Influence of soil type and land use on the nature of mobile colloids: implications for the metal transfer in soils

<u>CITEAU Laëtitia</u>, LAMY Isabelle, van OORT Folkert and ELSASS Françoise

INRA, Unité de Science du Sol, RD 10, 78026 Versailles cedex, France

Abstract

In this study, natural colloids circulating in gravitational waters were collected in situ with zero-tension lysimeters from different type of soils located in the same area contaminated by trace metals (Zn, Cd, and Pb). An agricultural soil (Luvisol), a forest soil (Podzol) and a soil under a metallophyte grassland (Luvisol) were chosen. Characterisation and localisation of trace metals on colloids were performed by transmission electron microscopy coupled with Energy Dispersive X-ray Analysis (AEM). Mobile colloids were found to be different according to soil type and land use. In the podzol, organic colloidal matter migrates in association with Fe and Al. In the luvisols the nature of colloids is closely linked to the leaching of clay and iron. Colloids containing Zn were organic (bacteria) or mineral (phyllosilicates, Fe-oxyhydroxydes and Ca- or Al-phosphates). 70 to 90 % of Pb was present in colloidal form except for the forest soil whereas Zn and Cd were mostly in dissolved form. The partitioning of metals in solutions in different fractions according to their metal form stability was done by an ion exchange method. Pb was in the form of stable or slowly labile complexes whereas Zn and Cd were essentially in the form of free ion or labile complexes. The stability of Pb-forms and the main presence of colloidal forms of Pb can be related in soil solutions. Consequently colloids seem to be implicated in the Pb transfer in soils whereas their role for Zn and Cd seem to be minor depending on soil type.

Keywords: mobile colloids, gravitational water, heavy metals, land use, analytical electron microscopy

Introduction

Mobile soil colloids have been extensively studied in recent years for their implications in contaminant transport through the soils and for their potential impact on the groundwater quality (Denaix *et al.*, 2001; Karathanasis, 1999). However colloidal transport of contaminants was rarely evidenced in field studies but especially by laboratory column experiments. Consequently, data on the importance of colloid-facilitated transport of contaminants under real field situations are necessary (Kretzschmar *et al.*, 1999).

A large variety of organic and inorganic materials may be found in colloidal forms in soil solution. These colloids are either directly inherited from soil (phyllosilicates, oxides, mineral weathering products, humic substances) or neoformed in soil solution (carbonates, Fe-, Al-, Ca-phosphate). The nature of mobile colloids in soils can be influenced by soil physico-chemical characteristics and by the chemistry of soil solution. Due to the scarcity of field studies, little is known about the chemical composition of mobile colloids circulating in soil solution according to the soil type and to our knowledge no information exists on the effects of land use on the presence and the nature of colloids in soil solution.

Therefore in this work, the studied colloids were natural colloids circulating in gravitational waters of soils, collected *in situ*. The aims of this study were: (i) to determine the importance of the nature of soil on the nature of mobile colloids; (ii) to determine the speciation of metals in gravitational waters in distinguishing soluble and colloidal forms; and (iii) to assess the role of colloids in the transfer of trace metals through soils to groundwater.

Materials and Methods

A specific site was chosen for this study, where soils were contaminated for 60 years by industrial atmospheric fallout containing mainly Zn, Pb, and Cd produced by a zinc-smelter complex (van Oort *et al*., 2001b). Three soils different in type and in land use were selected in the agricultural perimeter of the former industrial complex: a luvisol, cultivated in maize, a forest soil (a Podzol) under *Pinus sylvestris* stand and a highly polluted soil under a metallophyte grassland (Luvisol). The main physico-chemical characteristics of the soils studied are given in Table 1.

Table 1 Main physico-chemical characteristics of the soils (surface horizon).

Land use	Soil type	pH	Metal content in soil (surface horizon) mg kg^{-1}			Mineralogy (X-ray diffraction)
			Zn	Cd	Pb	
Agricultural soil	Luvisol	6.5	400	3.5	100	Quartz, Feldspath, kaolinite, illite, smectite
forest	Podzol	4.0	150	2	240	Quartz, feldspath, kaolinite, illite
Metallophyte grassland	Luvisol	6.0	2,400	33	520	Quartz, feldspath, illite, smectite, chlorite

Gravitational water was collected *in situ* by zero-tension lysimeters placed at the lower part of the pedological horizons of soils. In this work, results will be given for the surface horizon. Gravitational water was collected at least once a month depending on rain events during 2 years. The collected soil solutions were filtered at 5 µm and ultracentrifugated at 270,000 g during 270 min to isolate soil colloids on a microgrid. The supernatant containing the dissolved fraction was pipetted and acidified before analysis. The proportion of metals in colloidal forms was calculated from the difference in metal concentrations before and after ultracentrifugation. The colloidal phases deposited on Ti or Au microgrids during the ultracentrifugation were characterised and trace metals were localised on these colloids by coupling transmission electron microscopy observations (TEM Philips 420 at 120 kV) with elemental chemical analysis using an energy dispersive spectrometer (EDS Link).

Tests of stability of metal forms in solution were performed by using an ion exchange method derived from that developed by Holm *et al*. (1995). Metal forms were separated in three fractions according to an operationally defined stability design by using different contact times with a cation exchange resin (Chelex 100): (i) the free ions and labile complexes, (ii) the slowly labile complexes and (iii) the stable complexes.

Results and Discussion

Nature of soils and nature of colloids (Citeau *et al.*, 2001)

In gravitational waters collected in the plough-layer of the agricultural soil (Figure 1a), a mixture of mineral and organic colloids with variable nature was observed. Organic colloids existed frequently as biocolloids (bacteria, fungi) and also as organic matter either isolated or as coatings on mineral colloids. The latter were dominantly inherited from the soils (phyllosilicates and iron oxi-hydroxides). Neoformed inorganic colloids (Ca- and Al-rich phosphates) were also observed probably due to fertilisation practices in agricultural soils.

Colloids in gravitational water collected from O and A horizons of the podzol (Figure 1b) were dominantly organic. The organic phases were amorphous and were found frequently in association with Fe and Al oxi-hydroxides.

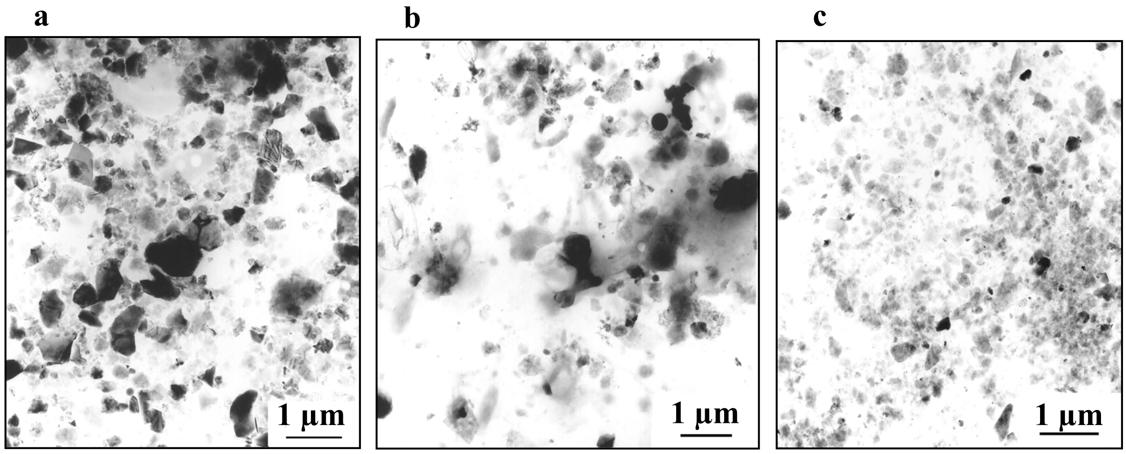

Figure 1 Transmission electron microscopy (TEM) images of colloids isolated from gravitational waters of the surface horizons of **a.** the agricultural soil, **b.** the forest soil and **c.** the soil under the metallophyte grassland.

In the soil solution collected in the surface horizon of the soil under the metallophyte grassland (Figure 1c), exclusively mineral colloids inherited from the soil were observed, such as phyllosilicates and iron oxi-hydroxides. The absence of colloidal organic compounds in spite of the presence of overlying litter and organic matter-rich horizons as well as the absence of biocolloids seem to be related to the biogeochemical disfunctioning of this highly polluted soil (Table 1) (Balabane *et al.*, 1999; van Oort *et al.*, 2001a).

The nature and the morphology of colloids circulating in gravitational waters of selected soils appeared closely linked to the soil functioning (Podzol, Luvisol). In the Podzol, organic colloidal matter migrates in association with Fe and Al and in the luvisols the nature of colloids appears related to the leaching of clay and iron. Moreover, land management such fertilisation practices can induce the formation of new colloids such as colloidal Ca- or Al-phosphate phases in the soil solution of the agricultural soil. In the same way, a biological disturbance induced by a strong metal pollution seems to have a consequence on the colloidal composition of the soil solution such as the absence of organic and biocolloids.

Importance of metal colloidal phases

The importance of metal colloidal phases are presented Figure 2 for all the results obtained during 24 months of monitoring. Percentage of colloidal forms for each metal vary with time, and with the soil type. Nevertheless, in the forest soil, all metals were essentially in dissolved form probably due to the low pH of the soil solution (pH between 3.5 and 4). In gravitational waters of both luvisols, Pb was dominantly in colloidal form (70 to 90 %) whereas for Zn and Cd the importance of the colloidal phases varied according to the land use. Indeed, for the soil under the metallophyte grassland, 40 to 50 % of Zn and Cd were present in colloidal forms whereas for the agricultural soil they were essentially in dissolved form.

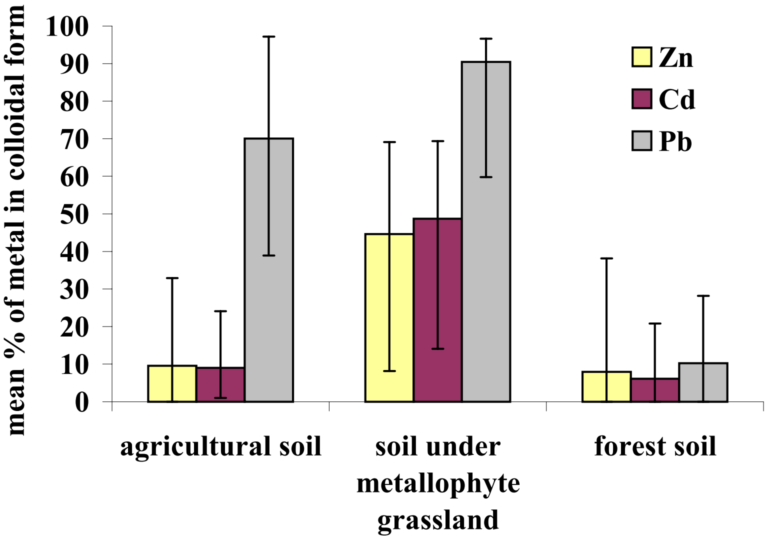

Figure 2 average percentage of metals in the colloidal form in gravitational water of the surface horizon of the agricultural soil, the soil under the metallophyte grassland and the forest soil.

The importance of metal colloidal phases in the gravitational waters of soils is related to the chemistry of the soil solution (pH, organic carbon) and probably to the nature of colloids which is governed by soil type and land use.

Colloidal forms of metals

Different colloidal forms of metals were found, organic or mineral. Only Zn and sometimes Pb were detected by EDS due to the relatively high EDS detection limit (approximately 500 mg kg^{-1}).

50 to 75 % of the analysed particles for respectively the agricultural soil and the soil under the metallophyte grassland contained Zn whereas in the forest soil only a minority of colloidal particles contained Zn. For the gravitational waters of the agricultural soil and the soil under metallophyte grassland, Zn was found associated with phyllosilicates inherited from the soils, mostly smectites and interstratified clays associated with high amounts of iron. Some individual particles of Fe-oxyhydroxydes were also carrier of Zn. In the agricultural soil, Zn was also detected associated with Al-

or Ca-phosphates. Biocolloids (bacteria, fungi) (Figure 3) and organic matter, either isolated or as coatings on mineral colloids were found associated with Zn in the gravitational waters of surface horizons of the forest soil and the agricultural soil.

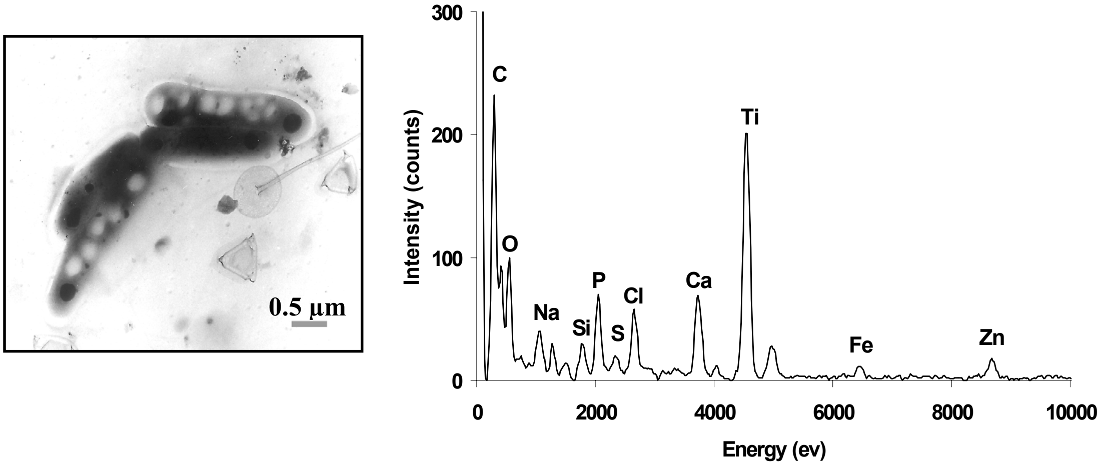

Figure 3 TEM image and EDS analysis of bacteria containing Zn.

Stability of metallic forms in solution

The results of the ion exchange method applied to gravitational waters of surface horizons of the three soils studied after a 5 µm filtration are shown in Figure 4 for Zn and Pb.

Almost all Zn (and also Cd not shown) was present in soil solution as free ion or labile complexes (> 95 %) for the three soils. Pb was also dominantly in a free-ion form or as labile complexes in gravitational waters of the forest soil whereas for the agricultural soil and the soil under the metallophyte grassland slowly labile and stable complexed forms can be found in significant amounts. As already shown (Figure 2), Pb was in majority in colloidal form for these two soils whereas in the forest soil Pb was essentially in dissolved form. The presence of slowly labile and stable complexes of Pb in soil solution can be associated to the presence of colloidal forms.

Conclusion

Specific soil physico-chemical conditions, induced by soil type and land management, govern the nature of colloids circulating in gravitational waters. Our results show that colloids are involved in the mobilisation of metals but their importance depends on the metal, the soil type and the land use. Pb was found in majority in colloidal form (except for the forest). It is hypothesized that links between colloids and Pb are stable. Consequently colloids could have a real role in facilitating the transport of Pb through the soil profile. Zn and Cd are mostly found in dissolved form (except for the soil under the metallophyte grassland) as free ions or labile complexes. Then these metals can likely interact with reactive soil constituents during migration towards the water table and colloids seem to have only a minor role in their transport through the soil profile.

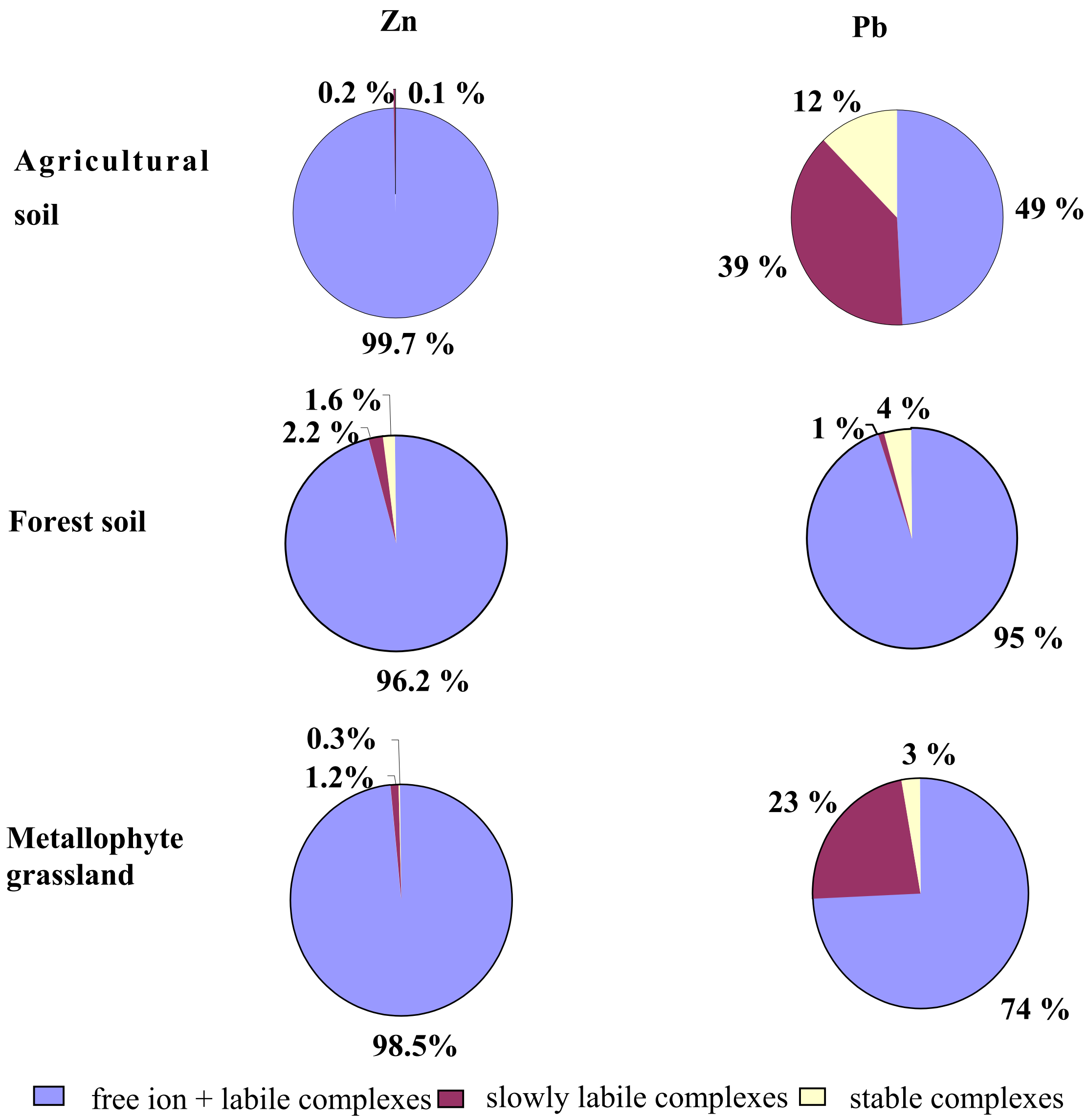

Figure 4 Distribution of metal forms according to their stability with the resin Chelex in gravitational waters of surface horizons of the three soils studied.

Acknowledgements

This study was supported financially by the French ministry of environment (no 98142) and by a grant from ADEME for L.C.

References

Balabane, M., D. Faivre, F. van Oort and H. Dahmani-Muller. 1999. Mutual effects of soil organic matter dynamics and heavy metals fate in a metallophyte grassland. Environ. Pollut. 105:45-54.

Citeau, L., I. Lamy, F. van Oort and F. Elsass. 2001. Nature of soils and nature of mobile colloids in gravitational water: a field study. C.R. Acad. Sci., Earth and Planetary Sciences, 332:657-663.

Denaix, L., R.M. Semlali and F. Douay. 2001. Dissolved and colloidal transport of Cd, Pb, and Zn in a silt loam soil affected by atmospheric industrial deposition. Environ. Pollut. 114:29-38.

Holm, P.E., T.H. Christensen, J.C Tjell and S.P. McGrath. 1995. Heavy metals in the environment, speciation of cadmium and zinc with application to soil solutions. J. Environ. Qual. 24:183-190.

Karathanasis, A.D. 1999. Subsurface migration of copper and zinc mediated by soil colloids. Soil Sci. Soc. Am. J. 63:830-838.

Kretzschmar, R., M. Borkovec, D. Grolimund and M. Elimelech. 1999. Mobile subsurface colloids and their role in contaminant transport. Adv. Agron. 66:121-193.

van Oort, F., M. Balabane, H. Dahmani-Muller, A.G. Jongmans and J. Nahmani. 2001a. Approche intégrée du fonctionnement d'une pelouse métallicole. *In* Baize, D. and M. Tercé (eds.). les éléments métalliques dans les sols. Approches fonctionnelles et spatiales, Inra-Editions, Versailles.

van Oort, F., J.P. Gaultier, R. Hardy and H. Bourennane. 2001b. Distributions spatiales et stratégies d'échantillonnage. *In* Baize, D. and M. Tercé (eds.). Les éléments mé talliques dans les sols. Approches fonctionnelles et spatiales, Inra-Editions, Versailles.