiked soils (lack of ageing) and to confounding factors such as higher salinity and acidification. For different metals, empirical 'leaching–ageing' or 'lab-to-field' factors translating that difference have been identified in toxicity tests and adopted in risk assessment, however, for Pb this factor is not well established (Smolders et al., 2009). The toxicity of Pb to *F. candida* in environmentally contaminated soils was compared with corresponding soils spiked with $Pb(NO_3)_2$ (Lock et al., 2006). The Pb doses required to reduce the reproduction of *F. candida* in freshly spiked soils by 50% ranged 2200–3200 mg Pb/kg and corresponding doses in the field contaminated soils were at least a factor of two larger. In a field trial conducted in Nagyhörcsök (Hungary) in 1991 (Kádár et al., 1998), Pb was applied as $Pb(NO_3)_2$ at three rates with the highest application rate equivalent to about 250 mg added Pb/kg soil. During the first year after application, the grain yield of maize was significantly reduced by 28% at the highest Pb application whereas toxic effects disappeared in subsequent years.

The fraction of isotopic exchangeable metal in soil is a suitable index to identify the 'ageing' reaction and to denote the difference in metal (Zn, Cu) toxicity between soils freshly spiked with metal salts and well equilibrated soils or field-contaminated soils (Hamels et al., 2014). No such comparison between isotopic exchangeable metals and metal toxicity has yet been made for Pb but the chemical data suggest that the ageing reactions of Pb are not strongly pronounced. For example, the isotopically exchangeable Pb fraction is only 2-fold larger in freshly spiked soil compared to field contaminated soils (Degryse et al., 2007). An extensive survey in a British catchment affected by Pb mining showed that the isotopically exchangeable Pb fraction was 80% in most acid soils, decreasing to about 30% near pH 7 (Marzouk et al., 2013). This study also showed that Pb was clearly more labile than zinc. Soils contaminated by petrol-derived Pb also had somewhat larger isotopically exchangeable Pb fractions than soils in which Pb was derived from sewage sludge application or from Pb-containing minerals (Mao et al., 2014).

Toxicity in Pb^{2+}-salt spiked soils is confounded by the associated pH decrease (Speir et al., 1999) which results from the displacement of protons by Pb^{2+} on the sorption surfaces. In addition, application of Pb^{2+} salts (e.g., $PbCl_2$) increases the salinity of the soil solution and may induce salinity stress (Stevens et al., 2003). These factors do not occur where atmospheric deposition of the alkaline PbO (e.g., Pb smelters) is the source of soil Pb or where the emissions are gradual, thereby allowing time for leaching of excess salts. The confounding effects of salinity and acidification on metal toxicity are found for all metals but these confounding factors become increasingly important for those metals where large doses, e.g. >20 mmol divalent metal/kg soil, are required to elicit a response. Such might be the case for Pb because of its large immobilisation in soil. It was calculated that leaching is essential for the identification of genuine Pb toxicity to plants in soils with pH > 5 where strong Pb^{2+} sorption requires high Pb^{2+} salt doses to invoke toxicity (Stevens et al., 2003). Leaching, however, does not remove the acidification induced by the sorption of Pb^{2+} on the variable charge binding sites in soil. Leaching of soil reduced toxicity of copper (Cu) salt amended soils to barley seedlings and it was shown that the additional Ca uptake in non-leached soils (due to increased solution Ca^{2+} in spiked, non-leached soils) contributes to the confounding factors (Schwertfeger and Hendershot, 2013b).

This study was designed to compare Pb toxicity between well equilibrated, leached, and pH-corrected soils and soils freshly spiked with Pb^{2+} salts and to identify factors involved in that difference. Lead toxicity in spiked soils was tested in soils under three treatments after spiking, i.e. spiked, spiked + leached + pH corrected, or aged (5 years) after spiking with leaching and pH correction. These different treatments allow the separation of the different factors altering toxicity (i.e., salinity, acidification, equilibration time) and may suggest which soil manipulations are required for normalizing the results of Pb toxicity tests conducted in freshly-spiked to field-contaminated soils. The toxicity tests in this study included a variety of organisms (plants, soil microbial processes and invertebrates) to cover a range of organisms with potentially different exposure routes.

2. Materials and methods

2.1. Experimental design

Three different soils were spiked with Pb salts and toxicity was compared among three treatments with stepwise increasing complexity, i.e. (A) freshly spiked soils, (B) spiked soils which are leached and pH corrected and (C) spiked but aged soils, the latter including the leaching and pH correction. Toxicity was measured with six different assays (7 endpoints) and thresholds are reported as metal concentrations measured in soils after each soil treatment.

2.2. Soil sampling and characterization

Three uncontaminated topsoils with varying soil properties were collected from Spain (BA), the United Kingdom (WB) and Belgium (TM). The soil BA was from arable land and classified as calcic luvisol, contained 16% clay and 10% $CaCO_3$; soil WB was from grassland and classified as dystric luvisol, containing 30% clay. Soil TM was from arable land and classified as haplic luvisol with 12% clay. Soils were collected with a metal spade from the plough layer, or for grassland, from the surface horizon after clearance of the grass thatch layer. The time between sampling and cold storage was never more than one week, followed by storage at 4 °C until drying. The soils were air-dried, sieved through a 4-mm sieve, and stored at room temperature prior to soil characterization and spiking.

The carbon concentration in soil was measured by ignition with an elemental analyzer (EA112, CE instruments). Organic carbon was calculated as the difference between total C and carbonate C. The carbonate C was determined from pressure increases after addition of HCl to the soil in closed containers (including $FeSO_4$ as a reducing agent). Soil moisture at pF 0 (saturation) and pF 1.9 (80 cm suction) was determined by the sandbox method using 100 cm^3 soil cores (P1.80-1, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands). Aqua regia–soluble metal concentrations in all soil treatments, including unspiked