Land application of sewage sludge: A soil columns study

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Abstract

A column study was conducted to assess the potential Cr, Ni, Cu, Zn, Cd and Pb movement through a reconstructed soil profile to which surface composted sewage sludge was applied. Sewage sludge was mixed into the top 100 mm of each column at the rates of 357 (H), 223 (M) and 22 Mg·ha^{-1} (L). Treatment H was calculated according to the critical soil concentration and treatments M and L were calculated according to the amount of metals which may be added to agricultural land on 10 yr average (M) and 1 yr (L) according to European legislation. Soil columns were leached with 5 000 mℓ of water. After leaching, soil columns were sampled at depth intervals of 0 to 100, 100 to 300, 300 to 500 and 500 to 840 mm. Metal balance accounted for over 97% of metals and over 86% of metals were retained in the first 100 mm of the column. The average percentage of metals leached decreased in the order Cd (0.04%) > Cu (0.02) ~ Ni (0.02) ~ Zn (0.02) > Pb (0.01) ~ Cr (0.01). The maximum metal concentration in leachates was lower than the limit value for irrigation water but metal concentrations exceeded the drinking water levels for Pb and Ni in all treatments. Thus, harmful health effects may result from the application of sewage sludge.

Keywords: metals, sewage sludge, soil and water pollution

Introduction

Sewage sludges are inevitable by-products of wastewater purification. Over the past decades, there has been a significant increase in sewage sludge production from wastewater treatment plants due to the major limitations in wastewater disposal and the increase in the percentage of households connected to central treatment plants. Consequently, the world is currently undergoing a rapid increase in sludge production that is expected to continue in coming years.

At the moment, the conventional uses of sewage sludges include industrial utilisation, landfill, combustion and composting for farmland utilisation (Sánchez Monedero et al., 2004). Composted sewage sludge applied to agricultural land to improve soil fertility is a widespread practice in Mediterranean areas. Compost supplies a high content of organic matter with favourable effects on soil physical, chemical and microbiological properties. Organic matter improves soil structure, infiltration rate, aggregate stability to raindrop impact and water holding capacity of the soil (Sort and Alcañiz, 1999). Indeed, the addition of organic residues reduces soil loss and runoff (Ojeda et al., 2003). However, composted sewage sludge has a high metal and soluble salts content which could constitute a toxic threat to plants and a contamination source due to its potential lixiviation to groundwater.

Several countries have regulated the use of sewage sludge in agriculture to avoid harmful effects on soil, vegetation, animals and human being. For example, European Communities (European Community, 1986) and the United States of America (USEPA, 1997a) have fixed limit values for concentrations of metals in soil and sewage sludge for use in agriculture and have determined limit values for amounts of metals which may be added annually, based on a 10-year average in European legislation or 20-year average in American regulations. Nevertheless, regulations in European countries and the USA differ largely with respect to requirements of organic waste quality and the quantities of pollutants which can be added to the soil (Düring and Gäth, 2002). For this reason, both field and laboratory experiments are necessary to measure the critical load which can be supported by different soils.

Various researchers have studied the potential lixiviation of metals after sewage sludge applications in different soils. Berti and Jacobs (1998) studied distribution of trace elements Cr, Ni, Cu, Zn, Cd and Pb in a Typic Hapludaf after application of sewage sludge at total rates of 240, 690 and 870 Mg·ha^{-1} over a period of 10 years and observed that > 90% of metals applied were recovered from surface soil. Sloan et al. (1998) obtained similar percentages of metals recovery in sandy-loam soils after cumulative biosolids loadings of 0, 60, 120 and 180 Mg·ha^{-1}. McGrath and Lane (1989) concluded that metals movement was practically limited to a depth of 100 mm.

However, metal movement occurs and metals leaching through the soil could contaminate groundwater (Reynolds et al., 2002; Emmerich, 1982; Singh et al., 2000).

Soil column studies can be an appropriate methodology to assess metals movement in soils since the possible errors caused by sampling or plant uptake can be avoided. For example, Vogeler (2001) used leaching columns to study copper transport trough a dryland Dystric Fluventic Eutochrept and an Ustollic Haplargid, or more recently, Voegelin et al. (2003) used soil columns to investigate the potential of metal release in response to soil acidification in non-calcareous and neutral soil.

The main objective of this work was to study the balance of metals in a reconstructed soil profile to which three treatments of a composted sewage sludge were applied. The experiment was completed with the measurement of electrical conductivity

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of leachates to assess soluble salts movement. The selected sewage sludge was from the Alcalá de Henares treatment plant (Madrid, Spain) and presented a typical composition for this kind of solid wastes (Polo et al., 1995). The soil used was classified as Luvisols (WRB, 1998) which represents 650×10^6 ha in the world and is extensively used in agriculture.

Materials and methods

Soil characterisation

The soil samples were air-dried, crushed, and sieved through a 2 mm mesh. Soil metal content was determined after extraction by digestion with 3:1 (v/v) concentrated $HCl\text{-}HNO_3$ following 3051a method (USEPA, 1997b) and measurement by Varian 10/20 atomic absorption spectrophotometer with graphite furnace. Initial pH and electrical conductivity (EC) were determined in a ratio soil: water of 1:2.5 ($g \cdot m\ell^{-1}$). Final soil EC was determined in a saturated extract (EC_{se}). pH was measured by a Crison micro-pH 2000 according to the method of Thomas (1996) and EC with a Crison 222 conductivimeter following Rhoades' method (1996). Organic carbon (OC) content was determined by the Walkley-Black method (Nelson and Sommers, 1996). N content was determined by the Kjeldahl method (Bremner, 1996) with a Büchi 435 digestor. Soil cation exchange capacity CEC was determined with $NH_4OAc/HOAc$ pH 7.0 (Sumner and Miller, 1996). Soil cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) moved with $NH_4OAc/HOAc$ pH 7.0 were measured using a Perkin Elmer 2280 atomic absorption spectrophotometer. Soil texture was determined according to Bouyoucos (1962) and soil moisture characteristics according to Richards (1954). Soil colour was measured by a Minolta Chromameter calibrated with Munsell Color Charts (Munsell Color Co., 1998).

Sewage sludge characterisation

Sewage sludge was air-dried, crushed and sieved through a 2 mm mesh. A fraction was crushed and sieved through 0.074 mm mesh. This fraction was used to determine total carbon (TC), organic carbon (OC), N and total content of Cr, Ni, Cu, Zn, Cd, Pb, Ca, Mg, Na and K. EC and pH were determined in a saturated extract. Total carbon (TC) was determined by ashing at 540ºC (Nelson and Sommers, 1996). Organic carbon (OC) was analysed by the Walkley-Black method (Nelson and Sommers, 1996). Dissolved organic carbon (DOC) was extracted by agitation for 1 h using a soil: water ratio of 1 g soil to 10 mℓ water and determined by the Walkley-Black method. Total humified substances (THS), humic acids (HA) and fulvic acids (FA) were extracted according to Schnitzer (1982). N was determined by the Kjeldahl method (Bremner, 1996) and phosphorus (P) according to Watanabe and Olsen (1965). Total content (TC_m) of Cr, Ni, Cu, Zn, Cd, Pb and Ca, Mg, Na and K in sewage sludge was determined following 3051a method (USEPA, 1997b). Ca, Mg, Na and K were determined using a Perkin Elmer 2280 atomic absorption spectrophotometer. Metals bound to organic carbon (OC_m) were released with 30% H_2O_2 and HNO_3 at pH 2.0 and 85 ºC. After cooling, 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added to prevent adsorption of extracted metals onto the oxidised sediment (Tessier et al., 1979). Metals bound to dissolved organic carbon (DOC_m) were analysed in a DOC extract (see above). Metals were measured using a Varian 10/20 atomic absorption spectrophotometer with graphite furnace.

Leachates and irrigation water characterisation

The metals content of leachate samples was measured by atomic absorption spectrophotometer with graphite furnace. Also, leachate EC was measured.

Irrigation water EC was 91 $\mu S \cdot cm^{-1}$, 25ºC and it was classified as C1S1 according to Richards (1954). Therefore, its content in Cl^- and SO_4^{2-}, less than 1 $cmol_{(+)}/\ell$, did not influence soluble salts movement through soil columns. The metals content of the irrigation water was below the detection limit.

The analyses of soil, composted sewage sludge, leachates and irrigation water were done in quadruplicate.

Metals and salts transport

Solute movement through soil has been studied by many authors. The most widely used model is the convection-dispersion equation (CDE) (Parker and Van Genuchen, 1984; Biggar and Nielsen, 1967). This model has two terms: the first term describes convection and the second one represents diffusion of solutes in the solution:

$$D\frac{\partial^2 C}{\partial z} - U\frac{\partial C}{\partial z} - \frac{\partial C}{\partial t} = 0 \qquad [1]$$

where:

C is solute concentration
z is soil depth
t is the time taken between soil surface and depth z
D is the diffusion coefficient of the solute
U is the real solute velocity.

The CDE model can be solved by using the Laplace equation (Vallochi, 1985) resulting in a Fickian distribution probability function (pdf). This Fickian pdf can be fitted to a Lognormal pdf when z is constant (Jury and Roth, 1990). Analysis of lognormal distribution can be done according to Parkin and Robinson (1992). Thus, mean lifetime of solutes in the soil columns μ_τ can be calculated according to the equation:

$$\ln \mu_\tau = \frac{\sum C_i \cdot v_i \cdot \ln t_i}{\sum C_i \cdot v_i} \qquad [2]$$

where:

C_i is solutes concentration
v_i is leached volume on the day t_i.

The mean solute concentration in leachates (C_{mean}) can be calculated using the next equation:

$$C_{mean} = \frac{\sum C_i \cdot v_i}{\sum v_i} \qquad [3]$$

where:

C_i is solute concentration
v_i is leached volume on the day t_i.

Experimental design

The soil profile was sampled in terms of horizons. Afterwards, soil samples were packed into columns by horizons to approximate the field bulk densities of each horizon Ap: 1.368 $kg \cdot m^{-3}$, B1t: 1.276 $kg \cdot m^{-3}$, B2t: 1.231 kg m^{-3} (Emmerich et al., 1982). Columns to hold the soil were made from 1m lengths of PVC pipe (114 mm i.d.). Columns were closed at the bottom with a plastic mesh of 2 mm. The last 60 mm of each column was filled up with coarse sand without metals and organic matter. Composted sewage sludge collected from Alcala de Henares water treatment

TABLE 1
Critical soil concentration and limit value for amounts of metals which may be added to agricultural land on 10 yr average and 1 yr allowed by European Legislation (kg·ha^{-1})

	Cu	Zn	Ni	Cd	Pb
Critical soil concentration[a]	150	480	120	9.6	480
10 yr average allowed by European legislation[b]	120	300	30	1.5	150
1 yr allowed by European legislation[b]	12	30	3	0.15	15

Note:
[a] Critical soil concentration (kg·ha^{-1}) is calculated from critical soil concentration (mg·kg^{-1}) (Kabata-Pendias and Pendias, 1992) for a bulk density = 1 200 kg·m^{-3} and a depth = 0.10 m.
[b] (European Community, 1986)

TABLE 2
Soil properties

H	D (mm)	Texture			Colour		Soil moisture characteristics	
		Sand (%)	Silt (%)	Clay (%)	Dry	Wet	33 (kPa)	1 500 (kPa)
Ap	0-300	46.0	34.0	20.0	8.3 YR 4.9/4.3	7.3 YR 3.2/3.1	17.43	9.08
B1t	300-500	40.0	16.0	44.0	7.4 YR 4.7/4.8	6.9 YR 3.7/3.9	27.21	15.85
B2t	500- 840	35.0	10.0	55.0	8.4 YR 4.5/4.3	8.7 YR 4.1/3.8	32.22	16.31
H	**EC (1:2.5) (µS cm^{-1}, 25°C)**	**pH (1:2.5)**	**OC (%)**	**N (%)**	**Ca (mg/kg)**	**Mg (mg/kg)**	**Na (mg/kg)**	**K (mg/kg)**
Ap	350 ± 20[a]	5.21 ± 0.01	1.23 ± 0.05[*]	0.064 ± 0.05	387 ± 50	109 ± 8	125 ± 20	102 ± 3
B1t	550 ± 40	5.62 ± 0.03	0.58 ± 0.02	0.046 ± 0.04	3590 ± 319	680 ± 28	151 ± 37	121 ± 5
B2t	1 190 ± 130	6.33 ± 0.05	0.48 ± 0.02	0.030 ±0.04	4389 ± 298	743 ± 30	148 ± 31	122 ± 3
H	**Cr (mg/kg)**	**Ni (mg/kg)**	**Cu (mg/kg)**	**Zn (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**	**CEC (cmol$_{(+)}$/kg)**	
Ap	1 090 ± 60	18.6 ± 1.6	9± 1	17 ± 1	0.38 ± 0.03	24.8 ± 1.1	13.26 ± 2.25	
B1t	120 ± 30	18.0 ± 1.5	6 ± 1	19 ± 1	0.06 ± 0.01	25.4 ± 1.6	27.68 ± 1.05	
B2t	110 ± 20	17.9 ± 0.9	4 ± 1	20 ± 1	0.07 ± 0.01	21.0 ± 1.2	33.39 ± 2.55	

Note: H: Soil horizon. D: Depth interval. EC: Electrical conductivity. OC: Organic carbon content. CEC: Cation exchange capacity. [a] Mean values ± SD

plant was mixed into the top 100 mm of each column and was added to each column according to the following treatments: 364.5 g (High H – equivalent to 357 Mg·ha^{-1}), 227.8 g (Medium M-equivalent to 223 Mg·ha^{-1}) and 22.8 g (Low L-equivalent to 22 Mg·ha^{-1}). Sludge was crushed to pass a 2 mm sieve to improve the mixture between soil and sludge. Dosage H was calculated according to the critical soil concentration, above which toxicity is considered to be possible (Kabata-Pendias and Pendias, 1992). Dosages M and L were calculated according to the limit values for amounts of metals which may be added to agricultural land on a 10 year-average (M) and 1 year (L) allowed by European Legislation (European Community, 1986) (Table 1). A completely randomised design was implemented with the three soil treatments and a control soil (C). Each treatment was replicated four times resulting in 12 soil columns treated with sewage sludge and 4 untreated columns.

Over the duration of the study, 5 000 mℓ of water was applied to each of the columns and 6 pore volumes of water was leached from each of the columns simulating the drainage regime of a Mediterranean climate. Irrigation consisted of 500 mℓ every 15 to 20 d. Soil columns were maintained at unsaturated moisture and under steady state (time-independent) water flow conditions over 174 d. After each irrigation, leachates were collected over a 48-h period by a funnel (area: 12 000 mm^2) located in a 750 mℓ capacity bottle.

Finally, columns were sectioned and soil samples were collected at four depth intervals: 0 to 100 mm, 100 to 300 mm, 300 to 500 mm and 500 to 840 mm. Analytical concentrations of Cd, Cr, Cu, Pb, Ni and Zn were determined in the soil samples. A metals mass balance was completed by determining the metals content of the leachates.

The risk of groundwater salinisation by sewage sludge application was studied by measuring the electrical conductivity of leachates, since EC correlates well with the dissolved salts concentration (Barbarick et al., 1980).

Results and discussion

Soil properties

Soil properties are shown in Table 2. Soil is classified as Typic Palexeralf by USDA-SSS Soil Taxonomy (USDA, 1999) and as Luvisol by FAO (WRB, 1998). Soil profile was A-B1t-B2t and presented an argillic horizon whose illuviation clay content increased with depth. The metal content of the soil did not exceed the limit values for concentrations of metals in soil fixed by Eu-

TABLE 3
Sewage sludge properties

TC (%)	OC (%)	THS (%)	HA (%)	FA (%)	DOC (%)	N (%)
28.6±0.2[a]	12.8 ± 0.1	3.80 ± 0.14	2.47 ± 0.10	1.33 ± 0.09	0.26 ± 0.01	1.5 ± 0.1
P (g/kg)	**EC (dS m^{-1}, 25ªC)**	**pH**	**Ca (g/kg)**	**Mg (g/kg)**	**Na (g/kg)**	**K (g/kg)**
1.2 ± 0.1	7.1 ± 0.5	6.65 ± 0.06	45 ± 2	7.1 ± 0.3	0.6 ± 0.2	5.1 ± 0.7

Note: TC: Total carbon. OC: Organic carbon. THS: Total humified substances. HA: Humic acids. FA: Fulvic acids. DOC: Dissolved organic carbon. EC: Electrical conductivity.
[a] Mean values ± SD

TABLE 4
Metals content of sewage sludge: total content (TC_m), bound to total organic carbon (OC_m) and dissolved organic matter (DOC_m)

Fraction	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
TC_m	518 ± 29[a]	63 ± 2	377 ± 3	1344 ± 17	1.7 ± 0.2	229 ± 11
OC_m	25 ± 3	30 ± 2	68 ± 5	247 ± 14	1.07 ± 0.08	1.68 ± 0.11
DOC_m	1.99 ± 0.05	3.60 ± 0.21	7.67 ± 0.14	9.89 ± 1.46	0.03 ± 0.01	1.30 ± 0.05

Note: [a] Mean values ± SD

ropean (European Community, 1986) and Spanish regulations (CEE-CM, 1998; MAPA, 1990); and these contents were normal for this type of soil (Polo et al., 1995).

Composted sewage sludge properties

Tables 3 and 4 show sewage sludge composition. The metal content of the composted sewage sludge was below the limit values for concentrations of metals in sewage sludge fixed by European Regulation (European Community, 1986). The ratio of THS/OC (0.13) confirmed that the sewage sludge organic matter had not undergone a high degree of transformation and it was not very humified. The polymerisation index HA/FA (1.86) was normal for composted sewage sludge (Iakimenko et al., 1996). The DOC of the sewage sludge was high due to FA and organic compounds produced during the composting process (Fletcher and Beckett, 1987). These organic substances can bind to Cr, Ni, Cu, Zn, Cd and Pb forming soluble organic complexes which can move down soil columns.

The ratio OC_m/TC_m decreased as follows: Cd 0.63 > Ni 0.48 > Cu 0.18 = Zn 0.18 > Cr 0.05 > Pb 0.01) and the ratio DOC_m/OC_m was in the following order: Pb 0.77 > Ni 0.12 > Cu 0.11 > Cr 0.08 > Zn 0.04 > Cd 0.03. These results show that Pb was first and Cd last in the order of metals bound to DOC which follows the stability order of organic-metal complexes described by Klassen et al. (2000). The positions of Ni and Pb in the above sequence depend on the Ni and Cu content of the soil organic matter (McBride, 2001). Zn and Cd are in the last positions which can be related to their low capacity for occurrence in organic complexes (Hay, 1984).

Mass balance of metals

Mass balance of metals was calculated after determining the initial metals content of the soil treated with sewage sludge, the final metals content of the soil at four depth intervals: 0 to 100 mm, 100 to 300 mm, 300 to 500 mm and 500 to 840 mm, and the total Cr, Ni, Cu, Zn, Cd and Pb leached from the soil columns.

The percentage (of initial metals content of the soil treated with sewage sludge) of leached Cr, Ni, Cu, Zn, Cd and Pb from soil columns (Table 5) ranged from 0.10% (Cd, treatment H) to 0.01% (Cr, Pb, treatments H, M, L, C). The lixiviation of each metal (Fig. 1) increased with the doses which had a significant effect on the metals' mobility. The low percentage of leached metals could be caused by clay content (data for whole soil profile 39.17%), which could influence the metals' retention. It must be pointed out that clay minerals and oxides of iron occur in the clay size fraction (< 2 µm). Indeed, soil colour (Table 2) indicated a high content of iron oxides (Scheinost and Schwertmann, 1999) that are excellent scavengers for trace metals (Tessier, 1979). Obtained results have been compared with the results obtained in three soils with different clay content (Table 6) to which surface composted sewage sludge was applied at the rate H. Results show that since the P-value in the ANOVA test is less than 0.05, there is a statistically significant relationship between clay content (%) and total percentage of leached metals at the 95% confidence level (Fig. 2). Moreover, the R-squared statistic indicates that the model as fitted explains 92% of the variability in total percentage of leached metals at the confidence level. The correlation coefficient equals -0.96, indicating a relatively strong relationship between clay content (%) and total percentage of leached metals at the 95% confidence level. These results are in agreement with the results reported by other authors that have described the influence of clay size fraction in metals retention (Alloway, 1995; Kabata-Pendias and Pendias, 1991). For example, McGrath and Loveland (1992) observed that the retention of Cr and Ni in topsoils increased with the increment of the clay size fraction, Kiekens (1995) that the maximum Zn adsorption by soils increased with the percentage of clay in soils with similar pH and Kabata-Pendias and Pendias (1991) observed, that usually, total soil content of Cr, Ni, Cu, Zn, Cd, Pb was related to soil texture being higher in clay soils than in silty or sandy soils.

The average of leached metals expressed as a percentage of initial content (Table 5) followed the sequence:

$$\begin{aligned}&\text{Cd } (0.04\%) > \text{Cu } (0.02) \sim \text{Ni } (0.02) \sim \text{Zn } (0.02)\\ &> \text{Pb } (0.01) \sim \text{Cr } (0.01) \qquad [4]\end{aligned}$$

These results are in agreement with those of other authors. Singh

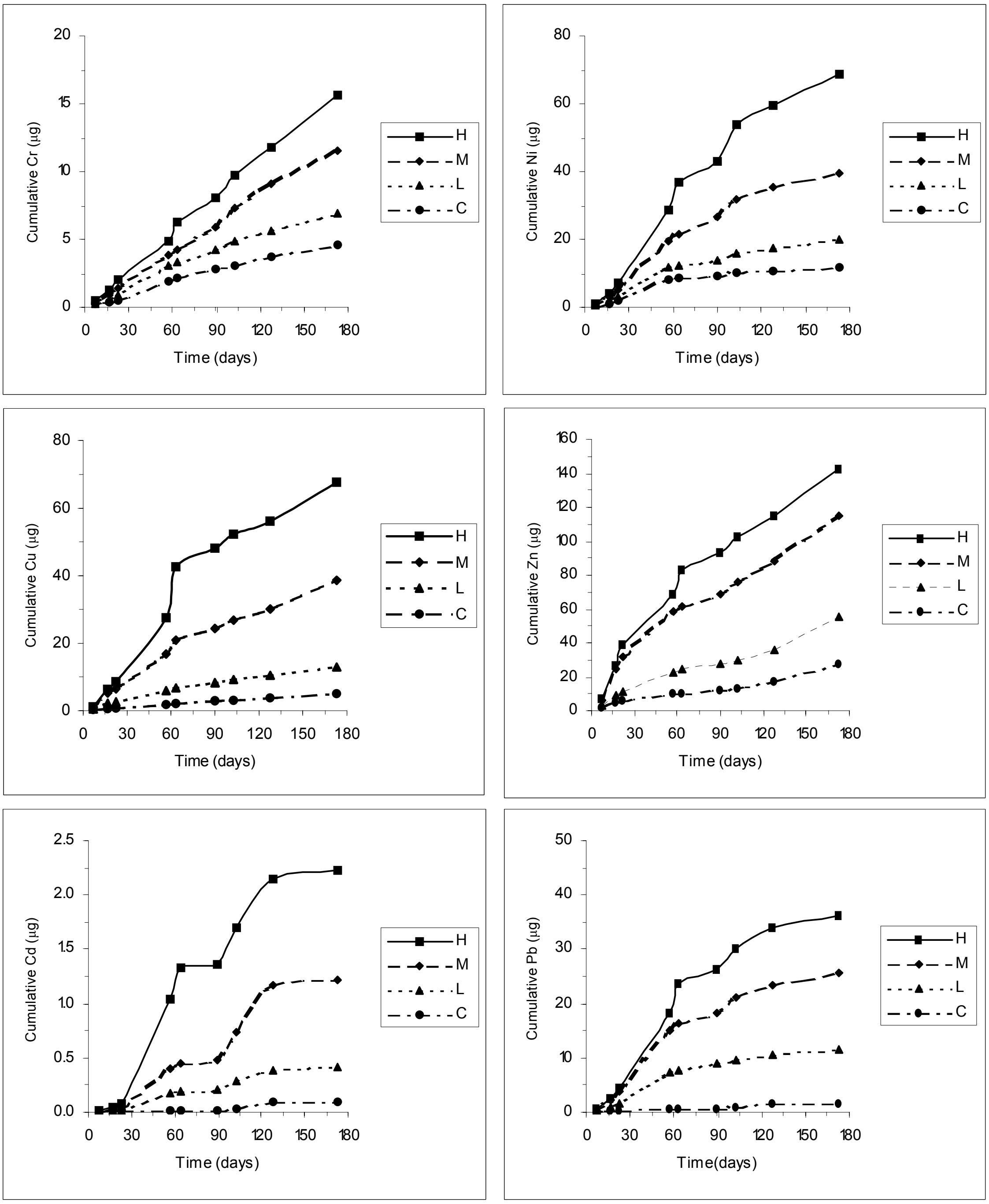

Figure 1
Amounts of metals leached from soil columns as a function of experimental time

TABLE 5
Leached metals from soil columns expressed as a percentage of soil initial content

Treatment	Cr	Ni	Cu	Zn	Cd	Pb	Total
			% of total applied				
H	<0.01a[a]	0.04 ± 0.01a[b]	0.04 ± 0.01a	0.03 ± 0.01a	0.10 ± 0.01a	0.01 ± 0.01a	0.21± 0.01a
M	<0.01a	0.02± 0.01ab	0.03± 0.01ab	0.03± 0.01a	0.06± 0.01b	<0.01ab	0.14± 0.02b
L	<0.01a	0.01± 0.01b	0.02± 0.01b	0.02± 0.01ab	0.02± 0.01c	<0.01ab	0.08 ± 0.02c
C	<0.01a	0.01± 0.01b	0.01± 0.01bc	0.02± 0.01ab	0.01± 0.01cd	<0.01ab	0.04± 0.01d
Average	<0.01	0.02±0.01	0.02± 0.01	0.02± 0.01	0.04± 0.04	<0.01	

Note: [a] Mean values ± SD [b] Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan method (Manugistic, 2000).

TABLE 6
Main properties and leached metals from three different soils treated at the rate H

CEC[a] (cmol$_{(+)}$/kg)	pH[a]	OC[a] (%)	Clay[a] (%)	Cr (%)	Ni (%)	Cu (%)	Zn (%)	Cd (%)	Pb (%)
17.04	6.7	4.6	31.36	0.02± 0.01[b]	0.12± 0.01	0.07± 0.01	0.04± 0.01	0.31± 0.01	0.02± 0.01
19.23	8.2	1.5	28.86	0.02± 0.01	0.14± 0.01	0.09± 0.01	0.03± 0.01	0.41± 0.01	0.04± 0.01
11.46	8	2	11.63	0.02± 0.01	0.15± 0.01	0.14± 0.01	0.03± 0.01	0.67± 0.01	0.02± 0.01

Note: [a]Data for whole soil profiles. [b]Mean values ± SD

TABLE 7
Maximum metal concentration ($C_{maximun}$), mean metal concentration (C_{mean}) in leachates and metals' mean lifetime

Treatment	Metal	$C_{maximun}$ (μg/ℓ)	C_{mean} (μg/ℓ)	μ_t[a] (day)
H	Cr	11.81±0.91a[bc]	7.47±0.20a	79±2
M		7.41±0.07b	5.23±0.26b	79±3
L		5.25±0.23c	3.71±0.14c	73±1
C		3.54±0.62d	2.40±0.12d	73±2
Average				**76±4a[d]**
H	Ni	62.98±2.43a	32.8±0.63a	72±2
M		44.79±0.18b	17.93±0.56b	68±3
L		21.14±0.36c	10.58±0.47c	65±1
C		16.60±1.09d	6.05±0.52d	55±2
Average				**63±7b**
H	Cu	76.69±0.43a	32.37±1.37a	69±1
M		57.13±0.53b	17.51±0.32b	69±3
L		14.33±0.25c	10.58±0.47c	64±3
C		4.40±0.15d	6.05±0.52d	75±4
Average				**70±5ab**
H	Zn	262.50±1.61a	68.61±1.79a	58±3
M		137.83±2.57b	52.02±2.06b	60±6
L		47.10±5.22c	29.09±0.74c	72±3
C		25.51±4.40d	14.51±0.49d	74±5
Average				**68±9ab**
H	Cd	2.81±0.32a	1.06±0.03a	74±2
M		1.14±0.13b	0.55±0.03b	87±3
L		0.39±0.03c	0.22±0.02c	80±1
C		0.24±0.03d	0.05±0.01d	93±3
Average				**84±8c**
H	Pb	40.61±0.52a	17.4±0.75a	64±2
M		34.96±0.67b	11.60±0.49b	63±2
L		14.23±0.21c	6.07±0.35c	61±2
C		2.54±0.56d	0.84±0.09d	66±7
Average				**64±6b**

Note: [a] Metals' mean lifetime in soil columns. [b]Mean values ± standard deviation. [c]For each metal, values followed by the same letter are not significantly different (*P* = 0.05) using Duncan method (Manugistic, 2000). [d] For each average, values followed by the same letter are not significantly different (*P* = 0.05) using Duncan method (Manugistic, 2000).

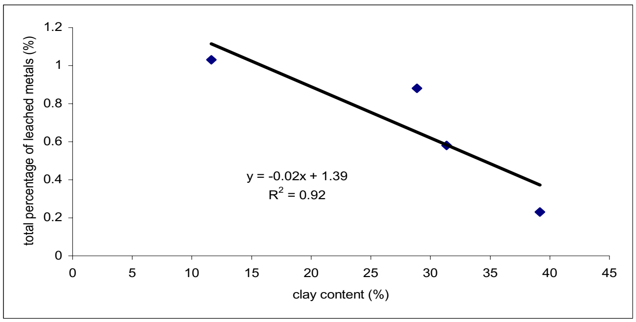

Figure 2
Percentage of metals leached from different soils as a function of clay content

et al. (2000) obtained a similar sequence for metals leached with H_2O at pH 4. Cd was the most leached metal according to Sidle and Kardos (1977) who found, in a soil amended with sewage sludge, 6.6% of Cd at 120 cm soil depth. Welch and Lund (1989) measured a higher Zn concentration (0.37%) in sandy soil (50% sand) and a higher Cd mobility was described by Schmitt and Sticher (1991). Pb mobility was lower than Zn and Cd due to the formation of insoluble organic-Pb complexes (Camobreco et al., 1996).

The displacement of Cr, Ni, Cu, Zn, Cd and Pb through soil columns presented temporal differences (Table 7). The mean lifetime of metals in soil columns μ_τ followed the sequences:

Cd (84 days) > Cr (76) ~ Cu (70) ~ Zn (68) [5]

Cu (70) ~ Zn (68) ~ Pb (64) ~ Ni (63) [6]

Cd is on the borderline of soft Lewis acids according to ionic potential (IP) and Misono softness (Sposito, 1989), and its displacement depends on the presence of soluble organic compounds. The mean Cd lifetime was almost 87d, half of the experimental time (174 d), and therefore Cd was uniformly distributed. Cr distribution was similar to Cd distribution. However, Cr is classified as a strong Lewis acid by Misono softness, as is Al^{3+}, and their behaviour can be related to their high affinity for inorganic ligands such as H_2O and OH^- which are strong Lewis bases that can precipitate with Cr. Ni and Pb occupied the last positions in the mean lifetime of metals sequence and, therefore, their distribution was not very uniform. Ni is preceded by Cu in Irvin-Williams order according to their relative affinities for their adsorptions by the soil and therefore, Ni forms more stable compounds than Cu according to ionic radius^{-1} and electron configuration (Sposito, 1989; Fiabane and Williams, 1977). Indeed, Ni and Zn are located on the borderline between soft and strong Lewis acids and could have a similar behaviour to Ca^{2+}, Mg^{2+} and, therefore, could form stable soluble complexes with Cl^-, SO_4^{2-} and HCO_3^-, which are strong ligands (Hay, 1984). Finally, Pb is a soft Lewis acid, and its displacement depends on soluble organic compounds. Thus, each metal has different chemical properties, due to their atomic structures, which affect their displacement in the soil after sewage sludge application.

Mean metal concentrations (c_{mean}) and maximum metal concentrations ($c_{maximun}$) in leachates for all metals (Table 7) were

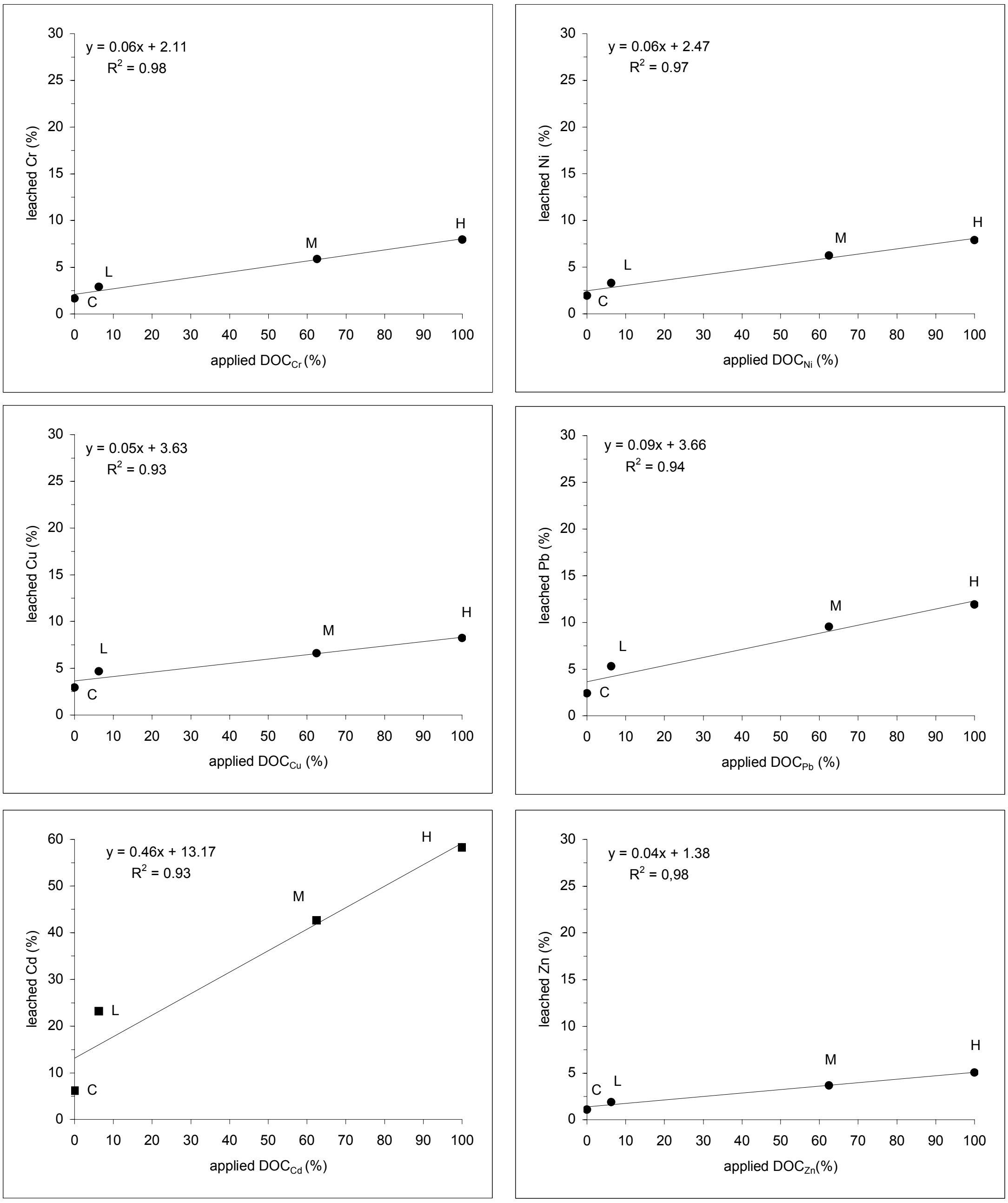

Figure 3

Leached metals as a function of applied metals bound to sewage sludge dissolved organic carbon by each treatment

below the limit values for irrigation water (Branson et al., 1975). Nevertheless, concentrations of Pb and Ni were greater than the guideline values for drinking water (WHO, 1996). Thus, potentially harmful health effects may result from the application of sewage sludge. Indeed, the risk of harmful effects increases in soils with less clay content due to the influence of clay in metal retention (Gascó et al., 2003).

Organic ligands of soil and sewage sludge can form organic-mineral complexes which can influence the displacement and fixation of metals. Soil organic matter may make an appreciable contribution to the capacity of the soil to fix metals by adsorption or complex formations (Bear, 1964). Metal movement may be related to the DOC of sewage sludge since some organic ligands have a high affinity for the metals and form soluble complexes (McBride et al., 1997).

The influence of DOC on metals lixiviation was studied. Figure 3 shows leached metals (leached$_m$, expressed as percentage of metals bound to DOC of sewage sludge added by each treatment) as a function of applied metals bound to DOC of sewage sludge added (applied DOC$_m$) by each treatment (expressed as percentage of metals bound to DOC of sewage sludge applied according to treatment H). The analysis of variance (ANOVA) showed that applied DOC$_m$ had a statistically significant effect on leached$_m$ at the 95.0% confidence level. These results confirmed that Cr, Ni, Cu, Zn, Cd and Pb were displaced in soils bound to DOC and leached metals increased with dose. Recently, Al-Wabel et al. (2002) suggested that DOC increased Cu and Zn mobility and only a small percentage of the total dissolved metals existed as free ions or organic complexes. For this reason, organically complexed forms of metals can account for the mi-

TABLE 8
Metal content of soil in the Typic Palexeralf columns

Depth	Cr		Ni		Cu		Zn		Cd		Pb	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
(cm)	(mg·kg^{-1})											
Control												
0-10	109±9[a]	94 ±7	19±2	17±1	9±1	8±1	18±2	16±2	0.40±0.03	0.36±0.04	25±1	24±1
10-30	109± 9	107±10	19±2	17±2	9±1	8±1	18±2	17±2	0.40±0.03	0.36±0.04	25±1	24±2
30-50	12±3	15±2	18±1	18±1	5±1	4±1	19±1	19±4	0.05±0.01	0.06±0.01	26±1	25±2
50-84	11±2	16±2	18±1	17±1	4±1	4±1	20±1	16±2	0.07±0.01	0.07±0.01	21±1	18±1
Treatment H												
0-10	168±10	146±10	28±1	27±3	84±7	77±5	286±13	272±11	0.65±0.05	0.59±0.08	137±6	123±2
10-30	108±5	103±4	17±1	17±1	10±1	8±1	18±1	15±1	0.38±0.03	0.34±0.04	24±1	21±3
30-50	12±3	23±3	18±1	18±3	5±1	11±2	19±1	30±7	0.05±0.01	0.11±0.02	26±1	35±4
50-84	11±1	18±1	18±1	17±1	4±1	6±1	20±1	28±5	0.07±0.01	0.10±0.02	21±1	30±4
Treatment M												
0-10	140±9	121±8	25±1	24±3	59±4	53±3	199±7	188±8	0.56±0.04	0.50±0.03	130±4	115±4
10-30	108±7	110±7	18±2	18±1	10±1	10±2	18±1	19±2	0.38±0.03	0.36±0.06	24±1	25±2
30-50	12±3	18±3	18±1	18±1	5±1	8±2	19±1	23±3	0.05±0.01	0.10±0.01	26±1	31±3
50-84	11±1	15±4	18±1	17±1	4±1	6±1	20±1	21±1	0.07±0.01	0.09±0.01	21±1	35±3
Treatment L												
0-10	121±8	105±7	19±1	19±2	15±2	14±2	38±4	33±5	0.40±0.03	0.38±0.04	28±1	26±1
10-30	104±7	106±5	19±1	19±1	9±1	9±1	18±1	19±2	0.37±0.03	0.35±0.02	25±1	27±1
30-50	12±3	16±1	18±1	16±1	5±1	6±1	19±1	20±2	0.05±0.01	0.08±0.01	26±1	23±2
50-84	11±1	17±2	18±1	16±1	4±1	4±1	20±1	21±3	0.07±0.01	0.07±0.02±	21±1	20±2

Note: [a] Mean ± SD

TABLE 9
Ratio between final metal concentration (C_f) of soil surface and the initial metal soil surface concentration (C_i)

Treatment	Cr	Ni	Cu	Zn	Cd	Pb
H	0.87±0.01a[a]	0.98±0.13a[b]	0.92±0.06a	0.95±0.06a	0.92±0.16a	0.90±0.04a
M	0.86±0.06a	0.97±0.14a	0.90±0.03a	0.94±0.04a	0.91±0.10a	0.90±0.01a
L	0.87±0.07a	0.93±0.05a	0.93±0.05a	0.88±0.17a	0.96±0.16a	0.93±0.03ab
C	0.87±0.08a	0.93±0.14a	0.89±0.11a	0.91±0.18a	0.97±0.16a	0.97±0.08b
Average[c]	0.87±0.06a	0.95±0.12bc	0.91±0.08b	0.92±0.13	0.95±0.14c	0.93±0.06c

Note: [a] Mean ± SD. [b] Values in a given column followed by the same letter are not significantly different (*P* = 0.05) using Duncan method (Manugistic,2000). [c] Average values followed by the same letter are not significantly different (*P* = 0.05) using Duncan method (Manugistic, 2000).

TABLE 10
Mass Balance of Cr, Ni, Cu, Zn, Cd and Pb recovered from soil columns

Treatment	Cr	Ni	Cu	Zn	Cd	Pb	Average
% of initial + added							
H	101± 3[a]	100± 3	102± 3	105± 5	102± 2	103± 4	102 ± 4
M	101± 3	98± 3	105± 6	100± 3	102± 3	105± 2	102 ± 4
L	102± 2	93± 4	102± 5	100± 3	100± 5	96± 3	99 ± 5
C	100± 3	96± 4	92± 13	93± 3	98± 7	94± 2	95 ± 7
Average	101± 3	97± 5	98 ± 10	98 ± 7	100 ± 5	99 ± 5	

Note: [a] Mean ± SD

gration of a substantial fraction of metals out of the soil surface (McBride et al., 1997).

Table 8 shows the final metal soil surface concentration (C_f) and initial metal soil surface concentration (C_i). The ratio C_f/C_i (Table 9) confirms that over 86% of metals were retained in the first 100 mm and that the metals' movement was limited to soil surface, which is in accordance with the findings of other authors (McGrath and Lane, 1989; Bergkvist et al., 2003; Emmerich et al., 1982).

Mass balances of Cr, Ni, Cu, Zn, Cd and Pb (Table 10) in soil columns, calculated for all profiles and not only for the superficial layer, recovered over 97% of initial metal content. These data were close to 100% for all metals since the soil and sewage sludge were homogenized and the soil and sewage sludge were mixed together before being packed into the soil columns, thus avoiding experimental errors due to the bypass flow through structural cracks, root channels, wormholes, and other highly conductive paths. Because of this, the recovery percentages were more accurate than those obtained in field experiments due to the bypass flow through structural cracks, root channels, wormholes, and other highly conductive paths. For example, Berti and Jacobs (1998) obtained trace element recoveries that ranged from 45 to 155% of the total applied. Dowdy et al. (1991) could only account for slightly less than half of the total added Cd and Zn in the top 1m of soil profiles.

Electrical conductivity evolution

Sewage sludge application produced an increase in soil ions which raised the soil electrical conductivity (Table 11), but it was, in all cases, under 4 dS·m^{-1}at 25 °C, which is the limit between normal and saline soils (Richards, 1954). Sewage sludge produced a saline pulsation which was measured by maximum electrical conductivity of leachates ($EC_{maximun}$) in the 22nd experimental day for all treatments (Fig. 4). The ECs of leachates were below the guideline value (2.78 dS·m^{-1}, 25 °C) fixed by the European Union (Council of the European Union, 1998). Mean electrical conductivity of leachates (EC_{mean}) and $EC_{maximun}$ increased in proportion to the amount of sludge applied, and so the dose of sewage sludge should be calculated carefully to avoid the risk of groundwater salinisation (Table 11).

TABLE 11
Electrical conductivity

Treatment	EC_{se}[a] (dS m^{-1}, 25°C)	EC_{mean}[b] (dS m^{-1}, 25°C)	$EC_{maximun}$[c] (dS m^{-1}, 25°C)	μ_t[d] (day)
H	2.07 ± 0.08a[e]	0.69 ± 0.03a	1.68 ± 0.08a	66 ± 2a
M	1.72 ± 0.07b[f]	0.38 ± 0.03b	1.04 ± 0.08b	57 ± 4b
L	0.57 ± 0.03c	0.11 ± 0.02c	0.22 ± 0.05c	58 ± 3b
C	0.11 ± 0.02d	0.06 ± 0.02d	0.11 ± 0.02d	62 ± 3a

Note: [a] Final soil electrical conductivity in saturation extract. [b] Mean leachates electrical conductivity. [c] Maximum leachates electrical conductivity. [d] Mean lifetime soluble salts. [e] Mean values ± SD. [f] Values in a given column followed by the same letter are not significantly different (*P* = 0.05) using Duncan method (Manugistic, 2000).

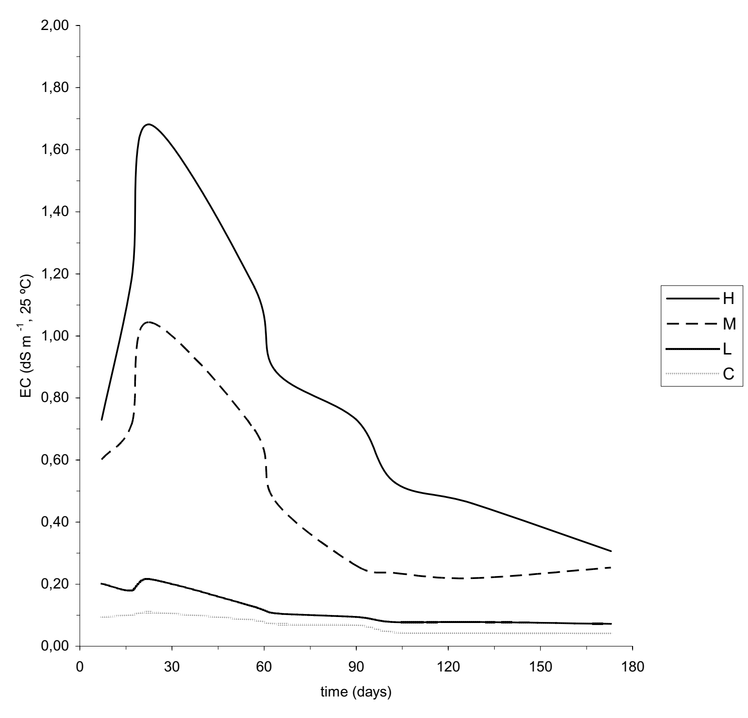

Figure 4
Electrical conductivity evolution

Conclusions

Mass balance recovered over 97% of the initial soil metal content and metal movement was limited to topsoil. The ratio C_f/C_i confirmed that over 86% of applied metals were retained in the top 10 mm and that the retention was similar for all metals. Total Cr, Ni, Cu, Zn, Cd and Pb leached from soil columns ranged from 0.01% to 0.10%. Results confirmed that metals were displaced through soil columns bound to dissolved organic carbon. Metal concentrations in leachates did not exceed the maximum allowed metal concentrations for irrigation water. Nevertheless, Pb and Ni concentrations in leachates were above the guideline values for drinking water in all treatments. Thus, potentially harmful health effects could occur after application of sewage sludge.

Sewage sludge application produced an increase in soil ion concentration which raised the soil EC to close to 4 dS·m^{-1}, 25°C, which is on the boundary between normal and saline soils. Electrical conductivity of leachates was below the guideline value fixed by the European Union.

Soil column experiments can provide rapid results about metal behaviour. These studies can serve as an aid in designing field experiments and the results can be used to assist in developing new regulations for sewage sludge use or disposal. .

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