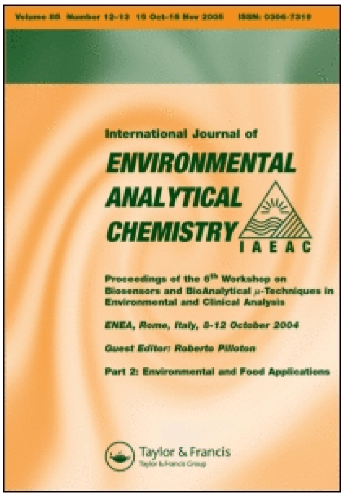

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MOBILITY OF HEAVY METALS IN SOIL PROFILES

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Mobility is a concept frequently used in soil science to estimate the risk of contamination of other environmental compartments. However some confusion exists over the definition of mobility, originating from the fact that this term is used in different fields. Consequently many operational parameters have appeared in relation to mobility estimation. This leads to great difficulties in comparatively interpreting practical data obtained under different conditions, and especially the biological significance of mobility. A standardization of the definition of mobility, taking into account the time scale, should be recommended.

Practical results obtained in reconstituted soil-vegetation systems are discussed, with a particular emphasis on the "mobility" of Cd, Cu and Zn. Several definitions were used to estimate the movement of heavy metals in the studied systems, i.e. the metal exports by plants or by gravitational water and the distribution of metals in the soil profile; this led to opposite conclusions about the mobility order of the three considered metals. However this apparent discrepancy can be resolved by taking into account the chemical species in the liquid phase.

KEY WORDS: Heavy metals, soil profiles, mobility, export balances, speciation.

INTRODUCTION

Mobility is a concept frequently used in soil science to estimate the risk of contamination of other environmental compartments by toxins, and especially by heavy metals[1,2]. However some confusion exists over the definition of mobility, originating from the fact that this term is used in different fields. Some environmental scientists will be particularly attentive to mass flows through ecosystems, to the possible contamination of food chains or of surface and ground water[3]; others are interested in the fertility and biological activity of soils and will focus on toxicity evaluation; other workers are more interested in the physico-chemical processes governing the migration and/or immobilization of metals in the soil and, as metal movements occur principally when the metals are in the aqueous phase in a dissolved form or associated with colloidal particles, will study essentially the solubility of metals or the reactivity and the fixation capacity of the soil surfaces[4–8]. Consequently many operational parameters appear in relation to mobility estimation, and this leads to great difficulties in comparatively interpreting practical data obtained under different conditions. Another difficulty arises from a confusion about the time scale: the definition of the mobility based on the quantitative determination of metal flows deals with already mobilized metals, the analysis of the soluble fraction concerns the metals actually in movement and the data obtained by a sequential extraction procedure give an indication of the potentially mobilizable metals. Some soil scientists use a mobility function with the determination of a soluble metal/total metal ratio under changing chemical conditions (pH, ionic strength or total metal load) to simulate the modification of environmental conditions[9–11]. This procedure seems to be the most promising for obtaining data to be used in predictive models, but additional work must be achieved to describe in a more quantitative way the time variation of the pH and of the total metal load of the soils and the consequent modifications which may occur in the soils.

In this work, mobile metals are considered as metal mass flows from the topsoil in other environmental compartments, namely the vegetation, the mineral subsoil and the gravitational water, and refer to the metals mobilized during the duration of the experiment or, in other words, to export balances. However, the estimation of mobility based on mass flows in plants, in subsoil and in water can lead to opposite conclusions about the mobility order of three heavy metals, cadmium, copper and zinc, even in a simple, modelized soil system. But, and this is the aim of the paper, this apparent discrepancy can be resolved by taking into account the chemical species in the liquid phase.

Material and methods

In an experiment planned to study movements of heavy metals in model soil profiles, we reconstituted soils in polyethylene lysimeters with sandy substratum as mineral subsoil and composted sludge as organic topsoil[12]. The experimental scheme used is shown in Figure 1. It was a three crossed factors experimental design: vegetation factor, with or without, pollution level factor, low or high total metal load of the

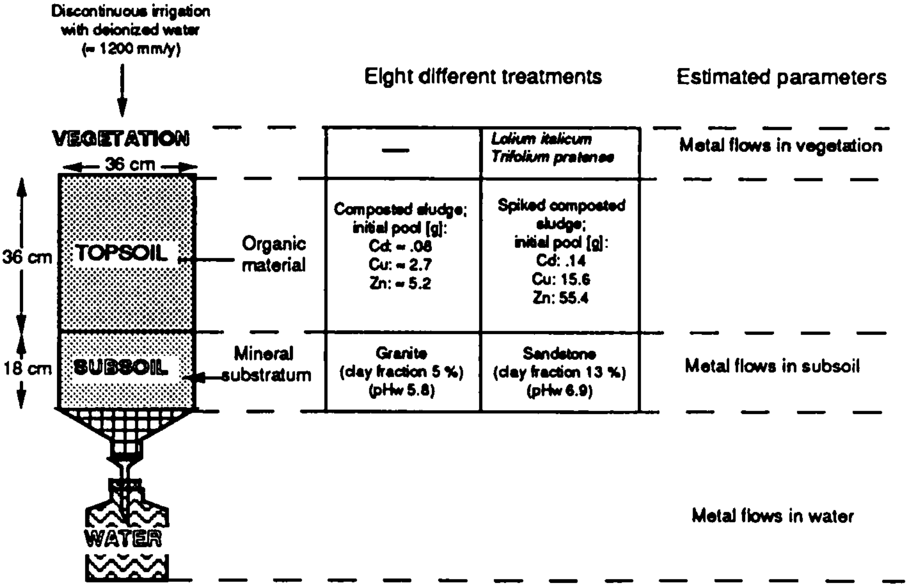

Figure 1 Flow chart of the experimental scheme used with various types of model soil systems.

composted sludge, mineral substratum factor, granite or sandstone. Eight model systems (four replicates) are compared. The metal flows in plants, in mineral subsoil and in water were assessed at the end of the experiment duration (from May 1985 through September 1988). The relationships between the different chemical parameters of the water were evaluated with simple and multiple correlation and regression analysis and the effects of treatments with variance analysis.

RESULTS AND DISCUSSION

Export balances

The export balances are presented in Table 1 and have already been discussed in detail for the vegetation and water[13]. These metal flows out of the topsoil varied from one system to another, from one compartment to another and from one metal to another. For each treatment and each compartment, a mobility order can be found based on the extent of relative metal flows; these mobility orders are presented in Table 2.

In the vegetation compartment, mobility orders are identical for each treatment, with the mobility of zinc greater than the mobility of cadmium greater than the mobility of copper; it is however not the case for the subsoil and water compartments.

Moreover, in the same treatment, the estimation of mobility by mass flows in the three compartments can lead to opposite conclusions about the mobility order of the three considered metals.

Figure 2 presents the relative metal flows for the treatment composted sludge on granite, the system having the widest range of pH and organic carbon load in the lysimetric water. The blocks are proportional to the losses by leaching in the gravitational water (grey blocks) and by absorption by plants (white blocks). If the mobility is measured by the extent of leaching, then Cu is more mobile than Zn, which is more mobile than Cd. If the mobility is measured by absorption by plants, then Zn is the more mobile metal, then Cd and Cu. An anomaly appears in the behaviour of copper which can be considered, in the same modelized system, as the more or less mobile metal depending on the point of view of the observer.

The effects of treatments on the exported metals in vegetation, mineral subsoil and gravitational water were evaluated with a variance analysis. Significant factors, with probability levels, are shown in Table 3. The substratum quality and pollution level of the composted sludge had a significant effect on the extent of metal exports in the gravitational water; this is not true for the exported metals in the vegetation, where the pollution level of compost alone is the influential factor for Cd and Cu export, the pollution level and the mineral substratum exerting an effect only on Zn export, nor for the export of metals in mineral subsoil, where only the pollution level of compost was a significant factor. The information obtained in the water compartment was characteristic of the different treatments. The composition of the gravitational waters, resulting from the interactions between the liquid and solid phases of soil, may give more valuable information to elucidate the different chemical reactions

Table 1 Metal export balances after a period of four years for the eight studied treatments. Metal quantities are given in mg, the italic figures refer to the proportion of initial pool of metal in compost.

		Compost/Granite				*Compost/Sandstone*			
Exported cadmium	Invegetation	no veg.		0.37	*0.43%*	no veg.		0.27	*0.38%*
	In subsoil	1.33	*1.56%*	0.39	*0.45%*	0.03	*0.05%*	n.d.	
	In waters	0.04	*0.05%*	0.04	*0.04%*	0.01	*0.02%*	0.01	*0.02%*
	Total	1.37	*1.61%*	0.79	*0.92%*	0.04	*0.06%*	0.28	*0.40%*
Exported zinc	In vegetation	no veg.		91.36	*1.62%*	no veg.		75.24	*1.60%*
	In subsoil	406.00	*7.20%*	361.90	*6.42%*	124.40	*2.65%*	133.80	*2.85%*
	In waters	6.31	*0.11%*	4.91	*0.09%*	3.34	*0.07%*	5.27	*0.11%*
	Total	412.31	*7.31%*	458.17	*8.13%*	127.74	*2.72%*	214.31	*4.56%*
Exported copper	In vegetation	no veg.		6.02	*0.21%*	no veg.		5.26	*0.22%*
	In subsoil	103.40	*3.58%*	93.10	*3.22%*	54.64	*2.24%*	136.70	*5.61%*
	In waters	9.19	*0.32%*	5.16	*0.18%*	4.41	*0.18%*	2.52	*0.10%*
	Total	112.59	*3.90%*	104.28	*3.61%*	59.05	*2.42%*	144.48	*5.93%*
		Spiked compost/granite				*Spiked compost/sandstone*			
Exported cadmium	In vegetation	no veg.		0.14	*0.10%*	no veg.		0.11	*0.08%*
	In subsoil	15.51	*11.00%*	16.92	*12.00%*	10.05	*7.13%*	10.09	*7.16%*
	In waters	0.76	*0.54%*	0.80	*0.57%*	0.12	*0.08%*	0.08	*0.06%*
	Total	16.27	*11.54%*	17.86	*12.67%*	10.17	*7.21%*	10.28	*7.29%*
Exported zinc	In vegetation	no. veg		282.65	*0.51%*	no veg.		174.16	*0.31%*
	In subsoil	2252.00	*4.06%*	2535.00	*4.57%*	2590.00	*4.68%*	1799.00	*3.25%*
	In waters	1276.89	*2.30%*	1074.25	*1.94%*	270.62	*0.49%*	234.96	*0.42%*
	Total	3528.89	*6.37%*	3891.89	*7.02%*	2860.62	*5.17%*	2208.12	*3.99%*
Exported copper	In vegetation	no veg.		4.32	*0.03%*	no veg.		3.47	*0.02%*
	In subsoil	495.60	*3.18%*	689.10	*4.42%*	616.80	*3.97%*	634.30	*4.08%*
	In waters	88.17	*0.57%*	99.66	*0.64%*	24.01	*0.15%*	32.40	*0.21%*
	Total	583.77	*3.75%*	793.08	*5.09%*	640.81	*4.12%*	670.17	*4.31%*

Table 2 Mobility orders estimation based on relative metal export balances after a period of four years.

Mobility estimation by	*Treatment*	*Mobility order*
Absorption in plants (% initial pool)	compost/granite	Zn > Cd > Cu
	compost/sandstone	Zn > Cd > Cu
	spiked compost/granite	Zn > Cd > Cu
	spiked compost/sandstone	Zn > Cd > Cu
Translocation in mineral (% initial pool)	compost/granite	Zn > Cu > Cd
	compost/sandstone	Cu > Zn > Cd
	spiked compost/granite	Zn > Cd > Cu
	spiked compost/sandstone	Zn > Cd > Cu
Leaching in water (% initial pool)	compost/granite	Cu > Zn > Cd
	compost/sandstone	Cu > Zn > Cd
	spiked compost/granite	Zn > Cu ≈ Cd
	spiked compost/sandstone	Zn > Cu > Cd

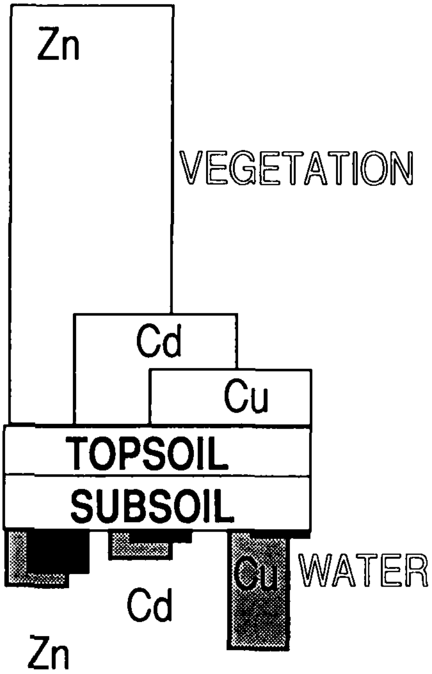

Figure 2 Metal flows in water and in vegetation after a period of four years for the system compost/granite. The white blocks represent the total exported metals in vegetation and the grey ones the total exported metals in water; the black blocks are an estimation of the flows of free metals in water (see text for further explanations). The areas of different blocks are proportional to the exported quantities of metals relative to the initial pool in compost.

Table 3 Analysis of variance of export balances.

Exported metals	*In vegetation*			*In mineral horizon*			*In waters*		
	S	*C*	*S* × *C*	*S*	*C*	*S* × *C*	*S*	*C*	*S* × *C*
Zinc	***	***	***		***		***	***	***
Copper		***			***		***	***	***
Cadmium		***		**	***		***	***	***

S: "mineral Substratum" factor.
C: "Compost" factor.
S × C: Substr.-Comp. interaction.
Accepted Ho
** Rejected Ho, P ≤ 0.01
*** Rejected Ho, P ≤ 0.001

occurring through the soil columns, to evaluate the actual mobility of chemical elements and to resolve the special behaviour of copper.

In Figure 3, correlations (presented as scattergrams) between total metal concentrations, pH and TOC are shown for the composted sludge/granite system. For Cd and Zn, the relationship between the solubility and pH is clear and consistent with the view that concentrations of zinc and cadmium increase with increasing acidity of interstitial water, and, considering the strong correlation between Cd and Zn, an analogy between the concentration patterns of cadmium and zinc can be expected; Cu shows no dependence on pH and will certainly exhibit a different concentration pattern.

The use of a linear regression model shows that pH alone was a significant descriptive variable for Zn and Cd concentrations, whereas the concentration of Cu

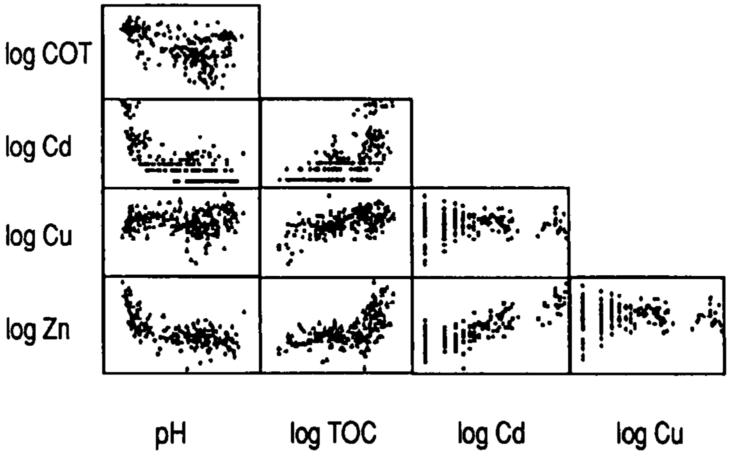

Figure 3 Correlations between pH, TOC and total metal concentrations in gravitational water of compost/granite system.

Table 4 Relationships between total metal concentrations, pH and TOC in the compost/granite system.

	Simple regressions	*Multiple regressions*	
	Coefficients (probability)	*Coefficients (probability)*	
	pH	*pH*	*log TOC*
log $[Cd]_{tot}$	−0.456 (*0.0001*)	−0.388 (*0.0001*)	+0.689 (*0.0001*)
log $[Zn]_{tot}$	−0.274 (*0.0001*)	*not significant*	*not significant*
log $[Cu]_{tot}$	*not significant*	+0.070 (*0.0001*)	+0.553 (*0.0001*)
log TOC	−0.098 (*0.0001*)	—	—

was best described with organic matter concentration and pH as independent variables (Table 4). The effect of an increase of pH was a decrease in Zn and Cd concentrations and no variation or a slight increase in Cu concentration, depending on which treatment was considered. This, together with the fact that total copper concentration was also proportional to the organic matter concentration was the sign of the association between organic matter and copper.

Concentration patterns of Cd, Zn and Cu are shown (solid lines) in Figure 4 for the composted sludge on granite treatment. The contrast between the behaviour of total copper in solution on one hand and of zinc and cadmium on the other hand is reflected in the general form of the concentration pattern: for Cu, the concentrations were rather constant, with periodical increase in the summer periods, for Cd and Zn, the higher concentrations were measured during the first period of the trial and then progressively decreased. The distribution of the probable chemical species was calculated using a thermodynamic computer program ADSORP2[14]. Hatched areas show the distribution of various species, e.g. free metal ion Me^{2+}, metals bound to inorganic ligands, Me-min (SO_4^{2-}, and/or HCO_3^-, OH^-, etc.) and metal complexed by organic matter, Me-org, obtained by computation. It is interesting to note that the behaviour of the $[Me^{2+}]$ curves (black areas on Figure 4) is similar for the three metals and that the differences observed in the total concentration patterns are related to the existence of bound species in lysimetric water, specially organic complexes in the case of copper.

A good fitting between the expected and practical metal species distributions was obtained with gel filtration and separations with an anion-exchange resin[14]. It was shown with a copper-selective electrode that the concentration of ionic copper in gravitational waters was a function of pH, that organic matter was never saturated with metal even in spiked compost systems, and so copper was essentially in bound form[15].

Therefore the special behaviour of Cu may be due to the fact that the availability for plants is proportional to the metal activity, that is to the ionic copper concentration in the soil solution, whereas the measured flows in the gravitational water are proportional to the total concentrations.

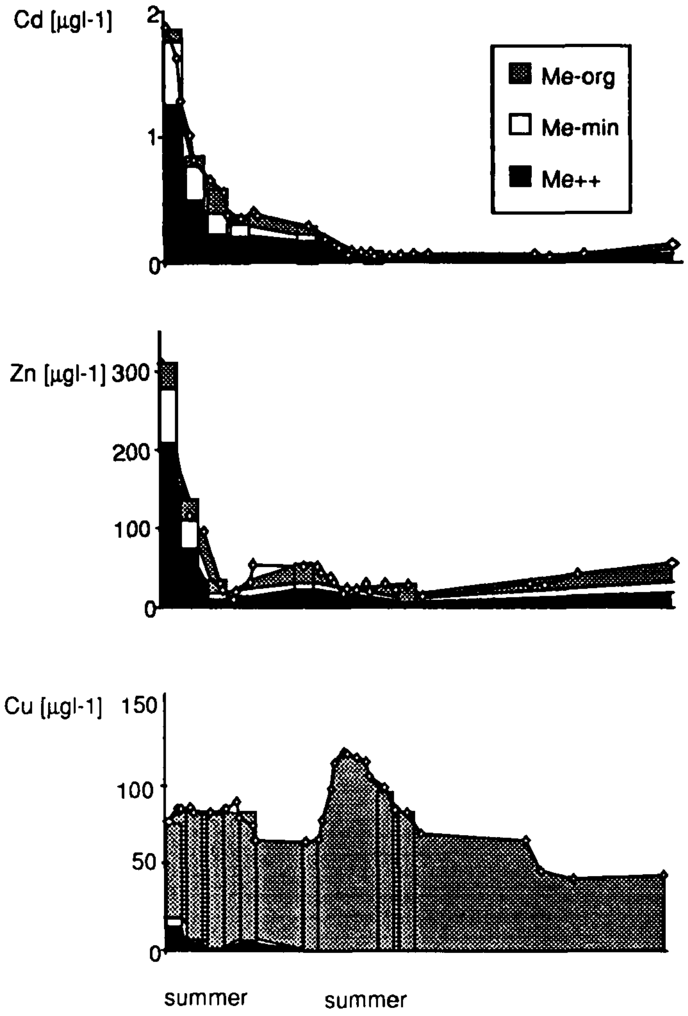

Figure 4 Concentration patterns and distribution of metal species in gravitational water of compost/granite system.

The observed anomaly in the mobility orders can be explained by taking into account the distribution of chemical species in the liquid phase and the very low activity of free Cu(II), a direct consequence of its strong affinity towards soluble organic ligands. When the leaching of organic matter is important, the mass flow of copper into water compartment is then enhanced compared to the other metals. If mobility had been measured by the determination of metal activity in the soil solution, we would certainly have: Zn more mobile than Cd, more mobile than Cu, in agreement with the mobility order measured in vegetation (see black blocks in Figure 2). We can so obtain an adequacy between the two mobility orders and, as plants seem to be good indicators for free metal concentrations, give at the same time an ecological significance to free metal.

The uptake by plants is a direct indication of the availability and mobility of the absorbed element but, for practical reasons, the determination of available metals with plants is unusual: it is a time-consuming practice, and the absorption of metal by plants can vary with plant species, plant development stage, and with many climatological and soil factors. Testing the mobility of metals with plants must be very strictly controlled and standardized.

Moreover one must be attentive to the fact that high levels of soil metals can induce a decrease in production, not always associated with an increase of metal concentration in plant tissues. The uptake by the roots always outweighed the loss by drainage in the systems with low content in heavy metals, but in the spiked systems, the absorption of metals by the roots was less than loss by drainage, despite the fact that the free Me(II) concentrations in the soil solution were higher in the spiked compost treatments. This low metal uptake by plants was related to the low production observed in the spiked systems and this in turn is linked to the phytotoxic processes occurring in vegetation[13].

In mineral subsoil, the interpretation is rather complicated and no simple general fixation rule could be laid down for the fixation of heavy metals. It is difficult to correlate the exports in the subsoil with the composition of the gravitational water because the accumulated metals in the mineral substratum were essentially extracted from soil solution and are therefore missing in the gravitational water.

The soil analysis data showed that different immobilization processes could be advanced: for Cu, immobilization was mostly due to the coagulation of Cu-organic complexes issued from the topsoil, and that this coagulation was more efficient for high pH; for Zn and Cd, retention was ensured partly by the coagulation of translocated organic and ferric compounds and also by a direct, pH-dependent adsorption of the free metal.

Interpretation

Considering the data from the analysis of composition of the water percolating out of the soil (TOC, pH and the distribution of metal species) and from the estimation of export balances, the following mechanism could be proposed (Figure 5):

Copper is firmly bound to organic matter in the composted sludge; the concentration of the ionic species, the "active" species and probably the available form for plants, is low and the copper flow in the vegetation compartment is reduced. As the drained soil solution penetrates the mineral horizon, dissolved organic matter with complexed copper can precipitate, acting as an immobilizing factor for copper; a fraction of the organic matter, especially important during the summer, remains in solution and migrates through the whole mineral horizon with associated copper: as a result, the copper flow is more important in water than in vegetation, the total copper concentration is proportional to the dissolved organic matter and the concentration of ionic copper is much lower than Cu-organic species; pH may also play a role in the translocation of copper: in controlling the dissolved organic matter

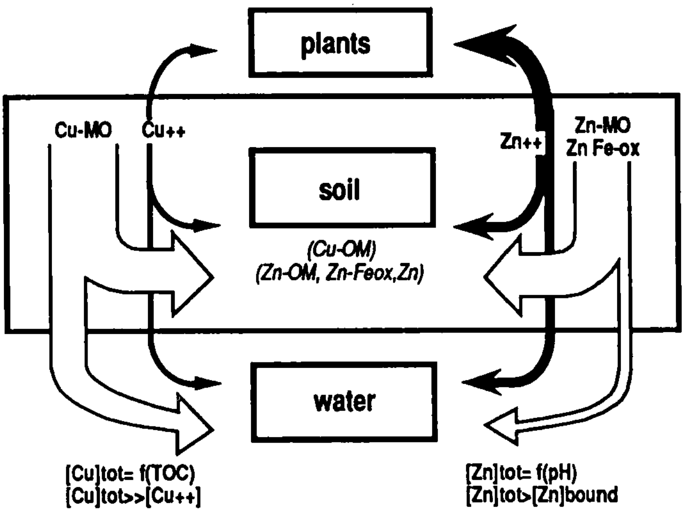

Figure 5 Mobility of copper and zinc through the model soil system.

concentration and its complexing behaviour (configuration and number of active sites in the organic molecules). The organic matter can exert at the same time a mobilization or an immobilization function: the physical state of the mobilizing agents will be perhaps the main factor on which the fate of copper will depend: if they are in a colloidal state, their insolubilization at the top of the subsoil is more probable than if they are in true solution; in contrast to copper, more zinc and cadmium exist in a free hydrated form Me^{2+} in the soil solution which is available to plants, giving important Cd- and Zn-flows in vegetation; fixation occurs in mineral substratum through the precipitation of organic matter and probably associated Cd and Zn and by a pH-dependent adsorption of the ionic metal species on active surfaces which strongly reduces the export in the water; the total cadmium and zinc concentrations in solution show no correlation with the concentration of dissolved organic matter and increase with acidification.

CONCLUSION

The results presented here are in general agreement with the ideas on processes controlling the fate of metals in environment, but that which distinguishes this work is that they were obtained in the same experimental vegetation-soil system.

Exports in vegetation, which are proportional to the concentration of the ionic species, can give an interesting estimation of mobility, when toxicity levels are not exceeded, especially in the surface horizons of agricultural land.

Analysis of the solid phase of a soil gives some information on the retention capacity of the active surfaces, but they are difficult to interpret because the metal concentrations in a soil are often the result of different surface reactions.

The data from soil solution analysis and especially the distribution of heavy metal species are the most interesting ones for an estimation of mobility; additional work should be developed to insure good sampling of soil solution and better measurements of metal activities, if possible in situ measurements; but metal activities are intensity values which give no indication of the probable evolution of the soil system and consequently of the fate of the metals: it is very important to give more attention to the role of time to make possible the elaboration of predictive models and to study in a quantitative way future trends in natural and polluted soils.

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