

Mobility of heavy metals in soils amended with sewage sludge

M. T. Morera, J. C. Echeverría, and J. J. Garrido

Departamento de Química Aplicada. Universidad Pública de Navarra. Campus Arrosadía, E-31006 Pamplona. Spain. E-mail: j.garrido@unavarra.es. Received 7 July 2000, accepted 30 April 2001.

Morera, M. T., Echeverría, J. C. and Garrido, J. J. 2001. **Mobility of heavy metals in soils amended with sewage sludge.** *Can. J. Soil Sci.* **81**: 405–414. Sewage sludges added to arable land can improve soil fertility and physical properties. However, the concentrations of heavy metals commonly found in sludges limits their application to soil. The purpose of this paper is to evaluate the mobility of heavy metals (Cd, Cu, Ni, Pb and Zn) in four soils amended with different rates (0, 80, 60 and 320 t ha⁻¹) of anaerobically stabilized urban sewage sludge. Total metal content in the sewage sludge was Zn >> Cu > Pb > Ni >> Cd. Sludge, soils and sludge-soil mixtures were fractionated by the Tessier sequential extraction procedure. The fractions extracted by H₂O₂/HNO₃ and NH₂OH.HCl were the most abundant pools for metals under study. The apparent mobility of metals in the sludge was Zn ≈ Cd ≈ Ni > Pb > Cu. The addition of sewage sludge in soils increased the percentages of metal extracted in non-residual fractions. ANOVA showed that the most significant increases were those of Zn, followed by Cu and Pb; there were no statistical differences (*P* < 0.05) for Ni and Cd. Exchangeable Zn from sludge was immobilized in basic soils. The other trace metals showed no fraction redistribution. The soils and sludge-treated soil samples were also extracted with EDTA and DTPA. Extraction with EDTA was more sensitive to soil type, whereas extraction with DTPA showed wider variation with metals. Both chelates seemed to be more effective to assess the mobility of metals added with the sludges at low concentrations than the Tessier's chemical partitioning.

Key words: Soils, sewage sludge, heavy metals, mobility

Morera, M. T., Echeverría, J. C. et Garrido, J. J. 2001. **Mobilité des métaux lourds dans les sols amendés avec des boues usées.** *Can. J. Soil Sci.* **81**: 405–414. L'addition de boues usées aux terres arables peut améliorer la fertilité et les propriétés physiques du sol. La concentration de métaux lourds dans les boues restreint toutefois une telle application. Les auteurs ont évalué la mobilité des métaux lourds (Cd, Cu, Ni, Pb et Zn) dans quatre sols auxquels avait été ajoutée une quantité variable (0,80, 60 et 320 t ha⁻¹) de boues usées urbaines stabilisées en anaérobiose. La concentration totale de métaux dans la boue était de Zn >> Cu > Pb > Ni >> Cd. La boue, le sol et le mélange sol-boue ont été fractionnés par la technique d'extraction séquentielle de Tessier. Les fractions obtenues par extraction dans H₂O₂/HNO₃ et NH₂OH.HCl contenaient la plus grande quantité de métaux de toutes les fractions examinées. La mobilité apparente des métaux dans la boue correspond à Zn ≈ Cd ≈ Ni > Pb > Cu. L'addition de boues usées au sol augmente la proportion de métal extrait des fractions non résiduelles. L'analyse de la variance révèle que c'est la concentration de Zn qui connaît la hausse la plus importante, le Cu et le Pb arrivant en second; les auteurs n'ont relevé aucune variation statistiquement significative (*P* < 0,05) pour le Ni et le Cd. Les ions Zn échangeables présents dans la boue sont immobilisés dans les sols basiques. Il n'y a pas redistribution des autres métaux à l'état de trace dans les fractions. On a aussi extrait les métaux présents dans le sol et le mélange sol-boue avec de l'EDTA et du DTPA. L'extraction à l'EDTA varie plus avec le type de sol tandis que celle au DTPA varie plus avec le métal. Les deux chélates semblent donner de meilleurs résultats que la méthode de fractionnement chimique de Tessier quand il s'agit d'évaluer la mobilité des métaux en faible concentration dans les boues.

Mots clés: Sols, boues usées, métaux lourds, mobilité

The use of sewage sludge as an organic amendment in agriculture is a widespread practice in many countries. Sewage sludges disposed of on arable land improve the fertility and physical properties of the soil. However, the high concentrations of heavy metals, commonly found in sludges, limit their application on land (Alloway 1995). Mobility, environmental diffusion and bioavailability of heavy metals present in the sewage sludge largely depend on soil physico-chemical characteristics and, likewise, on trace metal chemical forms (Obrador et al. 1998).

Several soil-related factors, namely pH, organic matter, Mn and Fe oxides, and clay content determine the chemical

associations of heavy metals and their availability to plants (Narwal and Singh 1998). Among these factors, pH has been regarded as a major variable regulating the metal mobility in soils (Heckman et al. 1987). The sorption and the precipitation of heavy metals are enhanced by increasing soil pH (Kiekens 1984; Alloway and Jackson 1991). These processes help to explain the decreased mobility normally found in soils with a basic pH.

Sequential extractions have been used to fractionate heavy metals in sludge (McGrath and Cegarra 1992; Petruzzelli et al. 1994) or sludge-amended soils to investigate their chemical distribution among the solid fractions

(Emmerich et al. 1982; McGrath and Cegarra 1992) and, indirectly, their mobility and plant availability (Dudka and Chlopecka 1990; Sims and Kline 1991; Tsadilas et al. 1995). Despite uncertainties related to the selectivity of the various extractants and to potential problems due to re-adsorption, sequential extraction procedures provide detailed information about the status of trace metals in soils (Pickering 1986; Echeverría et al. 1998). A procedure used extensively in soils and sediments is that of Tessier et al. (1979), which is based on five operationally defined fractions: exchangeable, carbonate, Fe-Mn oxides, organic, and residual. The exchangeable fraction is considered to be the most plant-available form (Petruzzelli 1989; Xian and Shokohifard 1989; Shuman 1991), whereas metals extracted in the residual fraction are considered to be less mobile and available in the short to a medium term (Brümer 1986). Application of sewage sludge to soil may alter heavy metal content in the fractions and enhance chemical forms potentially available (Pengxing et al. 1997).

Single chemical extractions with synthetic chelating agents such as **ethylene diamine tetraacetic acid (EDTA)** and **diethylene triamine pentaacetic acid (DTPA)** have been widely used to study relationships between metals in plants and soils. Single extractions are less time consuming than sequential extractions. They have been used as an alternative to sequential extractions in routine tests to evaluate plant availability and mobility of heavy metals in soils amended with sewage sludge (Lebourg et al. 1996). These extractants usually aim to extract the fractions that are water-soluble, easily exchangeable, and some of the organic bound metals, although they can also dissolve some of the carbonates and oxyhydroxides (Pickering 1986). The efficiency of these extractants is usually measured in terms of their ability to extract an amount of metal that correlates well with the plant content. Correlations vary according to the analyzed metal, soil and experimental conditions (Kuo 1990; Juste and Tauzin 1992). The metal ions extracted are not necessarily the same as the ions absorbed by the plant. They are only related by a satisfactory empirical relationship allowing for a rough prediction of the mobility of the metal.

The purpose of this study was to investigate the mobility of sludge-borne heavy metals added to four soils with different physico-chemical properties. In order to enhance these effects, sewage sludge was applied at rates (80, 160 and 320 t ha⁻¹) up to the maximum limit values established by the Spanish (R.D. 13110/1990) and European Community (86/278/EEC). Trace elements were sequentially extracted using the Tessier procedure from sludge, soils and sludge-treated soil samples. The soils and sludge-treated soil samples were also extracted with two solutions standardized for predicting plant availability, which include EDTA (pH 4.65) and DTPA (pH 7.30).

MATERIALS AND METHODS

Soils and Sewage Sludge

The four soil samples used in this study were collected in Navarra (Spain). According to soil taxonomy (Soil Survey

Staff 1975), the soils were Lithic Haplumbrept (Lh), Calcixerollic Xerochrept (Cx1 and Cx2), and Paralithic Xerorthent (Px). Calcixerollic Xerochrepts (Cx1 and Cx2) and Px were agricultural soils, whereas Lh was uncultivated (Echeverría et al. 1998, 1999a). Samples from the top 15 cm soil layer were air-dried, ground, and sieved through a 2-mm mesh before determining specific soils properties: (1) particle-size distribution by fractionation using wet sieving and sedimentation (Primo Yúfera and Carrasco Dorriens 1987); (2) mineralogical composition of clay fraction by a Siemens D500 X-ray diffractometer; (3) total amount of carbon and nitrogen by using a Carlo Erba EA 1108 elemental analyzer; (4) inorganic carbon (Loeppert et al. 1984); (5) pH (McLean 1982); (6) **cation-exchange capacity (CEC)** by Ca²⁺ saturation, displacement by 1 M sodium acetate and measurement of Ca²⁺ ions by atomic absorption spectroscopy (Jackson 1982); and (7) surface area by N₂ gas adsorption at 77 K (Echeverría et al. 1999b). Selected physical and chemical characteristics of soils are presented in Table 1. With the exception of the Lh soil, which is acidic and has a large organic C content, the other three soils had a basic pH, and contained a moderate or small percentage of organic C. The CEC values were similar to those found in references for illite (10–40 meq 100 g⁻¹) (Tan 1982; Alloway 1990), which was the most abundant phyllosilicate in soils under study. The BET surface area obtained from N₂ adsorption at 77 K of the soils ranged from 8 m² g⁻¹ for Lh to 50 m² g⁻¹ for Cx1.

The sludge was collected from the wastewater treatment plant of Arazuri that receives domestic and industrial water from Pamplona (Spain). It was a primary anaerobically digested sludge. Chemical properties of sewage sludge and total concentration, of Cd, Cu, Ni, Pb and Zn are presented in Table 2. The largest concentration was that of Zn followed by Cu, Pb, Ni and Cd. These concentrations are usually found in sludges with low inputs in industrial sewage, and were far below the Spanish and European Community limit values for agricultural use.

Soils Treatment with Sewage Sludge

Subsamples of each air-dried sieved (< 2 mm) soil were thoroughly mixed with the air-dried ground homogenized sludge in pots to produce mixtures equivalent in the field to application rates of 0 (reference), 80, 160 and 320 t ha⁻¹. Assuming an incorporation depth of 30 cm, the doses of sewage sludge, equivalent to 0, 80, 160 and 320 t ha⁻¹ were 0; 0.027; 0.053; and 0.107 g dry weight cm⁻³, respectively. These high application rates were an extreme treatment that would not be recommended in agricultural practice. Considering the concentration of metals in the sewage sludge, an annual dose of 80 t ha⁻¹ would be higher than the annual threshold for Zn according to Spanish and CEE regulations for the use of sewage sludge as soil amendment. The maximum amount of sewage sludge that could be added to the soils without going beyond the annual limit for Zn would be 56 t ha⁻¹. The soil-sludge samples were left to settle at field temperature for a month by periodically adding distilled water to keep moisture near field capacity. For each treatment, an integrated sample was prepared by mixing

Table 1. Selected physical and chemical characteristics of soils

	Lithic haplumbrept (Lh)	Calcixerollic xerochrept (Cx1)	Calcixerollic xerochrept (Cx2)	Paralithic xerorthent (Px)
Particle size (g kg ⁻¹)				
>50 (μm)	361	215	499	27
50–2 (μm)	408	410	291	579
<2 (μm)	231	375	210	394
Textural class	Loam	Clay loam	Loam	Silty clay
Main clay minerals ^z	I	I	M, C, I	I
Total C (g kg ⁻¹)	108	15	45	56
Inorganic C (g kg ⁻¹)	2	7	23	51
Organic C ^y (g kg ⁻¹)	106	8	22	5
Total N (g kg ⁻¹)	4.5	2	1.3	1.8
pH (saturated paste)	5	7.2	7.9	8.1
Cationic exchange capacity (meq 100 g ⁻¹)	17.3	23.9	10.7	14.8
Surface area (BET) ^x (m ² g ⁻¹)	8	50	30	25

^zI = illite, M = montmorillonite, C = chlorite.

^yObtained by difference.

^xAdsorption of N₂ at 77 K.

Table 2. Chemical characteristics of sewage sludge

pH	7.3
C/N rate	10.5
Dry matter (%)	31.7
<i>Fertilizing elements (%)</i>	
Organic carbon	22.6
Inorganic carbon	0.5
Total nitrogen	2.2
Potassium (K ₂ O)	0.2
Phosphorous (P ₂ O ₅)	3.5
<i>Heavy metals (mg kg⁻¹ dry weight)</i>	
Cd	3
Cu	325
Ni	95
Pb	201
Zn	1503

three portions taken from the surface, middle and bottom parts of the pots. These integrated samples were air-dried and crushed again to pass a 2-mm sieve prior to determining pH and studying the mobility of heavy metals by chemical extractions. Amendment with sewage sludge increased pH of Lh soil by one unit after the application of 320 t of sewage sludge ha⁻¹, but did not alter the pH of alkaline soils (Cx1, Cx2 y Px).

Metal Extraction Experiments

The metal distribution in sewage sludge and soil sub-samples from each treatment was assessed by the sequential extraction procedure of Tessier et al. (1979). The steps in the sequence were operationally defined in terms of the targeted forms as follows (Kim and Fergusson 1991): Fraction 1, exchangeable-weakly sorbed (8 mL, 1 M MgCl₂); Fraction 2, sorbed and/or carbonate bound (8 mL, 1 M NaOAc/HOAc, pH 5.0); Fraction 3, strongly sorbed to organic matter and/or strongly bound to easily reducible manganese oxides and amorphous iron oxides (20 mL, 0.04 M NH₂OH.HCl in 25% acetic acid); Fraction 4, very strongly bound or incorporated into organic matter or other

oxidizable species (8 mL, H₂O₂ 30% + 3 mL, 0.02 M HNO₃); Fraction 5, incorporated within resistant minerals (20 mL, HF 40%+4 mL, HClO₄ 70%). Suspensions were centrifuged at 3000 rpm for 10 min. Aliquots from the supernatants were removed, diluted up to 50 mL with distilled-deionized water and stored in polyethylene bottles to which 0.10 mL of HNO₃ (70%) were added for sample preservation. The rest of the extract was discarded and the residue was washed with 8 mL of distilled-deionized water; after centrifugation, the wash solution was discarded.

Extractable metal concentrations in soil subsamples from each treatment were also determined using EDTA and DTPA. In the EDTA extraction (Lakanen and Erviö 1971), 3 g of soil were extracted with 30 mL of 0.02 M EDTA + 0.5 M NH₄OAc (pH 4.65) for 1 h. In the DTPA extraction (Lindsay and Norvell 1978) 15 g of soil were extracted with 30 mL of 0.005 M DTPA + 0.1 M TEA (trietanolamine) + 0.01 M CaCl₂ (pH 7.30) for 2 h. The suspensions were placed in a thermostated water bath (Grant model SS40-2) at 298.0 ± 0.2 K, and shaken at 3 Hz. After the specified time for each extraction, suspensions were centrifuged at 3000 rpm for 10 min and the supernatants, acidified with 0.10 mL of HNO₃ (70%), were stored in polyethylene bottles for metal determination.

For each sample, sequential extraction and extractions with EDTA and DTPA were conducted in triplicate. Standards for all metals analyzed were prepared for each extraction in the same matrix as the extracting reagent to minimize matrix effects. Metal concentrations were determined by atomic absorption spectrophotometry (Perkin-Elmer mod. 2100). To determine total metal concentration in soils and sewage sludge triplicate sub-samples (1 g dry wt) were digested using the same procedure as that used for the residual fraction (Tessier et al. 1979).

Statistical Analysis

Sewage sludge treatment effects on content and mobility of heavy metals in soils were analyzed using variance analyses (ANOVA) based upon a design with three replications

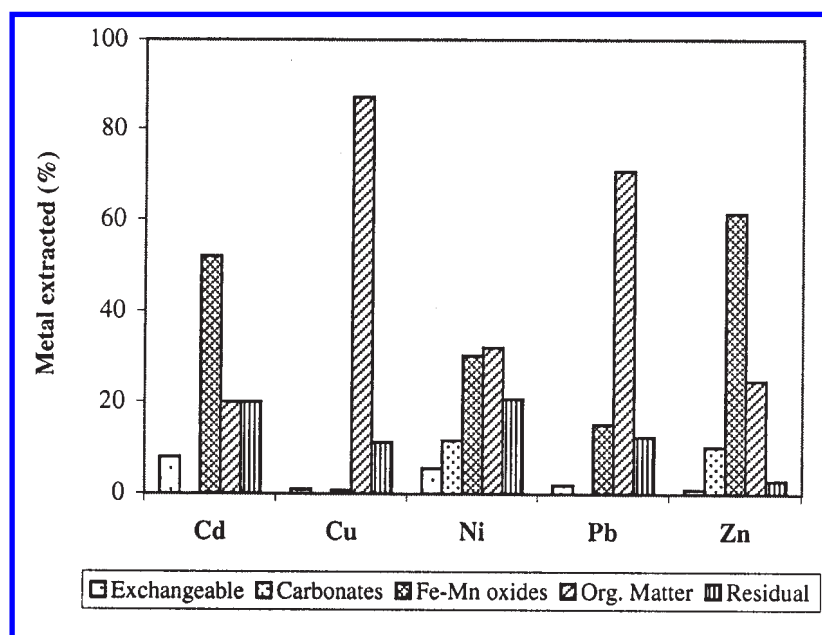


Fig. 1. Mean percentages of Cd, Cu, Ni, Pb and Zn in the Tessier partitioning of sewage sludge.

(Winer et al. 1991). A probability level of $P < 0.05$ was selected to establish statistical significance. We applied a multifactorial ANOVA to the percentages obtained from the Tessier fractions to evaluate the contribution to the total variance of sewage sludge rates (0, 80, 160, 320 t ha⁻¹), metals (Cd, Cu, Ni, Pb and Zn), soils (Cx1, Cx2, Px and Lh) and fractions (exchangeable, carbonates, oxides and organic matter). Similarly, we applied a multifactorial ANOVA to the percentages of metals extracted with EDTA and DTPA, including sewage sludge rates, metals and soils. SPSS Advanced Statistics 6.1 was used for this purpose.

RESULTS AND DISCUSSION

Heavy Metal Distribution in Sewage Sludge

Figure 1 shows, in percentages, the distribution of the chemical forms of Cd, Cu, Ni, Pb and Zn in the sewage sludge. The total percentage recoveries of metals extracted were Cd, 100; Cu, 99; Ni, 102; Pb, 91; and Zn, 93. The Fig. 1 reflects the predominance of the fractions extracted by H₂O₂/HNO₃ (organic matter) and NH₂OH.HCl (Fe and Mn oxides), with some differences among the metals. Copper and Pb were extracted mainly by H₂O₂/HNO₃ (87.2% and 70.6%, respectively); these results are consistent with the known affinity of copper and lead for organic ligands (Taylor et al. 1995). Copper appeared in somewhat more resistant chemical forms than Pb, since percentage of these metals released by NH₂OH.HCl were 0.7% for Cu and 15.1 for Pb. However, most of the Zn and Cd were extracted with hydroxylamine hydrochloride (61.3% and 52%, respectively). The findings for Ni were somewhere in between the other two groups, with similar percentages for H₂O₂/HNO₃ (32%) and NH₂OH.HCl (30.3%) fractions. More than 10% of Ni, Zn and Cd were found in easily mobilizable forms (exchangeable and NaOAc/HOAc extracted). Bearing in mind that fractions are extracted according to a gradient of

association stability with the solid phases (Martin et al. 1987), and that extractability decreases roughly according to the order of extraction (Harrison 1981); mobility of metals in the sludge was as follows: Zn ≈ Cd ≈ Ni > Pb > Cu.

Since the sum of the amounts of Cd, Cu, Ni, Pb and Zn extracted by NH₂OH.HCl (918 mg kg⁻¹) was larger than the total Fe and Mn content released in that fraction (881 mg kg⁻¹), it is highly unlikely that the metals extracted in this fraction were exclusively associated with Fe and Mn oxides. According to Kim and Fergusson (1991) some of the metals released in the oxide fraction are metals strongly sorbed to organic matter which were not extracted in previous fractions. Therefore, partitioning would reflect not only the contribution of geochemical phases, but also the diversity of reactive groups generated by the variety of active functional groups found in sludge organic matter and the different reactivity of metals.

Effects of Sewage Sludge Application on Total Content and Distribution of Heavy Metals in Soils

Total concentration of Cd, Cu, Ni, Pb and Zn in soils following application rates of 0 (reference), 80, 160 and 320 t ha⁻¹ of sewage sludge are included in Fig. 2. In control soils (0 t ha⁻¹) the total concentration of heavy metals was within the range of the most frequent values for natural soils (Adriano 1986; Kabata-Pendias and Pendias 1993). In general, the largest concentration corresponded to Lh, a soil derived from ophites. Amendment with sewage sludge increased the total concentration of Cu, Pb and Zn in soils. The rise reflected the sludge metallic content (Table 2) and the doses applied. The biggest increases corresponded to Zn, followed by Cu and Pb; there were no significant differences ($P < 0.05$) in the total concentration of Ni and Cd after the addition of sludge.

The metal distribution in the five fractions of the Tessier procedure corresponding to the sewage sludge-amended

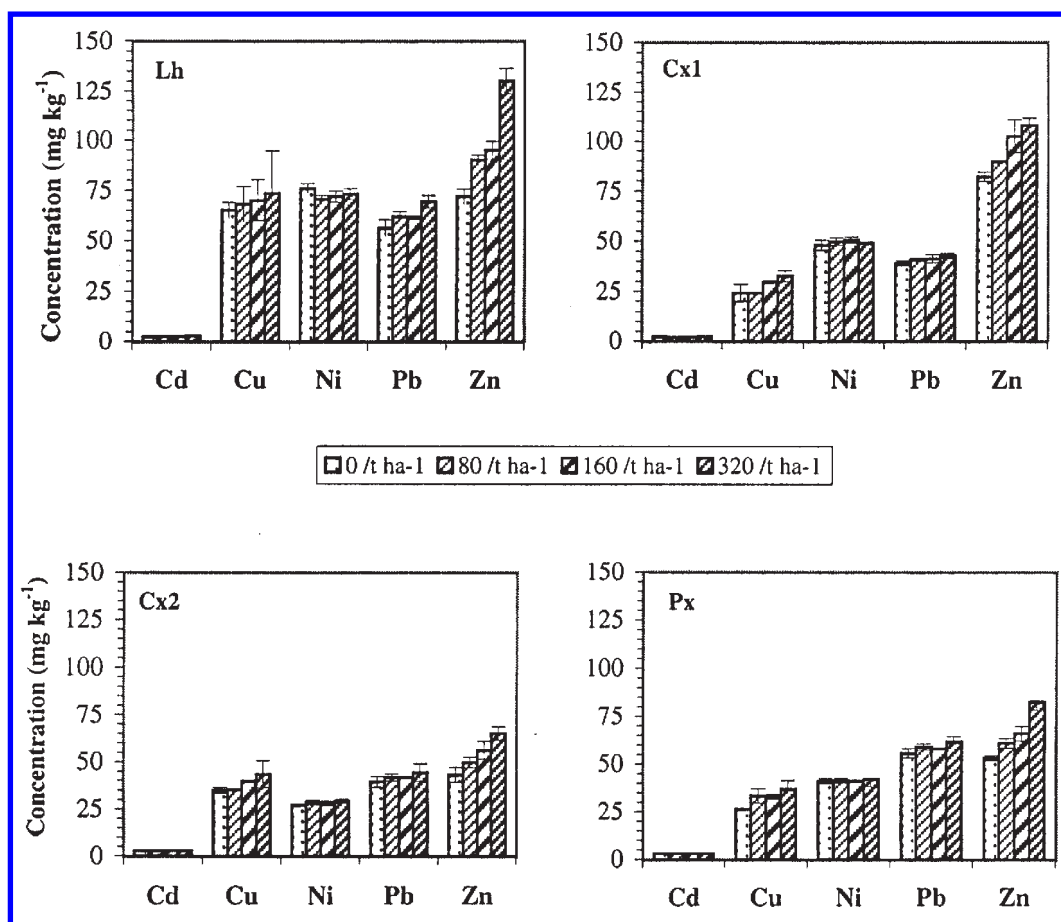


Fig. 2. Total concentration of metals in soils amended with sewage sludge. The results are the average concentration of three replicates and include the standard deviation.

soils differed according to the application rates, the metal extracted, and soil considered. On applying a multifactorial analysis of variance to all results, a positive correlation ($r^2 = 0.91$) was detected between sludge application rate and the overall mean percentage of metals extracted in non residual fractions, ranging from 35.4% for 0 t ha⁻¹ dose to 43.3% for 320 t ha⁻¹ (Table 3). The application of sewage sludge provided a source of heavy metals and enriched the soils in relatively mobile and available forms (Pengxing et al. 1997). The mean percentages released in the non-residuals fractions, including the results of the four soils and five metals, showed greater rises for NH₂OH.HCl, H₂O₂/HNO₃, and NaOAc/HOAc extractions than for exchangeable fraction (Table 3). The dissolution and consequently the mobility and bioavailability of metals added with sewage sludge are controlled mainly by organic matter and oxides that act as principal adsorbents and can prevent excessive mobilisation of heavy metals (McBride 1995). Soil carbonates decrease the availability of metals more for their effect on soil pH than for their adsorption capacity.

Table 3 shows that the increase in the overall mean percentage for metals extracted in the non residual fractions was brought about by Zn, Cu and Pb, but not by Ni and Cd, which is consistent with the metal level in the sewage sludge. The effect of the application doses on the four soils

Table 3. Mean percentages of metals extracted in the non residual fractions following different sewage doses

	Applied sewage sludge			
	0.0	80.0	160.0	320.0
	(t ha ⁻¹)			
	<i>Fractions^a</i>			
Exchangeable	y	0.2	0.2	0.1
Carbonates	1.9	2.7	3.1	3.4
Fe-Mn oxides	26.1	28.0	27.8	30.0
Organic matter	7.4	8.6	8.8	9.8
	<i>Metals^x</i>			
Cd	13.7	14.1	13.3	13.3
Cu	5.1	5.8	6.0	6.7
Ni	6.4	6.8	6.2	6.6
Pb	14.6	15.2	15.2	15.6
Zn	4.6	7.4	9.1	11.7
	<i>Soils^w</i>			
Lh	7.2	8.8	9.1	10.0
Cx1	6.7	7.0	7.4	8.7
Cx2	12.2	13.1	13.1	13.2
Px	9.5	9.5	10.2	11.6

^aAverage values including all studied metals and soils.

^yNo detected.

^xAverage percentages extracted in the four non residual fractions of the four soils.

^wAverage percentages extracted in the four non residual fractions of the five metals.

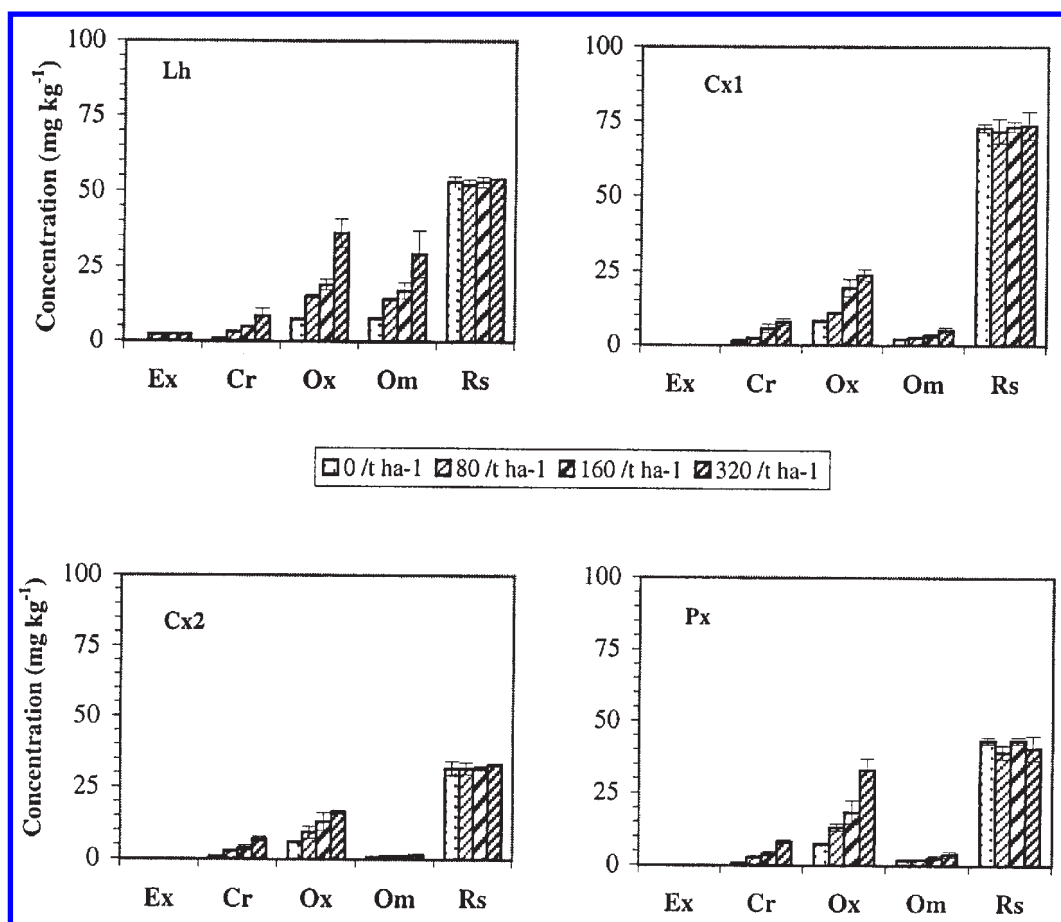


Fig. 3. Fractionation of Zn in the soils amended with sewage sludge (0, 80, 160 and 320 t ha⁻¹). The results are the average concentration of three replicates and include the standard deviation. (Ex, exchangeable; Cr, carbonates; Ox, Fe and Mn oxides; Om, organic matter; Rs, residual).

was slightly higher in the Lh soil than in the other three (Cx1, Cx2 and Px) because the apparent density of the Lh (0.58 g cm⁻³) was lower than that of Cx1 (1.05 g cm⁻³), Cx2 (1.14 g cm⁻³) and Px (1.19 g cm⁻³) soils; in the Lh soil the same sludge dose, in terms of t ha⁻¹, gave rise to a larger sludge/soil mass rate. The pH increase by almost one unit in the Lh soil following the addition of 320 t of sludge ha⁻¹ favoured the retention of metals, and therefore, the total average percentage of metal extracted was less than expected.

The global trends observed after applying a multifactorial ANOVA (Table 3) are depicted in detail in Figs. 3–5, which show the average concentrations of Zn, Pb and Cu extracted in the Tessier fractions of soils following application rates of 0, 80, 160 and 320 t ha⁻¹. In comparison with the control soils, sewage sludge addition statistically increased ($P < 0.05$) the concentration of Zn extracted by NH₂OH.HCl, NaOAc/HOAc and H₂O₂/HNO₃ (Fig. 3); the largest increases took place in oxides. As the Zn was mostly oxide-bound in sewage sludge (Fig. 1), its application to the soils increased the percentage of the reducible fraction (Fig. 3). There was no significant change in the Zn content extracted from the residual fraction. Exchangeable Zn was detected only in soil-sludge mixtures from the acidic soil (Lh), and was always below 2.5% of the total extracted in the five fractions. In Px, Cx1 and Cx2 soils immobilisation

of the exchangeable Zn from sludge took place. It was attributed to the basic pH and the buffering capacity of soils as a consequence of the presence of calcium carbonate (Px, 40%; Cx2, 19%; Cx1, 6%). On the contrary, acidity and the scarcity of carbonates in the Lh soil favoured the release of Zn from sludge (Parveen et al. 1994).

The only significant increase ($P < 0.05$) in the Cu concentration extracted following sludge application to soils corresponded to the fraction extracted by H₂O₂/HNO₃ (Fig. 4); there were no significant differences in the concentration obtained in the NH₂OH.HCl and residual fractions. The copper profile reflected its distribution in the sludge and in the soils control (0 t ha⁻¹), and no Cu redistribution was detected in the fractions. The organic matter contained by sewage sludge acts in soils both as a source of Cu but also as a major adsorbent for this metal; thus, the extraction and consequently the mobility of Cu was mainly controlled by organic matter (Planquart et al. 1999).

The main contribution of sludge to the partitioning of Pb was in the H₂O₂/HNO₃ fraction (Fig. 5), as a consequence of both the association of Pb with that fraction in sludge (70.6%) (Fig. 1), and the non existence of a redistribution of this metal. In Lh, Cx1 and Px soils increases were statistically significant ($P < 0.05$) for doses more than 160 t ha⁻¹; but in Lh soil they were significant only in NH₂OH.HCl fraction and for the maximum dose of 320 t ha⁻¹. Nickel and

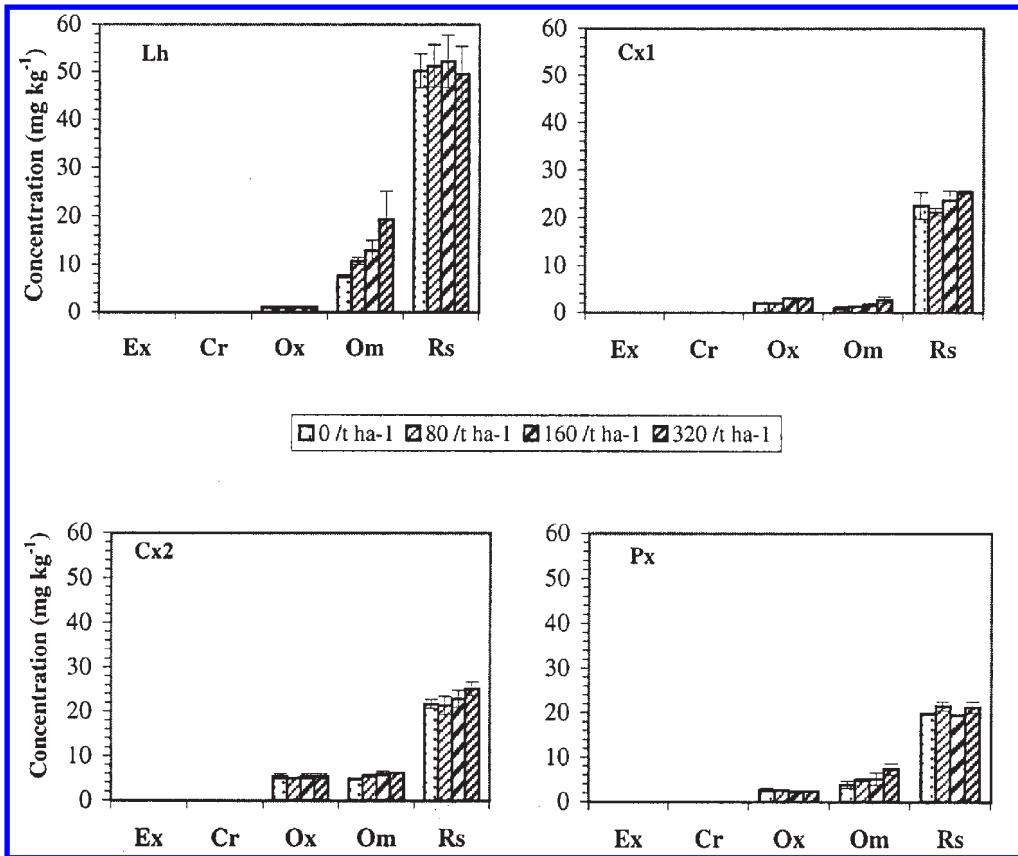


Fig. 4. Fractionation of Cu in the soils amended with sewage sludge (0, 80, 160 and 320 t ha⁻¹). The results are the average concentration of three replicates and include the standard deviation. (Ex, exchangeable; Cr, carbonates; Ox, Fe and Mn oxides; Om, organic matter; Rs, residual).

Cd concentrations extracted in the Tessier partitioning did not significantly increase with the sewage sludge application rates.

Effects of Sewage Sludge Application on Heavy Metal Extracted by EDTA and DTPA Solutions

Metal concentrations extracted with EDTA and DTPA are expressed as percentages of the total concentrations to eliminate the effect of the different amount of metals in the sewage sludge, and to be able to screen both chelates for their ability to extract metals. Table 4 shows that the three analyzed variables, sewage sludge dose, soil, and metal contributed significantly to the total variance; however, the contribution varied with the extractants. With EDTA (pH, 4.65) the type of soil contributed to the total variance more than the metal type or sludge rate. The differences in the carbonate contents of soils (Table 1) would explain that the soils was the variable with the largest contribution to the total variance for EDTA extraction (Batley 1987; Singh et al. 1996). On the other hand, the extraction with DTPA (pH, 7.30), prepared to avoid soil carbonate dissolution (Lindsay and Norwell 1978), was more sensitive to metal type.

The mean percentages extracted with EDTA and DTPA for the different sludge doses are shown in Table 5. Each result is the average value obtained by a given metal in the four soils (metal subgroup) or by a given soil in the five metals (soil subgroup). The average percentages of Cd, Cu, Ni,

Pb and Zn extracted with EDTA were approximately between 3 and 9 times larger than those obtained by DTPA, probably due to the higher concentration and lower pH of EDTA dissolution. In control soils (0 t ha⁻¹), both extractants removed more Pb and Cu than Cd, Ni or Zn.

For all metals and soils, the percentages extracted increased with sewage sludge rates (Table 5). For both extractants, the largest increases corresponded to Zn followed by Pb. For Cd, Cu and Ni the difference between the percentages extracted at the highest rate and the control was below 2.6%. Zinc was the metal with the largest concentration in the sewage sludge and it was also present in more mobile fractions than Pb and Cu (Fig. 1). Despite Cu concentration in sludge was 1.6 times larger than that of Pb, the smaller increase in the percentage of extracted Cu reflected that Cu formed more stable complexes with sludge's organic matter than Pb. The average percentages of Cd and Ni extracted with EDTA and DTPA increased slightly with increasing sewage sludge rates; this increment was not observed in the Tessier sequential partitioning. Consequently, both chelates seemed to be more effective to assess the mobility of metals added with the sludges at low concentrations than the Tessier's chemical partitioning.

The effectiveness of EDTA and DTPA to remove metals varied with soils. The average percentages extracted were lower in the acidic soil (Lh) than in calcareous soils (Table 5), probably because the complexing capacity of

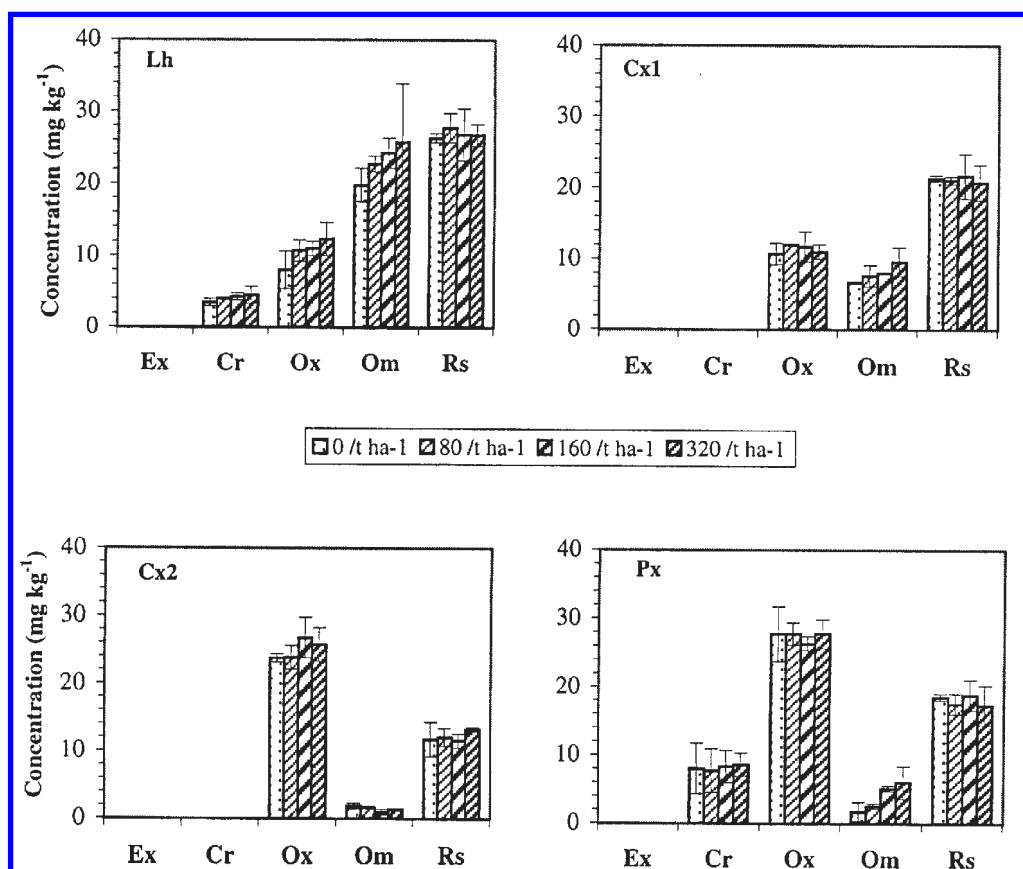


Fig. 5. Fractionation of Pb in the soils amended with sewage sludge (0, 80, 160 and 320 t ha⁻¹). The results are the average concentration of three replicates and include the standard deviation. (Ex, exchangeable; Cr, carbonates; Ox, Fe and Mn oxides; Om, organic matter; Rs, residual).

Table 4. ANOVA multifactorial on the percentages of Cd, Cu, Ni, Pb and Zn extracted with EDTA and DTPA in the soils (Lh, Cx1, Cx2 and Px) spiked with different doses of sewage sludge (0, 80, 160 and 320 t ha⁻¹)

	Sum of squares	Degrees of freedom	Mean square	F	Probability level
<i>EDTA</i>					
Soil	9069	3	3023	498	0.000
Metal	10007	4	2501	412	0.000
Sewage sludge doses	1292	3	431	71	0.000
Total	20368	10	2037	335	0.000
<i>DTPA</i>					
Soil	99	3	33	47	0.000
Metal	1351	4	338	484	0.000
Sewage sludge doses	168	3	56	80	0.000
Total	1618	10	162	232	0.000

EDTA and DTPA is not favoured at acidic pH (Harris 1992). In all soils, average percentages extracted increased with sludge doses. The squared correlation coefficients for the EDTA extraction ranged from 0.97 for Cx2 to 0.70 for Px; and for the DTPA extraction, the coefficients varied between 0.97 for Lh soil and 0.64 for Cx1. The soil with the largest percentage of carbonates (Px) showed the smallest increment in the metal extracted with increasing sludge

Table 5. Mean percentages of metals extracted with EDTA and DTPA for different sludge doses

		Applied sewage sludge			
		0.0	80.0	160.0	320.0
		(t ha ⁻¹)			
<i>EDTA</i>					
Metals ^z	Cd	15.4	16.1	16.5	16.9
	Cu	18.2	18.7	19.3	20.7
	Ni	6.3	6.6	6.9	7.4
	Pb	24.7	25.5	27.7	29.4
	Zn	5.3	11.7	17.8	26.7
Soils ^y	Lh	5.9	9.3	10.8	12.3
	Cx1	9.5	10.6	14.1	16.6
	Cx2	21.4	23.5	26.7	29.5
	Px	19.2	19.5	18.9	22.5
<i>DTPA</i>					
Metals ^z	Cd	1.9	2.4	2.4	2.8
	Cu	7.1	7.2	7.7	7.5
	Ni	0.7	0.8	1.1	1.4
	Pb	5.2	5.6	6.7	6.8
	Zn	1.7	4.2	6.4	9.1
Soils ^y	Lh	2.0	3.5	3.9	5.8
	Cx1	3.2	4.1	4.9	4.7
	Cx2	3.3	3.7	4.5	5.5
	Px	4.8	4.9	6.3	6.1

^zAverage percentages extracted including all soils.

^yAverage percentages extracted including all metals.

doses, and was largely attributable to buffering soil pH in basic soils (McBride 1995).

To sum up, the Tessier partitioning of Cd, Cu, Ni, Pb and Zn in the sewage sludge reflected the predominance of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{H}_2\text{O}_2/\text{HNO}_3$ extracted metals. Soil amendment with sewage sludge increased the total concentration of Cu, Pb and Zn. There were no significant differences in the total concentration of Ni and Cd after the addition of sludge. The rise mirrored the sludge metallic content and the applied doses. A positive correlation was detected between a higher sludge application rate and the overall mean percentage of metals extracted in non residual fractions. In the acidic soil, exchangeable Zn was detected in all soil-sludge mixtures; in calcareous soils, immobilisation of exchangeable Zn from sludge took place. Extraction with EDTA was more sensitive to soil type, whereas extraction with DTPA showed wider variation with metals. Both chelates seemed to be more effective to assess the mobility of metals added with the sludges at low concentrations than the Tessier's chemical partitioning. The Tessier procedure, much more laborious than selective extractions, showed significant differences only in the extractions with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $\text{H}_2\text{O}_2/\text{HNO}_3$.

ACKNOWLEDGEMENTS

This work was supported by a project of Instituto Nacional de Investigación y Tecnología Agraria y Alimentación (INIA SC94-026).

Adriano, D. C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York, NY.

Alloway, B. J. 1990. Soil processes and the behaviour of metals. Pages 7–28 in B. J. Alloway, ed. Heavy metals in soils. John Wiley and Sons, New York, NY.

Alloway, B. J. 1995. The origins of heavy metals in soils. Pages 38–57 in B. J. Alloway, ed. Heavy metals in soils. Blackie Academic and Professional, London, UK.

Alloway, B. J. and Jackson, A. P. 1991. The behavior of heavy metals in sewage sludge-amended soils. *Sci. Total Environ.* **100**: 151–176.

Batley, C. E. 1987. Heavy metal speciation in waters, sediments and biota from lake Macquarie, NSW. *Austral. J. Mar. Freshw. Res.* **38**: 591–606.

Boletín Oficial del Estado 1990. Madrid. **262**: 32, 339–40.

Brümer, G. W. 1986. Heavy metal species, mobility and availability in soils. Pages 169–192 in M. Bernhard, F. E. Brinckman, and P. J. Sadler, eds. The importance of chemical Aspeciation@ in environmental processes. Springer-Verlag, New York, NY.

Community European Council. 1986. Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). *Official J. Eur. Communities*, No. L 181/ 6-12.

Dudka, S. and Chlopecka, A. 1990. Effect of solid-phase speciation on metal mobility and phytoavailability in sludge-amended soil. *Water Air Soil Pollut.* **51**: 153–160.

Echeverría, J. C., Morera, M. T., Mazkiarán, M. C. and Garrido, J. J. 1998. Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environ. Pollut.* **101**: 275–284.

Echeverría, J. C., Morera, M. T. and Garrido, J. J. 1999a. Metal-induced chromium(VI) sorption by two calcareous soils. *Aust. J. Soil Res.* **37**: 431–443.

Echeverría, J. C., Morera, M. T., Mazkiarán, M. C. and Garrido, J. J. 1999b. Characterization of the porous structure of soils. Adsorption of nitrogen (77 K) and carbon dioxide (273 K), and mercury porosimetry. *Eur. J. Soil Sci.* **50**: 497–503.

Emmerich, W. E., Lund, L. J., Page, A. L. and Chang, A. C. 1982. Solid phase forms of heavy metals in sewage sludge-treated soils. *J. Environ. Qual.* **11**: 178–181.

Harris, D. C. 1992. *Análisis Químico Cuantitativo*; Editorial Iberoamericana, Mejico.

Harrison, R. M. 1981. Chemical association of lead, Cd, Cu and Zn in street dusts and roadside soils. *Environ. Sci. Technol.* **15**: 1378–1383.

Heckman, J. R., Angle, J. S. and Chaney, R. L. 1987. Residual effect of sewage sludge on soybeans: I. Accumulation of heavy metals. *J. Environ. Qual.* **16**: 113–117.

Jackson, M. L. 1982. *Análisis Químico de suelos*. 2nd ed. Omega, Barcelona, Spain.

Juste, C. and Tazuin, J. 1992. Comparison of the bioavailability of cadmium present in various fertilizers. *C.R. Acad. Agr. France* **78**: 71–79.

Kabata-Pendias, A. and Pendias, H. 1993. Trace elements in soils and plants. 4th ed. CRC Press, Boca Raton, FL.

Kiekens, L. 1984. Behaviour of heavy metals in soils. Pages 126–134 in S. Berglund, R. D. Davis and P. L' Hermite, eds. Utilization of sewage sludge on land: rates of application and long-term effects of metals. D. Reidel, Dordrecht, The Netherlands.

Kim, N. D. and Fergusson, J. E. 1991. Effectiveness of a commonly used sequential extraction technique in determining the speciation of cadmium in soils. *Sci. Total Environ.* **105**: 191–209.

Kuo, S. 1990. Cadmium buffering capacity and accumulation in Swiss chard in some sludge-amended soils. *Soil Sci. Soc. Am. J.* **54**: 86–91.

Lakanen, E. and Erviö, R. 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. *Acta Agric. Fenn.* **123**: 223–232.

Lebourg, A., Sterckeman, T., Ciesielski, H. and Proix, N. 1996. Intérêt de différents réactifs d'extraction chimique pour l'évaluation de la biodisponibilité des métaux en traces du sol. *Agronomie* **16**: 201–215.

Lindsay, W. L. and Norvell, W. A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* **42**: 421–428.

Loeppert, R. H., Hallmark, C. T. and Koshy, M. M. 1984. Routine procedure for rapid determination of soil carbonates. *Soil Sci. Soc. Am. J.* **48**: 1030–1033.

Martin, J. M., Nirel, P. and Thomas, A. J. 1987. Sequential extraction techniques: promises and problems. *Mar. Chem.* **22**: 313–341.

McBride, M. B. 1995. Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations protective? *J. Environ. Qual.* **24**: 5–18.

McGrath, S. P. and Cegarra, J. 1992. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soils. *J. Soil Sci.* **43**: 313–321.

McLean, E. O. 1982. Soil pH and lime requirement. Pages 199–224 in A. L. Page, R. H. Miller, and D. R. Keeney, eds. *Methods of soil analysis*. Part 2. Chemical and microbiological properties. 2nd ed. SSSA, Madison, WI.

Narwal, R. P. and Singh, B. R. 1998. Effect of organic materials on partitioning extractability and plant uptake of metals in an alum shale soil. *Water Air Soil Pollut.* **103**: 405–421.

Obrador, A., Rico, M. I., Alvarez, J. M. and Mingot, J. 1998. Mobility and extractability of heavy metals in contaminated sewage sludge-soil incubated mixtures. *Environ. Technol.* **19**: 307–314.

- Parveen, Z., Edwards, A. C. and Cresser, M. S. 1994. Redistribution of zinc from sewage sludge applied to a range of contrasting soils. *Sci. Total Environ.* **155**: 161–171.
- Pengxing, W., Erfu, Q., Zhenbin, L. and Shuman, L. M. 1997. Fractions and availability of nickel in loessial soil amended with sewage or sewage sludge. *J. Environ. Qual.* **26**: 795–801.
- Petruzzelli, G. 1989. Recycling wastes in agriculture: heavy metal bioavailability. *Agric. Ecosyst. Environ.*, **27**: 493–503.
- Petruzzelli, G., Ottaviani, M., Lubrano, L. and Veschetti, E. 1994. Characterization of heavy metals mobile species in sewage sludge for agricultural utilization. *Agrochimica* **38**: 277–284.
- Pickering, W. F. 1986. Metal ion speciation – Soils and sediments. A review. *Ore Geol. Rev.* **1**: 83–146.
- Planquart, P., Bonin, G., Prone, A. and Massiani, C. 1999. Distribution, movement and plant availability of trace metals in soils amended with sewage sludge composts: application to low metal loadings. *Sci. Total Environ.* **241**: 161–179.
- Primo Yúfera, E. and Carrasco Dorriens, J. M. 1987. *Química Agrícola*. Alhambra, Madrid, Spain.
- Shuman, L. M. 1991. Chemical forms of micronutrients in soils. Pages 113–144 in J. J. Mortvedt, F. R. Cox, L. H. Shuman, and R. H. Welch, eds. *Micronutrients in agriculture*. 2nd ed. SSSA, Madison, WI.
- Sims, J. T. and Kline, J. S. 1991. Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. *J. Environ. Qual.* **20**: 387–395.
- Singh, S. P., Tack, F. M. G. and Verloo, M. G. 1996. Solid-phase distribution of heavy metals as affected by single reagent extraction in dredged sediment derived surface soils. *Chem. Speciation Bioavailability* **8**: 37–43.
- Soil Survey Staff. 1975. *Soil taxonomy: a basic system of soil classification for making and interpreting soil surveys*. US Government Printing Office, Washington, WA.
- Tan, K. H. 1982. *Principles of soil chemistry*. Marcel Dekker, New York, NY.
- Taylor, R., Xiu, H., Mehadi, A., Shuford, J. and Tadesse, W. 1995. Fractionation of residual cadmium, copper, nickel, lead and zinc in previously sludge-amended soil. *Commun. Soil Sci. Plant Anal.* **26**: 2193–2204.
- Tessier, A., Campbell, P. G. C. and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**: 844–851.
- Tsadilas, C. D., Matsi, T., Baarbayiannis, N. and Dimoyiannis, D. 1995. Influence of sewage sludge application on soil properties and on distribution and availability of heavy metal fractions. *Commun. Soil Sci. Plant Anal.* **26**: 2603–2619.
- Winer, B. J., Brown, D. R. and Michels, J. M. 1991. *Statistical principles in experimental design*. 3rd ed. McGraw Hill, New York, NY.
- Xian, X. F. and Shokohifard, G. I. 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils. *Water Air Soil Pollut.* **45**: 265–273.

This article has been cited by:

1. K. R. Islam, S. Ahsan, K. Barik, E. L. Aksakal. 2013. Biosolid Impact on Heavy Metal Accumulation and Lability in Soiln Under Alternate-Year No-Till Corn–Soybean Rotation. *Water, Air, & Soil Pollution* **224**:3. . [[CrossRef](#)]
2. T. K. Pandit, S. K. Naik, P. K. Patra, D. K. Das. 2012. Influence of Lime and Organic Matter on the Mobility of Cadmium in Cadmium-Contaminated Soil in Relation to Nutrition of Spinach. *Soil and Sediment Contamination: An International Journal* **21**:4, 419-433. [[CrossRef](#)]
3. Ahmed M. Donia, Asem A. Atia, Rama T. Rashad. 2011. Fast removal of Cu(II) and Hg(II) from aqueous solutions using kaolinite containing glycidyl methacrylate resin. *Desalination and Water Treatment* **30**:1-3, 254-265. [[CrossRef](#)]
4. S. Kamali, A. Ronaghi, N. Karimian. 2011. Soil Zinc Transformations as Affected by Applied Zinc and Organic Materials. *Communications in Soil Science and Plant Analysis* **42**:9, 1038-1049. [[CrossRef](#)]
5. Sudarshana Sharma, Parmanand Sharma, A. K. Bhattacharyya. 2010. Accumulation of Heavy Metals in Wheat (*Triticum aestivum* L.) Seedlings Grown in Soils Amended with Electroplating Industrial Sludge. *Communications in Soil Science and Plant Analysis* **41**:21, 2505-2516. [[CrossRef](#)]
6. S. Kamali, A. Ronaghi, N. Karimian. 2010. Zinc Transformation in a Calcareous Soil as Affected by Applied Zinc Sulfate, Vermicompost, and Incubation Time. *Communications in Soil Science and Plant Analysis* **41**:19, 2318-2329. [[CrossRef](#)]
7. Geeta Tewari, Lalit M. Tewari, Prakash Chandra Srivastava, Bali Ram. 2009. Chemical transformation of copper in some sludge-amended soils. *Archives of Agronomy and Soil Science* **55**:4, 415-427. [[CrossRef](#)]
8. Silvana Irene Torri, Raúl Lavado. 2008. Zinc distribution in soils amended with different kinds of sewage sludge. *Journal of Environmental Management* **88**:4, 1571-1579. [[CrossRef](#)]
9. D. Gavalda, J.D. Scheiner, J.C. Revel, G. Merlina, M. Kaemmerer, E. Pinelli, M. Guiresse. 2005. Agronomic and environmental impacts of a single application of heat-dried sludge on an Alfisol. *Science of The Total Environment* **343**:1-3, 97-109. [[CrossRef](#)]
10. Saleh Kaoser, Suzelle Barrington, Maria Elektorowicz, Li Wang. 2004. Copper Adsorption with Pb and Cd in Sand-Bentonite Liners under Various pHs. Part II. Effect on Adsorption Sites. *Journal of Environmental Science and Health, Part A* **39**:9, 2241-2255. [[CrossRef](#)]