Soil Use and Management (2005) 21, 298–305 DOI: 10.1079/SUM2005324

Metal concentrations in agricultural and forestry soils in northwest Spain: implications for disposal of organic wastes on acid soils

M.E. López-Mosquera[1,*], R. Barros[1], M.J. Sainz[2], E. Carral[1] & S. Seoane[1]

Abstract. In Galicia (northwest Spain) the application of organic wastes to agricultural land is a common practice, which may increase total and bioavailable metal contents in the soil. In this study, total metal concentrations were determined in acid soils under different use (pasture, cropland, woodland) in an agricultural area where agro-industrial sludges are frequently recycled as manure. The aim was to establish baseline metal levels which could be used to determine the capacity of soils to absorb organic wastes. The estimation of baseline metal concentrations was carried out by two methods, one based on the analysis of means and geometric deviations, and another based on a modal analysis. Results suggested that the modal analysis procedure might be preferable when analysing data sets with a heterogeneous frequency distribution. In general, there was no significant difference in total metal concentrations when comparing soils from different land uses. Baseline levels for each metal indicated that all soils were suitable for organic waste application under current European Union (EU) legislation. From 2015, more restrictive metal limit values have been proposed by the EU, potentially preventing the addition of metal-containing wastes to pasture, cropland and woodland soils. The dissolved metal values in each soil were also estimated by empirical equations relating total metal concentrations, pH and organic matter content. Results showed that only the pasture soils would be suitable for organic waste disposal under the proposed EU metal limits for 2015, due to liming and substantial organic matter content. Total metal concentrations were insufficient to discriminate environmental risk in acid soils of different land use. The determination of baseline levels in reference areas and the estimation of soil metal bioavailability are suggested to define permissible values in the developing legislation.

Keywords: Baseline metal concentrations, dissolved metal concentrations, heavy metals, pasture, cropland, woodland, dairy sludge

INTRODUCTION

Metal concentrations in undisturbed soils depend on the geological substrates and soil forming processes (Alloway 1990; Kabata-Pendias & Pendias 1992). Agricultural activity may result in elevated levels of metals in soils. In particular, long-term addition of inorganic fertilizers and pesticides can increase total and available metal contents in agroecosystems. Superphosphate fertilizers have been related to slight or moderate soil contamination by cadmium (Rothbaum *et al.* 1986; Vassilev 2002), and calcium nitrate, widely applied as a nitrogen fertilizer, contains significant amounts of nickel (Verloo & Willaert 1990). Certain fungicides used to control plant diseases contain variable amounts of copper and zinc, which can increase availability of these elements in the upper soil horizons (Merry *et al.* 1983).

Similar problems can be expected from application of certain organic products. In the last decades, recycling of organic wastes as farmyard manure and sewage sludge to farmland has been considered an effective way to reduce other disposal practices such as incineration and landfill disposal (Sumner 2000). However, organic residues may contain elevated levels of metals. Significant levels of copper and zinc can be found in poultry and pig manures (Destain & Raimond 1983; Pomares & Canet 2001). Lead, copper, zinc and cadmium are common in sewage sludge and compost from urban solid wastes (Canet *et al.* 2000). As a consequence, long-term or excessive application of these organic residues may result in metal accumulation in soil. Siegenthaler *et al.* (1998) observed that long-term application of pig slurry and sewage sludge to Swiss agricultural soils raised zinc and cadmium levels up to or above legislated limits. Krogmann *et al.* (2000) made a prediction of metal levels in soil after the application of sewage sludge, dairy, poultry and pig manures for 100 years, and

[1]Escuela Politécnica Superior, Universidad de Santiago de Compostela, E-27002 Lugo, Spain. [2]Facultad de Veterinaria, Universidad de Santiago de Compostela, E-27002 Lugo, Spain.
*Corresponding author. Tel: +34 982 252231. Fax: +34 982 241835. E-mail: ellomo@lugo.usc.es

concluded that concentrations of certain metals may increase above background levels.

To study metal contamination of soils, it is considered essential to identify background concentrations under natural conditions, without strong human influence (Gough 1993). Background metal levels are also required to decide whether organic residues can be recycled to soils as manures and amendments. However, it is almost impossible to establish true natural background levels, since atmospheric deposition can contaminate soils with certain metals (Chen *et al.* 1999). For this reason, so-called baseline levels are normally assessed; they represent elemental concentrations specific for a given region and time, but are unlikely to be true background concentrations (Salminen & Tarvainen 1997). Background/baseline concentrations can only be reliably determined at a small spatial scale, due to large variation over relatively short distances (Ma *et al.* 1997). The closest estimation to a true baseline can be provided by unmanaged land, such as unproductive woodland, that has never been fertilized.

There is no specific legislation controlling manure application to agricultural soils. Only the EU Nitrates Directive (European Communities 1991) and codes of good agricultural practice (Xunta de Galicia 1999) suggest suitable timing and application rates for fertilizers, to minimize nitrate loss to water bodies. There are no specific rules controlling agro-industrial sludge application to soils in the European Union. By default, the use of these sludges as fertilizers is governed by Directive 86/278/EEC (European Communities 1986), which was originally directed at sewage sludges. This legislation states acceptable total metal concentrations for different soil pH values, with lower concentrations for more acidic soils. However, there is a general agreement that the total metal concentration in soil is not appropriate for environmental risk assessment, since it does not reflect bioavailability or chemical lability of a given contaminant (Traina & Laperche 1999).

Plants and microbiota take up metals from the soil solution; therefore, environmental quality objectives should be based on metal concentrations in soil solution rather than on total concentrations. Metal bioavailability depends on soil properties, mainly pH and soil organic matter (Kabata-Pendias & Pendias 1992). In this respect, Rieuwerts *et al.* (1998a, b) have emphasized the need to develop simple methods to predict bioavailable metal concentrations from existing and commonly available data on total metal concentrations and soil parameters such as pH and organic matter. Empirical relationships between concentrations of either dissolved metals or free metal ions and total soil metals, pH and organic matter content have been proposed by several authors, providing good descriptions of metal chemistry, principally in soils with levels of organic matter of 10% or less (Tipping *et al.* 2003). Citeau (2004) has recently compared bioavailable metal concentrations in soil water obtained from lysimeters to the corresponding estimations using equations reported by Butcher *et al.* (1989), McBride *et al.* (1997), Sauvé *et al.* (2000) and Tipping *et al.* (2003). Citeau concluded that dissolved metal concentrations obtained by Sauvé's equations best-predicted field Zn, Cd, Pb and Cu concentration in the soils studied.

Agro-industrial sludges are frequently recycled as manure in the soils of northwest Spain. In the present work, total metal concentrations in acid soils under different use (pasture, cropland, woodland) have been determined and compared to the corresponding dissolved metal values estimated by Sauve's equations, to assess whether they can be used to establish the capacity of the soils to absorb organic wastes. Unmanaged woodland soils in the study area were included to obtain baseline metal levels and determine the impact of the manuring and fertilizing practices on metal concentrations in pasture and cropland soils.

MATERIAL AND METHODS

Study area

An area of 30 km^2 was delimited in the municipality of Vilalba (Lugo, NW Spain). The climate is humid temperate with a mean temperature of 11.5 °C and mean annual precipitation of 1176 mm. The bedrock is the Alba-Vilalba series schist (ITGME 1975). Soils are mainly humic, haplic and gleyic Umbrisols (FAO-ISRIC-ISSS 1998), with slopes generally less than 2%. The soils are acidic, with a low effective cation exchange capacity (CEC_e), and usually have medium organic matter content and sandy loam or sandy clay loam texture.

The area is largely used for beef and dairy cattle kept on grassland, consisting mainly of mixtures of perennial ryegrass and white clover. Maize, wheat, kale and turnip are also produced for animal feed. The livestock are farmed intensively, with heavy use of inorganic fertilizers and cattle slurry, which are widely applied to grass and maize. Wheat, kale and turnip are commonly fertilized with inorganic NPK products and/or manured. All these crops have relatively high nitrogen (N) requirements and some of them may be overfertilized, particularly where farms use cattle slurry. Pesticides are rarely used for grassland, wheat, kale or turnip cultivation.

The grassland is also fertilized with agro-industrial sludge produced by a dairy processing and packaging plant in the study area. The initial waste product generated by the dairy plant is an effluent of milk, water (used for washing equipment), sodium hydroxide and nitric acid (used as cleaning products). The effluent undergoes a biological treatment that converts it into a semi-liquid sludge, hereinafter called dairy sludge.

Characteristics and application rates of wastes

The properties of cattle slurry and dairy sludge applied in the study area are presented in Table 1, together with EU metal limits in sludges for agricultural use (European Communities 1986). The cattle slurry has high N and K contents, but small amounts of metals. The sludge has significant amounts of N, P and Na, but low K and metal content. Both wastes provide crops with water (López-Mosquera *et al.* 2001).

Table 1. Main characteristics of cattle slurry and dairy sludge applied at the study area, and European Union metal limits in sludges for agricultural use (European Communities 1986).

	Cattle slurry	Dairy sludge	Directive 86/278/EEC
Dry matter ($g L^{-1}$)	18.2	20	
pH	7.1	7.1	
EC ($dS m^{-1}$)	4.0	3.4	
In %			
C	40.0	35.6	
N	5.1	6.2	
P	2.0	2.1	
K	9.6	1.1	
Ca	0.8	2.2	
Mg	0.7	0.4	
Na	2.4	3.2	
In mg kg^{-1}			
Cd	0.3	0.8	20
Cr	<0.06	14.8	1000
Cu	23.6	39.1	1000
Ni	6.8	11.6	300
Pb	0.5	18.3	750
Zn	115.3	347.4	2500

EC = electrical conductivity.

In grasslands, application rates of cattle slurry should meet N requirements of the cultivated grasses, according to the code of good agricultural practice for managing livestock manures (up to 170 kg N ha^{-1} yr^{-1}). An application at establishment of 20–40 m^3 ha^{-1} is recommended in autumn, and then successive annual applications of the slurry are made to provide 30–60 kg N ha^{-1} for grazed or cut forage. However, frequently the capacity of slurry storage tanks is insufficient for the number of cattle on the farm and farmers increase slurry rates above those recommended.

A single annual application of 80 m^3 ha^{-1} of dairy sludge to grassland at the beginning of the growing season is currently recommended to achieve best yields while favouring competition of clover against grass (López-Mosquera *et al.* 2001). Both cattle slurry and dairy sludge are surface broadcast to land by means of a tractor-drawn tank with splash-plate.

Soil sampling

Sixty sampling sites were selected for study: 34 in grass, 5 in wheat, and 4 in kale (cropland), and 17 under natural mixed deciduous woodland. The sites were selected from dairy and beef farms registered at the dairy plant for sludge disposal on their grassland. The selected farms had known histories of inorganic fertilizer and organic manure use, and woodland plots that had never been cultivated. All farms were located within 8 km distance from the dairy plant.

All 34 pasture soils were from fields habitually receiving dairy sludges, inorganic fertilizers and cattle slurry. The arable sites generally received only inorganic NPK fertilizers. The woodland plots had, to the best of our knowledge, never been fertilized, and were considered reference areas from which to obtain soil baseline metal levels.

At each site, 10 soil samples (0–15 cm depth) were taken using a 7 cm diameter corer, and then pooled to give representative samples. Sampling and sample processing avoided metal contamination (Ure 1990).

Soil sample analysis

The soil samples were air-dried and sieved through a nylon mesh to remove particles >2 mm. We determined texture, pH (in a 1:2.5 suspension soil/water or 0.1 M KCl, w/v), C by oxidation with potassium dichromate, N by the Kjeldahl method (Guitián & Carballas 1976), and effective cation exchange capacity (CEC_e) as the sum of exchangeable bases and Al extractable with 1 M NH_4Cl (Peech *et al.* 1947). Total Cd, Cu, Cr, N, Pb and Zn were determined by atomic absorption spectrometry (Varian Spectra 220 FS) on samples ground in an agate mortar to <0.1 mm and digested with HNO_3 in a microwave oven (US EPA 1995). The digestion procedure was quality-controlled by parallel analysis of the BCR® certified reference material BCR143R (Trace elements in sewage sludge amended soil).

All soils contained a high proportion of particles >0.05 mm, ranging from 43.5 to 87.3%. Textures were sandy loam or sandy clay loam. The mean chemical characteristics of the soils are presented in Table 2.

For each soil, dissolved metal concentrations of Cd, Cu, N, Pb and Zn were estimated from total metal concentration, pH and organic matter content, using the equations

Table 2. Chemical properties of the soils categorized by three land uses (woodland, pasture and cropland).[a] Ranges are given in parentheses.

	Woodland (n = 17)	Pasture (n = 34)	Cropland (n = 9)
pH (H_2O)	4.7a (4.4–5.0)	5.3b (5.1–5.6)	5.2b (5.0–5.5)
pH (KCl)	4.1a (3.8–4.3)	4.5b (4.2–4.8)	4.3a (4.1–4.4)
Organic matter (%)	4.7b (3.7–5.7)	7.5b (3.0–12.0)	2.7a (1.6–3.8)
N (%)	0.28a (0.19–0.37)	0.41b (0.34–0.58)	0.15a (0.08–0.22)
P ($mg kg^{-1}$)	4.3a (1.3–7.4)	37.8b (6.9–68.4)	44.5b (16.5–72.4)
Ca (cmol(+) kg^{-1})	1.65a (0.35–2.95)	2.33a (0.46–4.20)	1.78a (0.88–2.68)
Mg (cmol(+) kg^{-1})	0.47a (0.19–0.75)	0.46a (0.03–0.89)	0.30a (0.10–0.50)
K (cmol(+) kg^{-1})	0.42a (0.31–0.53)	0.48a (0.33–0.63)	0.51a (0.38–0.64)
Al (cmol(+) kg^{-1})	6.65b (3.83–11.50)	1.74a (0.24–4.79)	2.79a (2.13–4.62)
Al satn (%)	68.1b (54.7–81.5)	35.3a (17.3–53.3)	47.7a (32.3–63.1)

[a] For each soil characteristic, means followed by a different letter are significantly different at $P \leq 0.05$.

developed by Sauvé *et al.* (2000):

$$\log(\mathrm{Cd})_{\mathrm{dis}} = 3.42 - 0.47\,\mathrm{pH} + 1.08\log(\mathrm{Cd})_{\mathrm{T}} - 0.81\log(\mathrm{OC})$$

$$\log(\mathrm{Cu})_{\mathrm{dis}} = 1.37 - 0.21\,\mathrm{pH} + 0.93\log(\mathrm{Cu})_{\mathrm{T}} - 0.21\log(\mathrm{OC})$$

$$\log(\mathrm{Pb})_{\mathrm{dis}} = 1.81 - 0.37\,\mathrm{pH} + 0.56\log(\mathrm{Pd})_{\mathrm{T}}$$

$$\log(\mathrm{Zn})_{\mathrm{dis}} = 3.68 - 0.55\,\mathrm{pH} + 0.94\log(\mathrm{Zn})_{\mathrm{T}} - 0.34\log(\mathrm{OC})$$

$$\log(\mathrm{Ni})_{\mathrm{dis}} = 7.02 - 1.05\,\mathrm{pH} + 1.21\,log(\mathrm{Ni})_{\mathrm{T}} - 0.85\log(\mathrm{OC})$$

where $(\mathrm{M})_{\mathrm{T}}$ represents total concentration of each metal in the soil (mg kg^{-1}), OC is the percentage of organic carbon by weight, and $(\mathrm{M})_{\mathrm{dis}}$ is the quantity of dissolved metal (μg L^{-1}).

These equations were also used to estimate dissolved metal concentrations expected if metals were present in the local soils at the EU limits.

Statistical analyses

Dependent variables were compared between treatments by one-way ANOVA, with subsequent multiple comparisons by the Least Significant Differences Test for balanced samples, or the Scheffé test for unbalanced samples, and the non-parametric Mann–Whitney test for data not normally distributed (Zar 1984), using the SPSS statistics package. The level of significance for statistical analyses was established at $P \leq 0.05$.

As suggested by Tidball & Ebens (1976), baseline metal concentrations were expressed as geometric means and ranges of the element concentrations in the soils studied. This method, hereinafter 'baseline method 1', is widely used for determination of baseline metal concentrations in soils (Dudka 1993; Gough *et al.* 1994; Chen *et al.* 1999). Data were also subjected to a method based on a modal analysis to separate different normal populations within the data set. This method, hereinafter 'baseline method 2', was originally developed for the determination of background metal concentrations in marine sediments (Carral *et al.* 1995); as far as we know, this is the first use of this method for soils.

RESULTS AND DISCUSSION

Table 3 shows mean total concentrations of each metal in studied soils, and summarizes previously published data for other soils in Galicia and other regions of the world. Contents of Cd, Cr, Ni, Pb and Zn did not vary significantly between soils with different land uses, suggesting that manuring and fertilizing practices in the area had no significant impact on metal levels. The coefficients of variation for Cd and Pb were very high, as a result of very low concentrations of Cd in 14 soils from pasture, 3 from woodland and 4 from cropland, and a very heterogeneous frequency distribution of Pb concentrations within each land use (data not shown). Only Cu concentrations were significantly higher in arable soils than in pasture and woodland soils; this might be a consequence of the use of copper-containing fertilizers (Verloo & Willaert 1990).

In general, total metal concentrations in soils were within the ranges reported previously for other Galician soils

Table 3. Total metal concentrations (mg kg^{-1}) in soils categorized by three land uses (woodland, pasture and cropland), and data from published studies (local and international) for comparison.

Use	Cd	Cr	Cu	Ni	Pb	Zn
Woodland						
Mean	0.37a	41a	21a	25a	11a	52ab
Range	0.02–0.8	30.5–50.5	15.82–25.94	18.8–31.8	4.1–17.2[a]	35.6–68.4
CV (%)	57	25	24	26	61	32
No. of samples	17	17	17	17	17	17
Pasture						
Mean	0.39a	44a	23a	27a	12a	66a
Range	0.02–0.7	29.5–58.1	15.9–36.3	17.5–36.2	3.1–20.3	39.4–92.1
CV (%)	44	33	44	35	74	40
No. of samples	34	34	34	34	34	34
Cropland						
Mean	0.38a	47a	26b	30a	11a	67b
Range	0.02–0.9	36.1–57.4	21.4–31.3	21.7–37.9	6.2–16.2	50.1–82.9
CV (%)	34	23	19	27	45	25
No. of samples	9	9	9	9	9	9
Literature studies						
Local:						
Paz-González *et al.* (2000)	–	40.3	37.2	10.3	22.0	135.0
Fernández & Carballeira (2001)	–	37.8 – 169.7	2.3 – 54.2	0.3 – 55.0	12.9 – 59.3	10.5 – 99.3
International:						
Chen *et al.* (1999)	0.004–2.80	0.02–447	0.1–318	0.04–375	0.18–290	0.90–169
Kabata-Pendias & Pendias (1992)	0.37	47	13	13	22	45

Within columns, means followed by the same letter do not differ significantly at $P \leq 0.05$. CV = coefficient of variation.

(Paz-González *et al.* 2000; Fernández & Carballeira 2001), and for soils in other regions of the world (Kabata-Pendias & Pendias 1992; Chen *et al.* 1999), even though parent materials, climate and land use may differ.

Because there were no significant differences in total metal concentrations between the different land uses apart from Cu, data were pooled to estimate baseline metal concentrations. For Cu, pasture and woodland samples were used because concentrations in arable samples were significantly higher. Table 4 shows total metal concentrations estimated by baseline methods 1 and 2. With few exceptions, levels calculated by the two methods fell within the ranges reported by Dudka (1993), Gough *et al.* (1994) and Chen *et al.* (1999) for Polish, South Carolina (USA) and Florida (USA) surface soils, respectively. Zinc levels were considerably higher than those reported for South Carolina and Florida, reflecting larger Zn concentrations in the parent materials (Guitián *et al.* 1992).

To assess whether the two baseline methods gave similar results, a one-factor analysis of variance (factor *baseline estimation method*) was performed comparing metal concentrations only from soils with metal concentrations less than or equal to the corresponding baseline estimate (Table 5). Only Cd showed significant differences ($P \leq 0.05$) between the two methods; this is clearly a consequence of the high heterogeneity in the frequency distributions of this metal. Therefore, although both methods produced similar results for most metals, the method based on modal analysis (i.e. method 2) may be preferable to the more widely used method of Tidball & Ebens (1976) when analysing data sets with a very variable frequency distribution. The modal analysis method allows the identification of discrete Gaussian subpopulations within a data set, and the difference between subpopulations and the original distribution are assessed by a chi-squared test (Carral *et al.* 1995).

Metal baseline levels should be used to decide whether any fertilizer input may have an impact on soil metal content. The baseline concentrations of all metals were below the maximum concentrations specified by current EU legislation for sewage sludge application (Table 4), showing that all the soils were suitable for organic waste application. However, this would not be the case for Cr, Cu, Ni and Zn under proposed EU legislation for 2015. This means that, if the proposed new EU limits are adopted, even natural soils from forests which supposedly never received any waste or fertilizer would be unsuitable for sludge application. Only the baseline Pb concentration would be below the permitted concentration. Legislation is particularly exigent for acid soils, since metal solubility tends to increase at low pH and decrease at high pH (Rieuwerts *et al.* 1998a).

Total concentrations are not reliable indicators of metal bioavailability, since an important fraction of total values corresponds to metals strongly bound within soil particles and not normally available for organisms to take up (Rieuwerts *et al.* 1998a). Plants and soil microbiota are exposed to metals via the soil solution, therefore an estimate of soil metal bioavailabiltiy should be considered for quantifying contamination and environmental risks, instead of total values (Rieuwerts *et al.* 1998b; Sauvé *et al.* 2000).

Table 6 presents dissolved metal concentrations, estimated from total metal values, pH and organic matter content, in pasture, cropland and woodland soils, together with the dissolved metal concentrations expected if metals were present in the local soils at the EU metal limits.

The highest concentrations for all metals in solution were consistently found in woodland soils, and the lowest in cropland, particularly in pasture soils, even though grassland regularly received mineral fertilizers, cattle slurry and dairy sludge. These results can be explained mainly by differences in pH between soils with different land uses (Figure 1). It is known that metal solubility and bioavailability increase with decreasing soil pH (Xian & In Shokohifard 1989; Dudka *et al.* 1996), and woodland soils had significantly lower pH (both in water and KCl; $P < 0.05$) than the cropland and pasture soils (Table 2). Soils in northwest Spain are very acidic, as a result of acidic parent materials and much precipitation. Before cultivation, and especially when establishing grasslands in previous forestry soils, lime is usually applied (Mombiela & Mateo 1984), and after establishment, lime is applied every three to five years depending on the annual precipitation. The same is commonly done for wheat and kale crops, which explains higher pH values and lower dissolved metal concentrations in the arable and pasture soils than in the woodland soils.

Table 4. Mean concentrations of total metals (mg kg^{-1}) in soils of the data sets identified by baseline estimation methods 1 and 2. The 95% confidence limits are shown in parentheses. Also shown are baseline concentrations obtained by method 1 and reported in previous studies in other countries, and EU metal limits established for use of sludge in agricultural soils by the present legislation (Directive 86/278/EEC) and that proposed for 2015.

Method	Cd	Cr	Cu	Ni	Pb	Zn
Baseline 1	0.43 (0.36–0.51)	43 (40–47)	23 (21–25)	27 (25–29)	11 (9–13)	62 (56–68)
Baseline 2	0.14 (0.07–0.21)	42 (40–45)	24 (22–26)	28 (26–29)	10 (9–11)	59 (52–65)
Literature values (range)						
Dudka 1993		4–75	2–18	2–27		
Gough *et al.* 1994		6.8–29	0.35–5.2	0.96–4.6	5.7–15	2.8–12
Chen *et al.* 1999	0–0.33	0.89–80.7	0.22–21.9	1.70–48.5	0.69–42.0	0.89–29.6
Legislation						
Directive 86/278/EEC (soil pH < 7)[a]	1	100	50	30	50	150
Proposed limit values for 2015 ($5 \leq$ pH < 6)[b]	0.5	30	20	15	70	60

[a]European Communities 1986; [b]European Commission 2000.

Table 5. Descriptive statistics for the baseline sites identified by baseline estimation methods 1 and 2, showing the results of analysis of variance to compare metal levels between sites identified by each method.

	Cd[a]	Zn	Cu	Cr	Ni	Pb[a]
Sample size	$n_1 = 23$	$n_1 = 30$	$n_1 = 24$	$n_1 = 27$	$n_1 = 29$	$n_1 = 15$
	$n_2 = 23$	$n_2 = 30$	$n_2 = 31$	$n_2 = 25$	$n_2 = 33$	$n_2 = 25$
F value		0.00	1.90	0.03	1.18	
Z value[b]	0.242					112.5
α value[c]	0.19	1.00	0.18	0.86	0.28	0.04

n_1, n_2 = number of soils with metal concentration $\leq$ baseline value estimated by methods 1 and 2, respectively. [a]For Cd and Pb, data sets were compared by the Mann–Whitney U-test. [b]Level of significance for non-parametric tests. [c]Level of significance for parametric tests.

Table 6. Estimated dissolved metal concentrations in soils categorized by land use, and expected dissolved concentrations (both in $\mu g\,L^{-1}$) if metals were present in the local soils at the present EU metal limits or at those proposed for 2015. Number of samples are given in parentheses.

Use	log Cd	log Cu	log Ni	log Pb	log Zn
Woodland					
Mean	0.16b	1.51b	3.43c	0.52a	2.55b
	(17)	(17)	(17)	(17)	(17)
Pasture					
Mean	0a	1.36a	2.66a	0.25a	2.24a
	(34)	(34)	(34)	(34)	(34)
Cropland					
Mean	0ba	1.55b	3.15b	0.29a	2.45b
	(9)	(9)	(9)	(9)	(9)
Legislation					
Directive 86/278/EEC[a]	0.64	1.78	3.04	0.86	2.75
Proposed limit values for 2015[b] ($5 \leq pH < 6$)	0.32	1.41	2.67	0.95	2.38

For each metal, means followed by a different letter are significantly different at $P \leq 0.05$. [a]European Communities 1986; [b]European Commission 2000.

Liming reduces metal availability by converting the metals into less soluble forms that are less available for plant uptake (Krebs *et al.* 1998). A predictive model of metal concentrations in crops, derived from soil metal values, humus content and pH, has recently been proposed by Hough *et al.* (2003), showing the large dependence of Cd and Zn uptake on soil pH.

Apart from pH, organic matter content is another soil factor affecting dissolved metal concentration (Sauvé *et al.* 2000), but in our study this relationship was weak. The pasture and woodland soils had similar organic matter contents, higher than that of the cropland soils. However, significant differences ($P \leq 0.05$) were found between dissolved metal concentrations in pasture and woodland soils, suggesting that soil pH more than organic matter content is responsible for the variations in dissolved metal concentrations between soils. This is supported by the work of Sauvé *et al.* (2000), who, in a compilation of more than 70 studies, found that pH explained most of the variation for metals such as Cd and Zn. On the other hand, it cannot be ruled out that quality more than quantity of organic matter has a major influence on metal bioavailability, since it has been shown to play an important role in the mobility, availability and complexity of metals in soils (Barančíková & Makovníková 2003).

In soils from the three land uses, the dissolved concentrations of all metals except Ni were below those expected if metals were present in the local soils at the present EU limits. However, according to the proposed EU legislation for 2015, only pasture soils would be suitable for organic waste disposal. This reflects both the importance of liming and greater contents of soil organic matter in reducing metal bioavailability.

Our results indicate that determination of total metal concentrations is insuffucient for environmental risk

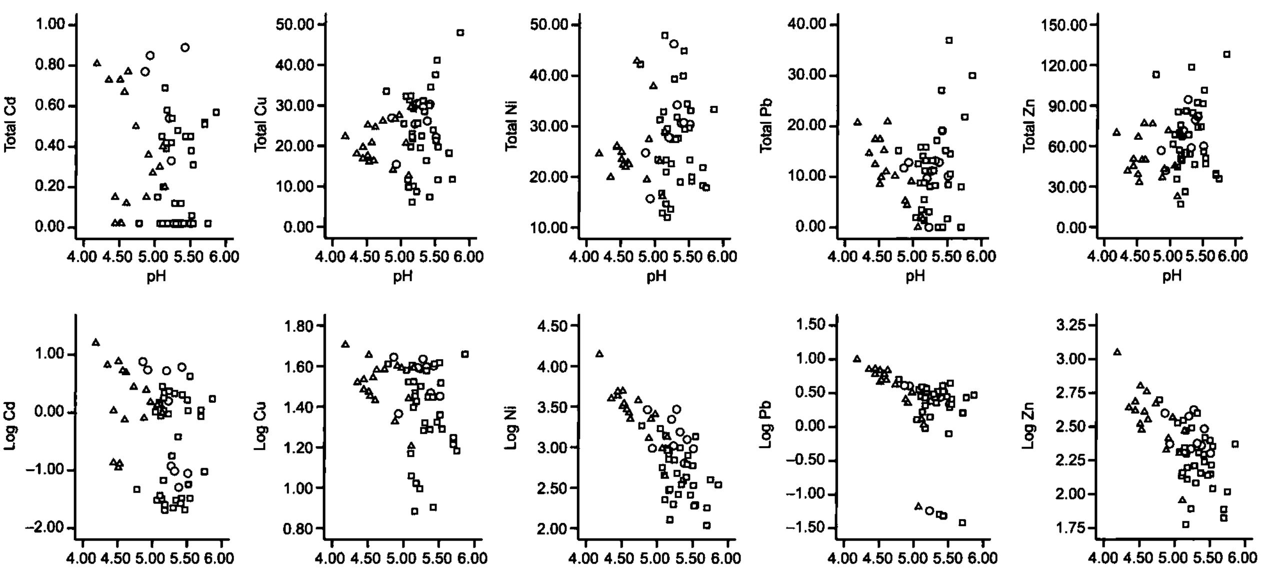

Figure 1. Total metal ($mg\,kg^{-1}$) and estimated dissolved metal concentrations ($\mu g\,L^{-1}$) of Cd, Cu, Ni, Pb, and Zn in individual samples of pasture (□), cropland (○) and woodland (△) soils, in relation to soil pH.

assessment in acid soils. It is important that the international legislation also takes into account the baseline metal concentrations in reference areas, and the use of simple methods that estimate metal bioavailability from total metal values and common soil factors, such as pH and organic matter. Estimations of dissolved metal, as used in the present work, or free metal-ion concentration, which have received much attention in recent years, could be useful tools for evaluating the capacity of acid soils for absorbing organic wastes.

ACKNOWLEDGEMENTS

We are grateful to Moisés Carballeira for kindly allowing us to carry our research at his farm. We also thank Cristina Vázquez and Susana Dopico for capable and skilful technical assistance. Financial support was received from Xunta de Galicia (project 29104A96), FEDER (project 1FD97-0334), Spanish Ministry of Science and Technology (project AGF99-0418-C02-02), and contract 1997/CE317 with Lactalis-Leche de Galicia S.A.

REFERENCES

Alloway DD 1990. Heavy metals in soils. John Wiley & Sons New York.

Barančíková G & Makovníková J 2003. The influence of humic acid quality on the sorption and mobility of heavy metals. Plant, Soil and Environment 49(12), 565–571.

Butcher B Davidoff B Amacher MC Hinz C Iskandar IK & Selim HM 1989. Correlation of Freundlich Kd and *n* retention parameters with soils and elements. Soil Science 148(5), 370–379.

Canet R Pomares F Albiach R Tarazona F Ibáñez MA & Ingelmo F 2000. Analyzing chemical properties of MSW compost. Biocycle 41, 72–76.

Carral E Puente X Villares R & Carballeira A 1995. Background heavy metal levels in estuarine sediments and organisms in Galicia (northwest Spain) as determined by modal analysis. The Science of the Total Environment 172, 175–188.

Chen M Ma LQ & Harris WG 1999. Baseline concentrations of 15 trace elements in Florida surface soils. Journal of Environmental Quality 28, 1173–1181.

Citeau L 2004. Etude des colloïdes naturels présents dans les eaux gravitaires de sols contaminés: relation entre nature des colloïdes et réactivité vis-à-vis des métaux (Zn, Cd, Pb, Cu). PhD Thesis INRA Versailles France. Avialable: http://www.inra.fr/ea/theses/citeau6. pdf [2004, 22 December]

Destain JP & Raimond Y 1983. La composition chimique du lisier, ses facteurs de variation et ses conséquences agronomiques. Revue de l'Agriculture 36, 39–49.

Dudka S 1993. Baseline concentrations of As, Co, Cr, Cu, Ga, Mn, Ni and Se in surface soils of Poland. Applied Geochemistry 2, 23–28.

Dudka S Ponce-Hernández R Tate G & Hutchinson TC 1996. Forms of Cu, Ni and Zn in soils of Sudbury, Ontario and the metal concentrations in plants. Water, Air and Soil Pollution 90, 531–542.

European Commission 2000. Working Document on Sludge – 3rd draft. Reference ENV.E.3/LM Brussels Belgium. Available: http://europa.eu.int/comm/environment/waste/ sludge/sludge_en.pdf [2005, 8 March]

European Communities 1986. Council Directive on the protection of the environment and in particular of the soil when sewage sludge is used in agriculture (86/278/EEC). Official Journal of the European Communities L181, 6–12 Brussels Belgium.

European Communities 1991. Council Directive on the protection of protection on waters against pollution caused by nitrates from agricultural sources (91/676/EEC). Official Journal of the European Communities L375, 1–8 Brussels Belgium.

FAO-ISRIC-ISSS 1998. World reference base for soil resources. World Soil Resources Reports No. 84. Food and Agriculture Organization Rome.

Fernández JA & Carballeira A 2001. A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environmental Pollution 114, 431–441.

Gough LP 1993. Understanding our fragile environment. Lessons from geochemical studies. Circular 1105, US Geological Survey National Center 509 National Center Reston VA 20192 USA.

Gough LP Severson RC & Jackson LL 1994. Baseline element concentrations in soils and plants, Bull Island, Cape Romain National Wildlife Refuge, South Carolina, USA. Water, Air and Soil Pollution 74, 1–17.

Guitián F & Carballas T 1976. Técnicas de análisis de suelos (Methods of soil analysis). Pico Sacro Publishers Santiago de Compostela Spain.

Guitián F & 44 coauthors 1992. Atlas Geoquímico de Galicia (Geochemical atlas of Galicia). Consellería de Industria y Comercio. Xunta de Galicia Santiago de Compostela Spain.

Hough RL Young SD & Crout NMJ 2003. Modelling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm. Soil Use and Management 19, 19–27.

ITGME 1975. Mapa geológico de España (Geological map of Spain). E 1:50 000 Villalba, Instituto Geológico y Minero de España. Servicio de Publicaciones Ministerio de Ciencia y Tecnología Río Rosas 23 E-28003 Madrid Spain.

Kabata-Pendias A & Pendias H 1992. Trace elements in soils and plants. CRC Press Boca Raton FL USA.

Krebs R Gupta SK Furrur G & Schulin R 1998. Solubility and plant uptake of metals with and without liming of sludge-amended soils. Journal of Environmental Quality 27(1), 18–23.

Krogmann U Heckman JR Boyles LS & Wiederhold C 2000. Land application of sewage sludge (biosolids): soil amendments and heavy metals. Fact Sheet FS956, Rutgers Cooperative Extension New Jersey Agricultural Experiment Station Rutgers. The State University of New Jersey New Brunswick NJ USA.

López-Mosquera ME Alonso XA & Sainz MJ 2001. Short-term effects of soil amendment with dairy sludge on yield, botanical composition, mineral nutrition and arbuscular mycorrhization in a mixed sward. Pastos 29(2), 231–243.

Ma LQ Tan F & Harris WG 1997. Concentrations and distributions of eleven metals in Florida soils. Journal of Environmental Quality 26, 769–775.

McBride M Sauvé S & Hendershot W 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. European Journal of Soil Science 48, 337–346.

Merry RH Tiller KG & Alston AM 1983. Accumulation of copper, lead and arsenic in some Australian orchard soils. Australian Journal of Soil Research 21, 549–561.

Mombiela FA & Mateo ME 1984. Necesidades de cal para praderas en terrenos a monte (Liming needs in sown meadows established in hill soils). Anales del INIA Serie Agrícola 25, 129–143.

Paz-González A Taboada-Castro T & Taboada-Castro M 2000. Levels of heavy metals (Co, Cu, Cr, Ni, Pb, and Zn) in agricultural soils of Northwest Spain. Communications in Soil Science and Plant Analysis 31, 1773–1783.

Peech M Alexander LT Dean L & Reed JF 1947. Methods of soil analysis for soil fertility investigations. USDA Circular 757. US Government Printing Office Washington DC 20402 USA.

Pomares F & Canet R 2001. Residuos orgánicos utilizables en agricultura: origen, composición y características (Organic residues used in agriculture: origin, composition and characteristics). In: Aplicación agrícola de los residuos ganaderos (Agricultural application of animal residues), eds J Boixadera & MR Teira, Universitat de Lleida Spain pp 1–16.

Rieuwerts J Thornton I Farago ME & Ashmore M 1998a. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chemical Speciation and Bioavailability 10(2), 61–75.

Rieuwerts J Thornton I & Ashmore M 1998b. Quantifying the influence of soil properties on the solubility of metals by predictive modelling of secondary data. Chemical Speciation and Bioavailability 10(3), 83–93.

Rothbaum HP Goguel RL Johnston AE & Mattingly GEG 1986. Cadmium accumulation in soils from long-continued applications of superphosphate. Journal of Soil Science 37, 99–107.

Salminen R & Tarvainen T 1997. The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. Journal of Geochemical Exploration 60, 91–98.

Sauvé S Hendershot W & Allen H 2000. Solid-solution partitioning of metals in contamined soils: dependence on pH, total burden, and organic matter. Environmental Science and Technology 34, 1125–1131.

Siegenthaler A Häni H & Stauffer W 1998. Long term effects of excessive organic waste application. In: Proceedings of the 8th International Conference of the FAO ESCORENA Network on Recycling of Agricultural, Municipal and Industrial Residues in Agriculture, eds J Martínez & MN Maudet, Cemagref Editions Rennes France pp 195–203.

Sumner ME 2000. Beneficial use of effluents, wastes, and biosolids. Communications in Soil Science and Plant Analysis 31(11–14), 1701–1715.

Tidball RR & Ebens RJ 1976. Regional geochemical baselines in soils of the Powder River Basin, Montana-Wyoming. In: Geology and energy resources of the Powder River Basin, ed RB Laudon, Wyoming Geological Association PO Box 545 Casper WY 82602-0545 USA pp 299–310 28th Annual Field Conference Guidebook.

Tipping E Rieuwerts J Pan G Ashmore MR Lofts S Hill MTR Farago ME & Thornton I 2003. The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. Environmental Pollution 125, 213–225.

Traina SJ & Laperche V 1999. Contaminant bioavailability in soils, sediments, and aquatic environments. Proceedings of the National Academy of Sciences USA 96, 3365–3371.

Ure AM 1990. Methods of analysis for heavy metals in soils. In: Heavy metals in soils, ed JB Alloway, Blackie London pp 40–80.

US EPA 1995. Method 3051: Microwave assisted acid digestion of sediments, sludges, soils, and oils. Test methods for evaluating solid waste, 3rd edn. US Environmental Protection Agency Washington DC USA.

Vassilev E 2002. Physiological and agroecological aspects of cadmium interactions with barley plants: an overview. Journal of Central European Agriculture 4(1), 65–75.

Verloo M & Willaert G 1990. Direct and indirect effects of fertilisation practices on heavy metals in plants and soils. In: Fertilisation and the environment, eds R Merckx H Vereecken & K Vlassak, Leuven University Press Belgium pp 79–87.

Xian X & In Shokohifard G 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc and lead in polluted soils. Water, Air and Soil Pollution 45, 265–273.

Xunta de Galicia 1999. Código Galego de Boas Prácticas Agrarias (Galician Code of Good Agricultural Practices). Consellería de Política Agroalimentaria e Desenvolvemento Rural, San Caetano E-15704 Santiago de Compostela Spain.

Zar JH 1984. Biostatistical analysis. Prentice-Hall Englewood Cliffs NJ USA.

Received July 2004, accepted after revisions March 2005.