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Factors affecting the three-dimensional distribution of exogenous zinc in a sandy Luvisol subjected to intensive irrigation with raw wastewaters

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Abstract

Massive volumes of raw wastewater have been spread on sandy Luvisols in the Paris region since 1899, causing major soil contamination with metallic trace elements (MTE). To identify the factors influencing the vertical and horizontal redistribution of MTE at the plot scale, a study was carried out of the three-dimensional distribution of zinc. The background and exogenous fractions of zinc in the contaminated soil were discriminated using correlations between zinc and iron defined from unpolluted soils of the area. At the surface, the spatial distribution of zinc is determined by the geometry of the irrigation system and the terrain topography. The highest concentrations are observed near the irrigation outlets and in areas of very slight slope. The exogenous zinc has migrated down to the base of the studied solums (1 m depth), and its subsurface distribution depends upon the physico-chemical properties of the horizons. In the E horizon, the trapping of exogenous zinc is governed by the number of available reactive sites, whereas in the Bt horizon it is a function of the vertical and lateral behaviour of the drainage. Moreover, lateral transfer of exogenous zinc occurs in the C horizon. In the case of soil contaminated with raw wastewater, the organization of water flow on the surface and in the subsurface is a determining factor in the redistribution of zinc within a plot.

Keywords: Wastewater irrigation, surface redistribution, subsurface redistribution, exogenous zinc, long-term

Introduction

Human activity, whether mining or agriculture, supplies major amounts of metallic trace elements (MTE) to soils (Alloway, 1990b; Juste & Robert, 2000). Once these MTE have accumulated in a soil, the problem arises of how they are transferred into the environment, i.e. their uptake by plants, their migration into groundwater, or their remobilization through erosion.

To identify the factors that govern MTE retention in soils, various complementary types of study have been carried out. These include laboratory batch tests to study the reactivity with MTE of various soil constituents and of the soil itself (Buchter *et al*., 1989; Zachara *et al*., 1991; Ledin *et al*., 1996; Elzinga *et al*., 1999); soil-column leaching to evaluate hydrodynamic aspects (Emmerich *et al*., 1982; Cornu *et al*., 2001; Kaschl *et al*., 2002), and, finally, *in situ* tests to take environmental factors into account (McGrath, 1987; McBride *et al*., 1997; Udom *et al*., 2004). These studies have shown that: (i) organic matter, carbonates, clay minerals and iron and manganese oxy-hydroxides are the main MTE-trapping phases (McBride, 1989; Alloway, 1990a; Sager, 1992); (ii) MTE migration in soil depends upon the chemical (type of constituents, pH, Eh; Alloway, 1990a; Sager, 1992; Kabata-Pendias, 1993; McBride, 1994; Charlatchka & Cambier, 2000) and physical properties of the horizons (permeability, structure; Camobreco *et al*., 1996; Simpson *et al*., 2004); and (iii) MTE migration is a slow phenomenon (Streck & Richter, 1997a) requiring long-term studies.

Nonetheless, almost all the available studies in the literature take into account one or more vertical soil profiles without considering their lateral interactions. This presents a major limitation as the authors then neglect the natural lateral variability of both pollution and soil properties in their interpretations.

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Effectively, soil pollution is not homogeneous and, in the surface horizon, shows variations at a scale of one to several metres (Assadian *et al.*, 1998; Sterckeman *et al.*, 2000; Bourennane *et al.*, 2006), depending on the way contaminants have been applied to the soil. This distribution evolves over time through the effects of ploughing as well as diffuse erosion (Williams *et al.*, 1987; Korentajer *et al.*, 1993; Zhao *et al.*, 2001; Zang *et al.*, 2003). Yingming & Corey (1993) estimated that, over about 20 years, 15–20% of the supplied MTE had been redistributed by ploughing and erosion. McGrath & Lane (1989) estimated this proportion to be 21–28% over about 40 years. However, few authors showed interest in the impact of the spatial variability of pollution on MTE migration in soil, even though Sterckeman *et al.* (2000) observed, in a site polluted by zinc and lead smelting activities, that the depth of zinc migration was a function of surface contamination.

In addition, numerous studies have shown that the physical and chemical properties of soil are horizontally variable at scales of one to several metres (Gaston *et al.*, 2001; Cichota *et al.*, 2003; Giltrap & Hewitt, 2004; Mzuku *et al.*, 2005), but few authors have studied the impact of such variations on MTE retention in soils.

Our aim was to determine the impact of these two parameters – spatial variability of pollution and of physico-chemical properties of soil – on the long-term three-dimensional redistribution of pollution in a sandy Luvisol, using zinc, a comparatively mobile MTE (Williams *et al.*, 1987; Lamy *et al.*, 2006), as a tracer of the pollution. A site that had been contaminated for over 100 years of irrigation with raw wastewater was analysed for: (1) the distribution of zinc in the surface horizon; and (2) the vertical migration down profiles. The concentrations of pollutant sorbed at depth were estimated after subtracting the local natural background level established by the Fe-MTE correlations method (Baize, 1997; Baize & Sterckeman, 2001; Lamy *et al.*, 2006). The causes of the distribution of exogenous zinc at the surface and at depth were then established by consideration of topography and irrigation-system geometry for surface pollution, and of pedological characteristics for the pollution at depth.

Material and methods

The Pierrelaye site

The study site is located at Pierrelaye, in the north-western suburbs of Paris. From 1899 to 2002, the year in which our study was carried out, crops were irrigated with raw wastewater, which caused major soil contamination with MTE (Bourennane *et al.*, 2006). The irrigation was organized in units of a dozen hectares, each unit being formed by one or more plots, surrounded by irrigation outlets. The area was used for vegetables and salad production until 1970, and subsequently for production of maize.

Soil

The soil underlying the study site is a sandy Luvisol (FAO, 1998), developed over a reworked sandy calcareous formation. It consists of a thick (~40 cm) cultivated horizon (Ap), sandy (7–11% of $<2\ \mu$m particles), and rich in organic carbon (2–3%); an eluvial horizon (E) of variable thickness (5–40 cm) with an $<2\ \mu$m content ranging from 3 to 16%; a sandy clayey horizon (Bt) (15–25% of $<2\ \mu$m particles) and of 15–55 cm thick; a sandy calcareous horizon (C) containing 14–45% $CaCO_3$ and 8–17% of particles $<2\ \mu$m (Table 1). No cracks or earthworm activity channels have been observed in the soil.

Table 1 Pedological characteristics of the soils

Profile	Horizon	Depth (cm)	$<2\ \mu$m (g kg^{-1})	$CaCO_3$ (g kg^{-1})	Org C (g kg^{-1})	Fe_M[a] (g kg^{-1})	CEC (cmol^{+} kg^{-1})
X_1	Ap	0–40	101	40	30.3	8.4	9.9
	E	40–80	61	< 1	1.7	3.5	4.0
	Bt	80–110	247	< 1	3.5	10.6	16.7
	C	110–120	79	138	3.7	3.5	5.0
X_3	Ap	0–45	71	20	17.1	6.0	6.8
	E	45–70	58	1	1.2	3.7	3.9
	Bt	70–95	243	1	3.0	9.7	16.7
	C	95–100	174	401	10.3	4.7	8.6
X_4	Ap	0–37	105	34	32.3	8.7	11.4
	E	37–70	65	< 1	1.9	3.8	4.7
	E/Bt	70–85	121	1	2.3	5.8	7.9
	Bt	85–100	152	19	3.3	6.7	10.6
	C	100–110	153	286	2.4	3.9	7.8
Y_1	Ap	0–40	85	28	30.4	7.2	12.1
	E	40–60	39	< 1	1.6	2.9	3.8
	Bt	60–80	180	< 1	2.8	8.1	13.5
	C_1	80–95	120	296	0.4	2.9	5.9
	C_2	95–105	98	252	3.1	2.6	5.4
Y_2	Ap	0–40	75	21	20.5	5.9	8.2
	E	40–46	149	< 1	3.0	6.9	10.2
	Bt	46–55	204	1	3.4	8.7	14.0
	C	55–65	111	447	3.5	3.1	5.5
Y_3	Ap	0–35	82	20	18.1	5.9	7.5
	E	35–70	93	< 1	1.7	5.4	5.6
	Bt	70–90	230	< 1	2.8	8.7	15.3
	C	90–110	78	180	0.6	3.5	4.9
Y_4	Ap	0–40	107	25	28.4	8.1	11.9
	E	40–65	32	1	0.8	2.6	1.9
	Bt	65–120	260	1	2.0	10.0	16.9
	C	120–130	90	202	1.7	4.2	5.9
Z_3	Ap	0–40	86	17	17.1	5.9	7.8
	E	40–50	158	< 1	2.7	6.5	10.4
	Bt	50–80	205	2	3.3	8.8	14.8
	C	80–100	143	319	1.2	4.3	7.5

[a] Fe_M is the free iron extracted according to the Mehra & Jackson (1960) method.

Sampling strategy

On the end of each irrigation outlet, the farmer fixed a flexible pipe, perpendicular to the slope, to convey the wastewater to the centre of the plots. Based on the geometry of the irrigation network and the topography, we defined the areas of influence of the various irrigation outlets within a plot. In one of these areas, we sampled the surface horizon at 21 randomly distributed points over about 1.7 ha (Figure 1).

For studying the vertical redistribution, eight solums were sampled with an auger drill to form three transects *X*, *Y* and *Z*, oriented in the slope direction (*X* and *Y*) and perpendicular to it (*Z*).

A digital elevation model (DEM) was drawn up from detailed topographical surveys by laser tachymeter. The elevation and slope of the sampling points were averaged over a radius of 10 m to take the micro-relief into account.

Estimating the local natural background

In soil, the total MTE concentration is equal to the naturally present MTE concentration (background MTE) plus that contributed by contamination (exogenous MTE). To differentiate between the two types of MTE in soil, we used the linear relationship that exists between MTE and major elements for uncontaminated horizons within a soil series (Baize & Sterckeman, 2001; Dère *et al*., 2006; Lamy *et al*., 2006). To establish this relationship, samples were taken along trenches in four unpolluted solums of the same type as the contaminated soils (sandy Luvisols), and located outside the wastewater spreading area, but at less than 2 km from the polluted area. As the surface horizon could be affected by diffuse pollution (pesticides and atmospheric pollution), only the subsurface horizons E, Bt and C were sampled (eight samples along four profiles). The background MTE concentrations in contaminated soil were then calculated from the iron concentrations measured in the contaminated soils, and from the MTE–Fe relationship established from uncontaminated soils.

Analyses

The samples were air dried and then sieved past 2 mm. The total zinc and iron concentrations of the horizons in polluted and reference soils were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), after total mineralization of the samples by HF + $HClO_4$ (Ciesielsky *et al*., 1997). For the surface horizons of the contaminated site, the organic carbon and total zinc concentrations were measured. For the transect samples, we also determined the grain size distribution (five fractions without decarbonatation), water pH, cobaltihexamine cationic exchange capacity (CEC), total $CaCO_3$ content and the free-iron content (FeM) extracted with the Mehra & Jackson (1960) method.

Results and discussion

Horizontal distribution

In the surface horizon, the natural background of zinc is negligible, of the order of 2% of the total concentration, i.e. below the analytical uncertainty of 5% (Ciesielsky *et al*., 1997). For this horizon, it is therefore not necessary to correct for background levels.

The spatial distribution of zinc in the surface horizon is shown in Figure 2. The maximum concentrations are observed at the top and the bottom of the plot. They

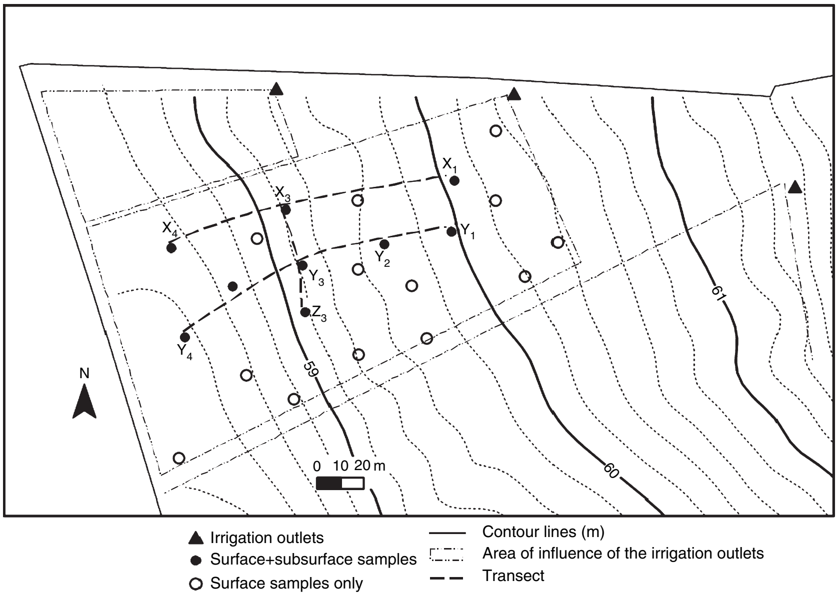

Figure 1 Map of soil-sampling locations within the plot.

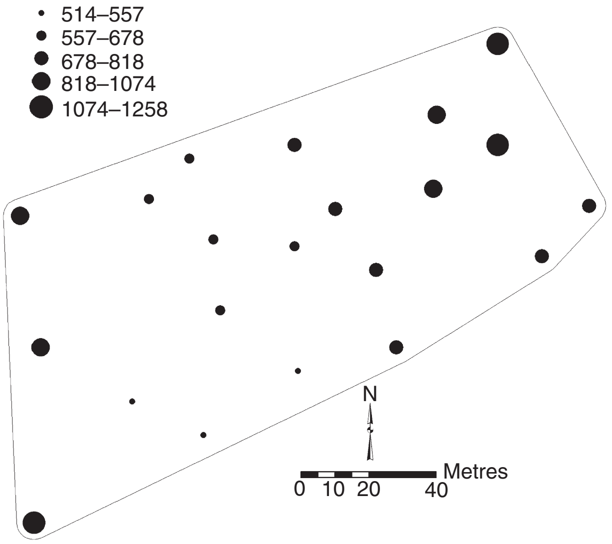

Figure 2 Total-zinc concentrations in the Ap surface horizon (mg kg^{-1}).

decrease with increasing distance from the irrigation outlet until 160 m, and then increase again when nearing the western edge of the plot (Figure 3) that corresponds to a flat area (Figure 1). The highest zinc concentrations are found in the areas where the slope is less than 1.2%, and the lowest in the parts with the steepest slope ($>1.5\%$; Figure 3). Eighty-six percent of the variability in zinc concentration in the surface horizon is explained by the slope and the distance from the irrigation outlet, as follows:

$$[\mathrm{ZnT_{Ap}}] = 2653 - 1568s + 530.4s^2 - 13.55d + 0.0484d^2 \quad r^2 = 0.86 \tag{1}$$

where [$\mathrm{ZnT_{Ap}}$] is the total zinc concentration in the Ap horizon (mg kg^{-1}); *s* is the terrain slope at the sampling point (%); *d* is the distance between the sampling point and the irrigation outlet (m).

The spatial distribution of zinc in the surface horizon corresponds to sedimentation patterns of the polluted particles present in the raw wastewater, i.e. high concentrations near the water outlets and in areas of slight slope. However, it is quite probable that this distribution has evolved over time because of soil tillage and diffuse erosion. Ploughing favours a spreading out of the pollution plume (Williams *et al.*, 1987; McGrath & Lane, 1989; Yingming & Corey, 1993), here along a northeast–southwest axis, and diffuse erosion accentuates the contrast in concentrations between areas of steep and gentle slopes, through removal of polluted particles on steep slopes and through their sedimentation on gentle slopes.

In this horizon the zinc concentration strongly correlates with the % calcium carbonate ($r = 0.99$) and with the % organic carbon ($r = 0.97$). Although zinc is strongly reactive with both compounds (Kiekens, 1990; Zachara *et al.*, 1991), it is quite probable that, here, this correlation marks a common origin, in addition to a chemical affinity. Marx *et al.* (1988) showed that a significant precipitation of calcium carbonate could occur in the surface horizon of a cultivated and abundantly irrigated soil, even under a temperate climate, and that the $CaCO_3$ precipitation is greatest near irrigation outlets. The correlation with % OC could be explained by the deposition of organic particles already enriched in metals during the irrigation with wastewater. This is consistent with the high zinc concentrations found near the outlets (indicating rapid deposition of the largest particles), and in the areas of shallow slope where water infiltration and particle sedimentation are more pronounced (Hairsine *et al.*, 2002; Santos *et al.*, 2003). Moreover, the organic carbon contents are greater than a normal sandy soil, which suggests that the carbon in the surface

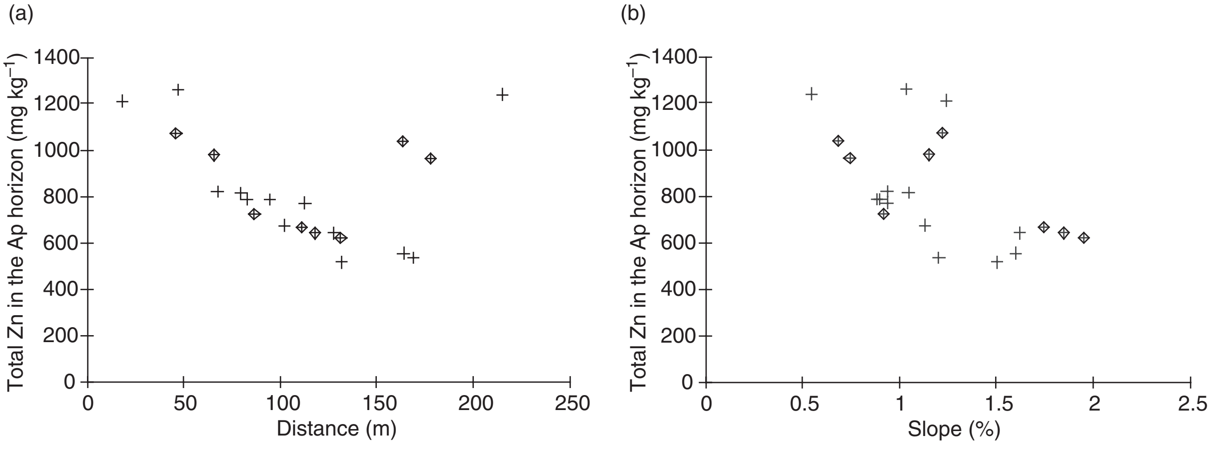

Figure 3 Total-zinc concentrations in the Ap horizon in terms of (a) the distance from the irrigation outlet and (b) the terrain slope. Diamonds denote surface samples from the transects.

horizon has been mainly brought in by the raw wastewater. The strong correlation between zinc concentrations and those of organic carbon and calcium carbonate indicates a common origin.

Vertical distribution

The zinc concentration profiles (Figure 4) show that significant migration has occurred. For X_1, Y_2, Y_3 and Y_4 profiles, exogenous Zn concentrations decrease with depth, although it increases in the Bt horizon for X_3, X_4, Y_1, and in the C horizon for Z_3 and Y_1.

E horizon

The exogenous-zinc concentrations in the E horizon are shown in Table 2. They represent 89–94% of the total measured concentration. There is no link between exogenous-zinc concentrations in the E horizon and that in the Ap horizon, contrary to the observations of Sterckeman *et al.* (2000). There is a significant correlation between free-iron concentrations, the CEC, the < 2-μm-fraction content and the organic carbon content ($r \geq 0.90$). We can thus consider that free-iron concentrations represent the total quantity of sites available for adsorption in the horizon. The relationship between exogenous-zinc concentrations in the E horizon and free-iron concentrations for the points X_1, X_3, X_4, Y_1, Y_2 and Y_4 (Figure 5) is:

$$[\mathrm{ZnE_E}] = 270\ \ln([\mathrm{FeM}]) - 138 \quad r^2 = 0.98 \tag{2}$$

where $[\mathrm{ZnE_E}]$ is the exogenous-zinc concentration in the E horizon (mg kg^{-1}) and [FeM] is the free-iron content (g kg^{-1}).

Profiles (X_4, Y_4) on the one hand, and (X_1, Y_1) on the other hand, have similar zinc concentrations in the Ap horizon and similar surface slopes (which implies identical water infiltration) (Figure 3). Thus the flux of zinc leaving the Ap horizon and traversing the E horizon is similar for X_4 and Y_4 on the one hand; and for X_1 and Y_1 on the other hand. The difference in exogenous-zinc concentrations in the E horizon observed between and within the two pairs of profiles can only be explained by their different potential for trapping the exogenous zinc: the more potential the trapping sites in the horizon, the more exogenous zinc will be trapped. The fact that there is a common relationship between the different points, defined by the free-iron content, suggests that the sorption sites are saturated. Y_2 has a smaller exogenous zinc concentration than X_1, X_4, Y_1 and Y_4 in the Ap horizon, and greater in the E horizon. However, Y_2 is located in an area of slight slope, which favours infiltration (Santos *et al.*, 2003), and thus the removal of

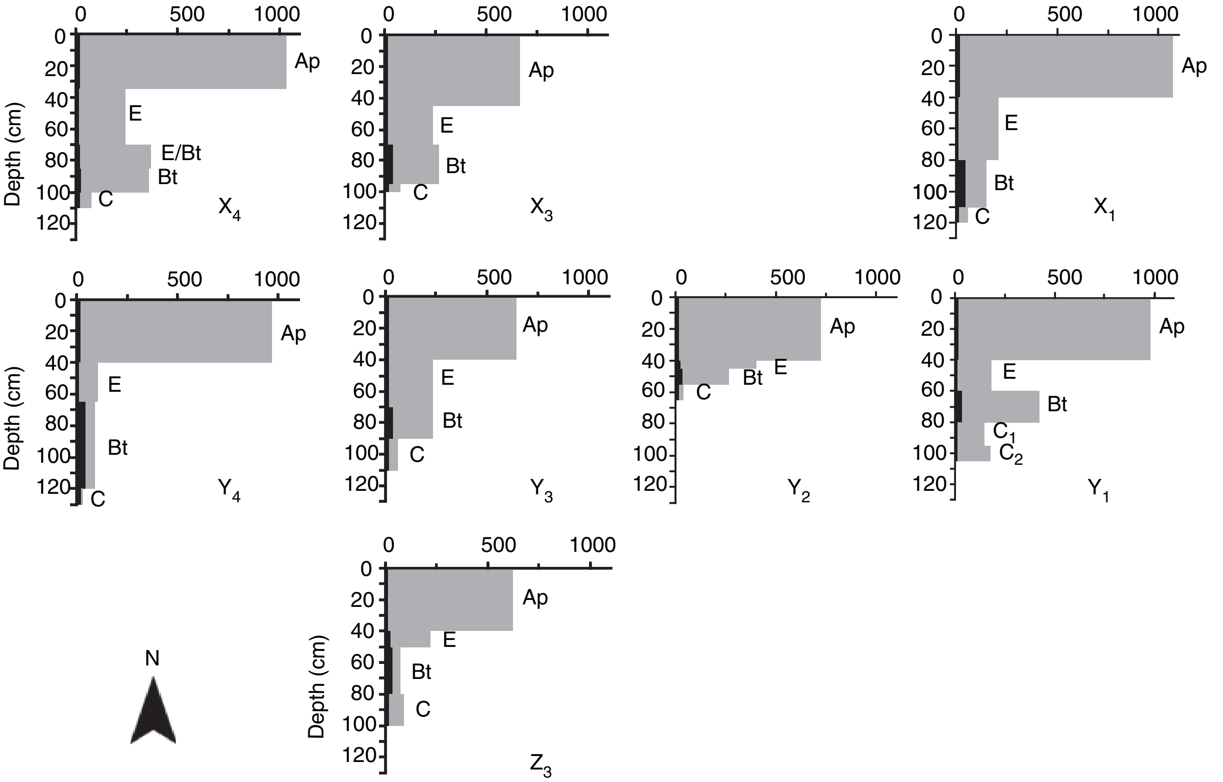

Figure 4 Profiles of exogenous (in grey) and background (in black) Zn concentrations (mg kg^{-1}) within the plot.

Table 2 Total-iron and exogenous-zinc concentrations in the soil horizons

Horizon	Profile number X_1	X_3	X_4	Y_1	Y_2	Y_3	Y_4	Z_3
Total Fe (g kg^{-1})								
Ap	11.8	8.5	12.7	10.9	9.2	8.9	11.9	8.7
E	6.7	7.0	7.4	5.4	15.0	10.9	4.6	14.5
Bt	27.7	24.9	15.4	19.6	19.7	22.8	26.6	21.1
C	8.7	12.3	10.7	7.6	7.4	9.1	11.9	10.3
Exogenous Zn (mg kg^{-1})								
Ap	1053	652	1014	962	708	627	946	607
E	194	221	229	169	378	217	100	196
Bt	101	226	331	387	232	196	44	36
C	46	54	55	133	26	44	9	71

$[Zn]_{Exogenous} = [Zn]_{Total} - [Zn]_{Background}$, with $[Zn]_{Background} = 1.63 \times [Fe] + 1.62$; $r = 0.96$ (r = Pearson correlation coefficient).

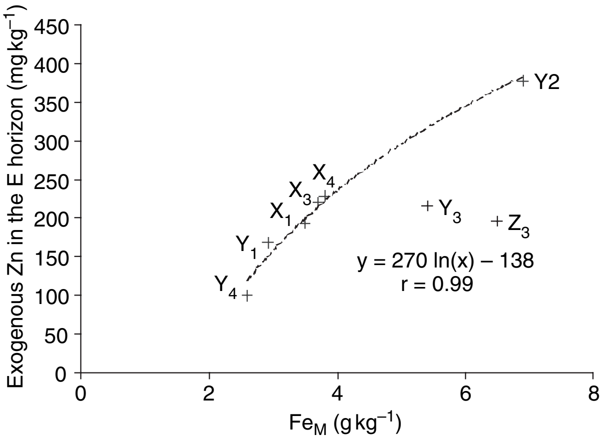

Figure 5 Exogenous-zinc and free-iron (Fe_M) concentrations in the E horizon (logarithmic regression excluding Y_3 and Z_3).

exogenous zinc from the surface Ap horizon. Because of its position in an area favouring downward pollutant flux, and because of high sorption potential (Table 1), the E horizon of profile Y_2 has trapped much exogenous zinc. The common relationship between the above points indicates that probably all sorption sites are occupied. The factor limiting the quantity of exogenous zinc trapped in the E horizon is, for all five profiles, the quantity of available sorption sites, and not the flux of pollutants.

Points Y_3 and Z_3 have smaller zinc concentrations than would have been expected in view of their free-iron contents. Together with X_3, they have similar exogenous-zinc concentrations in the E horizon, whereas their free-iron concentrations are different. Based on the exogenous-zinc concentrations in the Ap horizon and the terrain slope on surface (Figure 3), it can be assumed that the exogenous-zinc flux arriving in the E horizon must have been about the same for these three profiles. In the case of X_3, this quantity probably was enough to saturate the sorption sites, whereas in the case of Y_3 and Z_3, much richer in free iron, it was probably insufficient to saturate all the sorption sites. For these three profiles, it appears that it is the quantity of pollutant arriving in the E horizon that limits the quantity of exogenous zinc present in the E horizon.

Even though the surface slope is very gentle (2% at most), its variation seems to have a strong influence on the quantity of zinc leaving the Ap horizons. Comparing for instance profiles Y_2 and Z_3, it can be seen that their zinc concentrations in the surface horizon are close (607 mg kg^{-1} for Z_3, 708 mg kg^{-1} for Y_2). The free-iron content of the E horizons of the two profiles is similar but zinc concentrations of the E horizon of Y_2 (378 mg kg^{-1}) is nearly twice that of Z_3 (197 mg kg^{-1}). This difference is associated with double the gradient at Z_3 (1.95%) compared with that at Y_2 (0.92%), a difference which confers greater infiltration and less runoff at Y_2. The surface gradient thus is a determining parameter in the downward migration of zinc, as water infiltration occurs preferentially in areas of slight slope.

Bt horizon

The exogenous-zinc concentrations in the Bt horizon are shown in Table 2. They represent 50–93% of the total concentration of the horizon. They do not correlate with exogenous-zinc concentrations in the E horizon and show significant negative correlation with the contents in $< 2\ \mu m$ particles and free iron ($r = 0.71$ and 0.74 respectively). With the exception of Z_3, the points are aligned according to the equation (Figure 6):

$$[ZnE_{Bt}] = -2.66[< 2\,\mu m] + 792 \quad r = 0.88 \tag{3}$$

where $[ZnE_{Bt}]$ is the exogenous-zinc concentration in the Bt horizon (mg kg^{-1}) and $[< 2\ \mu m]$ is the $< 2\ \mu m$ fraction content in the Bt horizon (g kg^{-1}).

The fact that the exogenous-zinc concentrations correlate negatively with the $< 2\ \mu m$ contents is probably because of

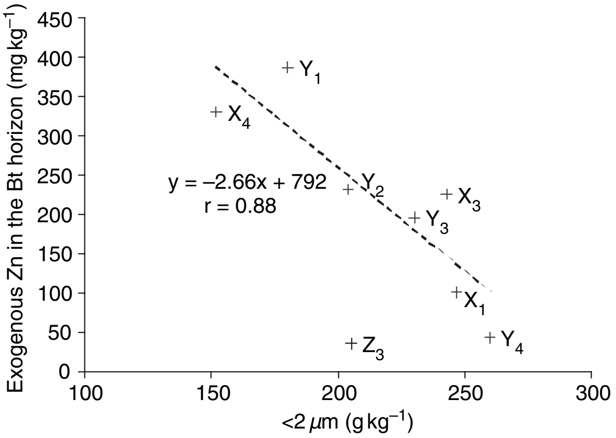

Figure 6 Exogenous-zinc concentrations in the Bt horizon in terms of the < 2 µm fraction (Z_3 excluded).

the horizons permeability. Within a given soil type, for a given silt content, and in hydric conditions near saturation, the less the < 2 µm fraction content of the Bt horizon, the more permeable it is, which means that the water loaded with zinc can easily traverse the horizon, leading to higher exogenous-zinc concentrations in the horizon. Conversely, the greater the < 2 µm fraction in the horizon, the less it permeable is, leading to more lateral drainage of the water on the Bt horizon to the detriment of vertical drainage. In this case, the behaviour would resemble that of a Planosol. Jamagne (1978), in his theoretical Luvisol evolution sequence, indicated that Planosol type profiles can appear under strongly hydromorphic conditions, which is probably the case here in view of the massive quantities of wastewater discharged (1–4 m year^{-1}). In addition, Presley *et al.* (2004) showed that irrigation accelerates the pedogenetic evolution of a soil, because of a stronger alteration of minerals and an increased illuviation of clays. According to Baize & Girard (1995), characteristics of Planosols are: (i) less than 300 g kg^{-1} of < 2 µm in the less clayey horizon; (ii) more than 250 g kg^{-1} of < 2 µm in the most clayey horizon; (iii) a difference of < 2 µm content greater than 200 g kg^{-1}; and (iv) a transition zone between the two horizons that is less than 8 cm in depth, with a < 2 µm content in the clayey horizon that is more than double that of the E horizon if the latter is less than 200 g kg^{-1}. Based on these morphological criteria, the profiles X_1 and Y_4 are at the boundary between Luvisols and Planosols (Table 1), and it is thus probable that the water behaviour in these two profiles is close to that in Planosols.

Therefore, the profiles with a high exogenous-zinc concentration in the Bt horizon reflect mainly vertical water flow (the water with zinc traverses the Bt horizon and the zinc is trapped in the horizon), whereas the profiles with low exogenous-zinc concentrations in the Bt horizon reflect water flow with a strong lateral component.

However, notwithstanding a < 2-µm-fraction content of 205 g kg^{-1} (which is small for a Bt horizon), profile Z_3 also shows a low exogenous-zinc concentration in the Bt horizon of 36 mg kg^{-1}. We saw above that the E horizon of this profile was not yet saturated in zinc. Therefore probably, at present, exogenous zinc is almost exclusively trapped in the E horizon for this profile, and that an increase in exogenous-zinc concentration of the Bt horizon must wait until almost all sorption sites in the E horizon are occupied.

C horizon

The exogenous-zinc concentrations in the C horizon are shown in Table 2. They represent 30–91% of the total concentrations in the horizon. They do not correlate with the < 2 µm fraction contents, nor with the $CaCO_3$ contents of the C horizon, nor with exogenous zinc concentrations of the Bt horizon. However, Z_3 has a particular behaviour as the exogenous-zinc concentration is higher in the C horizon than in the Bt horizon (72 mg kg^{-1} in the C horizon against 36 mg kg^{-1} in the Bt horizon). As exogenous zinc is mainly trapped in the E horizon for this profile, the supply of exogenous zinc in the C horizon via preferential flow paths across the Bt horizon seems improbable. A possible explanation might be the existence of lateral influx directly into the C horizon.

Because of the many phenomena playing a role, i.e. the quantity of zinc leaving the Ap horizon, the quantity of zinc retained in the E horizon, the quantity that can traverse the Bt horizon, the quantity of potential trapping phases in the C horizon, and the occurrence or not of lateral influx, it is difficult to draw up one general mechanism to explain Zn concentrations in this horizon. The cumulative effect of the many factors involved is shown by greater spatial variability of exogenous-zinc concentrations at depths than at the surface. In eight profiles, the standard deviation of exogenous-zinc concentrations in the surface Ap horizon is 23%, 37% in the E horizon, 66% in the Bt horizon and 75% in the C horizon.

In our case, water flows (and especially lateral water transfer) play a major role in the redistribution of zinc at the plot scale. These results differ from earlier work (Streck & Richter, 1997a,b; Seuntjens *et al.*, 2002) in which the adsorption capacity of the horizons, determined in laboratory batch tests, satisfactorily explained the distribution of zinc and cadmium at the plot scale, and in which the hydrodynamic properties of the horizons had almost no influence on the quantities of MTE trapped in them. Other authors have shown the insufficiency of purely thermodynamic modelling to explain the MTE-concentration profiles, especially in the case of preferential transfer via soil macropores (Sidle *et al.*, 1977; Zhang & Xu, 2003) or in the presence of horizons with contrasting physical properties (Seuntjens *et al.*, 2001).

Our work has shown the importance of lateral water transfer in determining the MTE distribution in soil.

Conclusions

In the surface horizon, the spatial distribution of zinc depends on the organization of water flow at the surface, itself governed by the geometry of the irrigation system and terrain topography. The largest zinc concentrations were observed near the irrigation outlets and in areas of slight slope.

For the lower horizons, no statistical link exists between exogenous-zinc concentrations in E, Bt and C horizons, and the contamination in the surface horizon. In the E horizon, the quantity of exogenous zinc depends upon the number of available reactive sorption sites and the quantity of pollutants arriving in the horizon, which is a function of the zinc concentration in the Ap horizon and the terrain slope. In the Bt horizon, the exogenous-zinc concentration is mainly governed by the permeability of the horizon. Smaller $<2\,\mu$m fractions favour the vertical drainage of water, and thus the adsorption of zinc in the Bt horizon, whereas greater $<2\,\mu$m fractions favour lateral drainage at the interface of the E and Bt horizons, thus reducing the extent of trapping in the horizon. For the C horizon, the parameters that influence the fixing of exogenous zinc in the horizon are difficult to identify, in view of the cumulative effect of the several parameters that together control the exogenous-zinc concentrations in the overlying horizons.

Finally, the water flows in the soil appears to be a major determining factor in the horizontal and vertical distribution of exogenous zinc within the studied plot. Consequently, it is important to discuss the migration of exogenous MTE in terms of physical properties of the soils (especially permeability) as well as in terms of chemical properties of the horizons (i.e. their reactivity to MTE). For modelling, this implies the use of a coupled 3D chemistry and transfer model that takes into account the lateral solute transfer in soils.

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