Determination of chemical availability of cadmium and zinc in soils using inert soil moisture samplers

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Abstract

A rapid method for extracting soil solutions using porous plastic soil-moisture samplers was combined with a cation resin equilibration based speciation technique to look at the chemical availability of metals in soil. Industrially polluted, metal sulphate amended and sewage sludge treated soils were used in our study. Cadmium sulphate amended and industrially contaminated soils all had >65% of the total soil solution Cd present as free Cd^{2+}. However, increasing total soil Cd concentrations by adding $CdSO_4$ resulted in smaller total soil solution Cd. Consequently, the free Cd^{2+} concentrations in soil solutions extracted from these soils were smaller than in the same soil contaminated by sewage sludge addition. Amendment with $ZnSO_4$ gave much greater concentrations of free Zn^{2+} in soil solutions compared with the same soil after long-term Zn contamination via sewage sludge additions.

Our results demonstrate the difficulty in comparing total soil solution and free metal ion concentrations for soils from different areas with different physiochemical properties and sources of contamination. However, when comparing the same Woburn soil, Cd was much less available as Cd^{2+} in soil solution from the $CdSO_4$ amended soils compared with soil contaminated by about 36 years of sewage sludge additions. In contrast, much more Zn was available in soil solution as free Zn^{2+} in the $ZnSO_4$ amended soils compared with the sewage sludge treated soils. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Heavy metal enrichment of soil by anthropogenic activity is unavoidable, and large areas of land untouched by either agriculture or direct industrial activity are known to be increasing in heavy metal content (Jones et al., 1987). In Britain, regulation and legislation regarding heavy metal contamination of soil is based on total metal concentrations. No account is taken of the total and free ion concentrations in soil solution, even though it has long been recognised as the medium through which beneficial and/or potentially toxic elements exert their effects on organisms (Whitney and Cameron, 1903). The determination of total metal con-

centration in soil solution and the qualitative and quantitative assessment of the chemical species present provides a rational and generic basis for assessing the bio-availability and potential toxicity of that metal.

The three most common techniques for collecting soil solution are water displacement, centrifugation and extraction by suction. In heavier clay and silt soils, displacement is difficult and the volume of solution which can be collected is limited. Centrifugation is time consuming and the sample collected often requires further filtration or centrifugation. Suction cups made of a number of different materials including nylon, Teflon and ceramics have been used. However, ceramic samplers are known to suffer from adsorption of charged groups, particularly trace elements, phosphorus and ammonium ions (Grossman and Udluft, 1991). Although Teflon is the ideal material (Litaor, 1988), it is

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expensive, and therefore unsuitable for large-scale trials. Hence, there is a need for a rapid, effective and relatively inexpensive method of obtaining soil solution. In this paper, we report on the use of a new sampler design for the extraction of soil solution. The porous plastic samplers used in this study have no cation exchange capacity, which avoids the problem of sorption, and the pore size of 0.2 μm ensures the solution collected is free from microbial and colloidal contamination.

Using these porous plastic samplers we determined the availability of Cd and Zn in soils amended with (1) individual metal sulphates, (2) the same soils contaminated by additions of sewage sludge from 1942–61 (McGrath, 1984) and (3) soils with elevated metal concentrations due to industrial activity. It is often assumed that the proportion of metals in soil solution is much greater in artificially amended soils compared with soils polluted by industry over long periods of time. Korcak and Fanning (1985) found that both uptake by corn and extractability of Zn and Cd using diethylene-triaminepentaacetate (DTPA) was greater in metal salt amended soils compared with soils receiving an equal loading of metals through sewage sludge addition. However, Ham and Dowdy (1978) found no difference in Zn, Cu or Cr uptake by soybeans in soils to which the

metal was added either as a salt or in sewage sludge. Therefore, a secondary aim was to determine whether Cd and Zn added as sulphate salts were more available, in terms of total and free metal ion concentrations in soil solution, than those entering the soil through other routes.

2. Materials and methods

2.1. Heavy metal amendment of soil and selection of industrially polluted soils

Soil was sampled from plots of a long-term liming experiment at Woburn in south-east England. The pH experiment was established in 1963 on soil belonging to the Cottenham series (Typic Udipsamment) and has been maintained at pHs ranging from 4.5 to 7.0 (Bolton, 1977). Moist soil samples were sieved to <3 mm, thoroughly mixed and separated into 1-kg (dry weight basis) portions. Metal sulphate solutions of either Cd or Zn (25 ml kg^{-1} soil oven-dry basis) were added to raise the total metal concentration to the maximum permitted under current European Union guidelines for Cd and Zn of 3 and 300 mg kg^{-1}, respectively, for agricultural soils receiving sewage sludge (CEC, 1986). The 1-kg portions were then thoroughly mixed using an electronic mixer before bulking to give 10 kg of soil (Table 1). These were then incubated moist for 2 years at ambient temperatures in southern England. Soils were also sampled from seven sites throughout Europe which had a history of heavy metal contamination. The selection of soils included a range of pHs, textures and heavy metal contents (Table 2).

2.2. Extraction of soil solution

Rhizon soil-moisture samplers (SMS) were obtained from Rhizosphere Research Products, Wageningen, Holland (e-mail: info@rhizo.nl). These samplers consist of a length of porous plastic, capped with nylon at one

Table 1
Analysis of soils before and after metal sulphate addition at two loading rates

Soil pH	CEC (cmol kg^{-1})	Zn (mg kg^{-1})		Cd (mg kg^{-1})	
		Control	Amended	Control	Amended
4.5	7.7	53.0	307	0.45	4.3
5.1	8.6	58.0	330	0.37	3.1
6.3	10.6	53.0	354	0.36	3.6
7.0	16.1	54.0	345	0.31	3.7

CEC, cation exchange capacity.
pH values are means of three replicates ±0.1 SED. Metal concentrations are means of four replicates ±9% SED.

Table 2
Description and chemical analysis of soils from long-term contaminated sites in Europe

Soil	Texture	Contamination source	pH	CEC (cmol kg^{-1})	Total metal concentration (mg kg^{-1})			
					Cd	Cu	Ni	Zn
Arras, France	sandy loam	Zn smelter	7.6	29.0	23.8	44.8	17.6	1722
Avon, UK	sandy loam	Zn smelter	7.0	25.1	2.9	74.6	46.0	400
Bonn, Germany	loam	9.8 t ha^{-1} sewage sludge DW biannually since 1959	7.4	23.7	2.2	92.6	36.3	383
Bordeaux, France	sand	10 t ha^{-1} yr^{-1} sewage sludge DW since 1974	6.1	8.8	2.4	31.3	7.7	329
Felton, UK	mine spoil	geogenic/smelter	6.6	10.3	58.1	41.8	61.8	3259
Sala, Sweden	loam	Zn smelter	7.5	47.0	13.8	56.1	12.6	2166
Woburn, UK	sandy loam	19 t ha^{-1} yr^{-1} sewage sludge DW from 1942–61	6.4	13.3	4.4	52.2	25.5	210

CEC, cation exchange capacity; DW, dry weight.

end, and attached to a 5-cm length of polyethylene tubing at the other end. A nylon strengthening rod is present inside the porous tube and the polyethylene tube is joined to a female luer lock (Fig. 1).

All samplers were washed by forcing 60 ml of 5% (v/v) HNO_3 through the probe, followed by 60 ml of de-ionized water and then dried at 30°C before use. One sampler was placed into each of three replicate 1.0-kg (dry weight) pots of the chosen soils. A glass rod was used to make a small primary hole in the soil, diagonally from the lip of the pot. The sampler was first wetted using a slurry of the soil from the pot (1:5 w/v soil to water) before being gently pushed into the soil. The soil was then made up to 50% water holding capacity (WHC) by adding de-ionized water to the saucer of the pot. During the 2 weeks prior to extraction of the soil solution, the soils were gradually made up to 75% WHC. Soil solution was extracted by connecting a thick-sided glass bottle to the luer lock on the SMS via polyethylene tubing. This tube had a two-way valve attached to it. A suction pressure equivalent to 50 mm Hg was created in the glass bottle through the valve, and the valve turned so that this pressure was then applied to the SMS to extract the soil solution. The whole apparatus was left over night and yielded about 60 ml soil solution (Fig. 1).

2.3. Soil and soil solution analysis

Soil pH was determined using a 1:2.5 (w/v) soil to water mixture. Total metal concentrations were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES; ARL 3400) following the method of McGrath and Cunliffe (1985), and small concentrations of Cd by graphite furnace atomic absorption spectrometer (GF-AAS; Perkin Elmer ZL 410) with Zeeman background correction.

The extracted soil solution was separated into several sub-samples for analysis. Two aliquots were acidified with either 5% (v/v) HCl or 0.3% (v/v) HNO_3 and used to determine total metal concentrations by ICP-AES or GF-AAS, respectively. Other aliquots of soil solution were used for determining dissolved organic carbon, pH and for the speciation analysis described below.

2.4. Determination of free Cd^{2+} and Zn^{2+} concentrations in soil solution

A cation exchange resin method was used to determine the concentrations of free metal ions in soil solution. The method relies on measuring the metal concentration before and after equilibrium is reached with a Ca saturated cation exchange resin. The proportion of the total

Calculation

$$M^{2+} = M_T (M_T - M_S) \times M^*_S \times M^{-1}_S \times (M^*_T - M^*_S)^{-1}$$
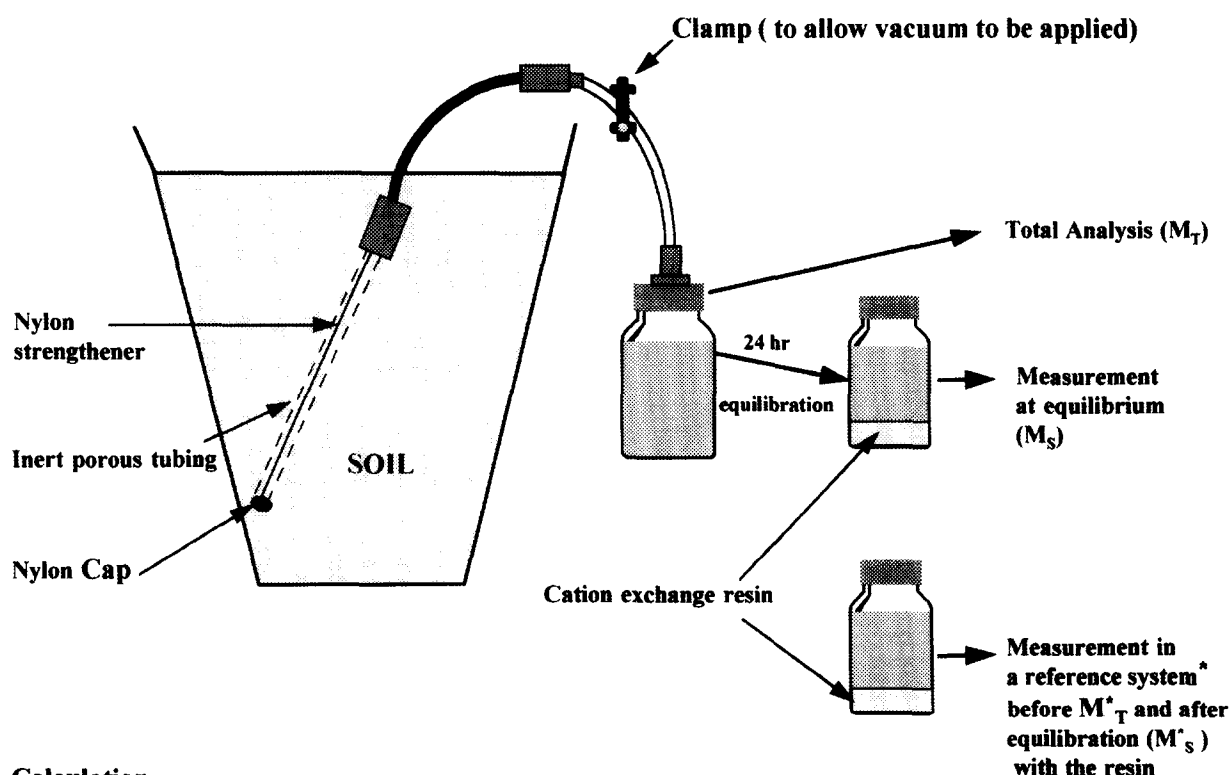
Fig. 1. Schematic of soil solution extraction procedure and chemical speciation determination.

metal in the environmental sample present as free metal ions can be calculated by comparison with a reference experiment. This method is described in detail elsewhere (Holm et al., 1995; Knight and McGrath, 1995).

3. Results and discussion

Unamended Woburn soils from the long-term liming field experiments, with bulk soil pHs > 5.1, had total Cd and Zn concentrations in soil solution which were very small and in most cases below the limit of detection (Table 3). The total Cd concentration in soil solution from the Cd amended soil, and the total Zn concentration in soil solution from the Zn amended soil, decreased from 475 to $2.9\,\mu g$ litre^{-1} and 1.262×10^5 to $1743\,\mu g$ litre^{-1}, respectively, with increasing pH (Table 3). The reduced solubility of Cd and Zn with increasing soil pH is in agreement with previous findings (Sanders et al., 1987; Lorenz et al., 1997). The most important factor controlling heavy metal availability in soil seems to be pH (Young and Japony, 1994). Increasing the soil pH has been shown to be more

effective at reducing heavy metal availability in contaminated soils compared with various organic matter amendments (Marschner et al., 1995). However, the proportion of free Cd^{2+} ions to total soluble Cd remained at $\geq 80\%$ across the pH range, except for the pH 7 soil, where about 50% of the total soluble Cd was present as free Cd^{2+} in soil solution. Similarly, the proportion of free Zn^{2+} ions to total soluble Zn remained at about 80% across the pH range (Table 3).

The total concentrations of Cd in the soil solutions extracted from the metal sulphate amended and the sewage sludge treated Woburn soils were quite different. Soils amended with $CdSO_4$, and with bulk pHs of 6.3 and 7.0, had 11 and $3.0\,\mu g$ total Cd litre^{-1} in soil solution respectively (Table 3; Fig. 2). Soil solution extracted from the same Woburn soil contaminated with heavy metals by past additions of sewage sludge, and with a pH of 6.4, had a total concentration of $38\,\mu g$ Cd litre^{-1}. The concentrations of total Zn and free Zn^{2+} in soil solutions from the $ZnSO_4$ amended Woburn soils were much greater than those found in the corresponding soil contaminated through long–term additions of sewage sludge (Table 3; Fig. 3). For example, $ZnSO_4$

Table 3

pH, organic carbon, total and free heavy metal concentrations in soil solution extracted from metal sulphate amended soils and industrially polluted soils

Soil	Bulk soil pH	Soil solution		Metal concentration in soil solution (μg litre^{-1})					
		pH	DOC (mg litre^{-1})	Cd	Free Cd	Zn	Free Zn	Cu	Ni
W-unamended		3.8	25 (3.3)	15.7 (1.7)	13.2 (0.9)	496 (69)	404 (59)	31 (3.1)	216 (25)
W-Cd	4.5	(0.1)	18 (1.5)	475 (61.8)	409 (31.2)	265 (33)	216 (30)	14 (1.8)	151 (19)
W-Zn			25 (3.1)	39.7 (5.5)	26.3 (4.6)	1.26×10^5 (1.3×10^4)	8.7 $(7.6) \times 10^4$	33 (0.7)	389 (32)
W-unamended		4.4	20 (3.7)	2.5 (0.1)	1.6 (0.1)	90 (4.9)	75 (8.7)	15 (1.3)	49 (3.3)
W-Cd	5.1	(0.2)	17 (1.4)	109 (12.6)	85.5 (37.9)	73 (6.4)	59 (5.9)	7 (4.5)	44 (1.3)
W-Zn			24 (2.9)	9.54 (2.0)	6.9 (4.6)	6.05×10^4 (2.7×10^4)	5.1 $(3.3) \times 10^4$	4 (1.0)	181 (8.9)
W-unamended		5.7	8 (2.1)	< DL	< DL	< DL	< DL	10 (5.3)	< DL
W-Cd	6.3	(0.1)	7 (1.3)	11.4 (1.6)	11.4 (2.5)	< DL	< DL	11 (1.0)	< DL
W-Zn			15 (1.7)	1.8 (0.1)	0.7 (0.4)	9672 (190)	7803 (780)	29 (18.5)	25 (13)
W-unamended		6.5	11 (1.3)	< DL	< DL	< DL	< DL	11 (4.0)	< DL
W-Cd	7	(0.2)	14 (1.7)	2.9 (0.3)	1.39 (0.2)	< DL	< DL	16 (7.1)	< DL
W-Zn			10 (0.2)	< DL	< DL	1743 (244.9)	1475 (290)	16 (3.5)	< DL
Industrially polluted									
Arras, France	7.6	7.3	13 (0.2)	46.7 (0.6)	38.9 (1.3)	154 (6.2)	88 (11)	63 (3.1)	53 (1.6)
Avon, UK	7	6.7[a]	18.6[a]	37.0 (1.4)	37 (2.0)	39 (2.0)	8 (0.3)	46 (1.7)	50 (6.7)
Bonn, Germany	7.4	7.5	35 (0.89)	34.7 (1.2)	33.3 (6.6)	36 (4.9)	3 (3.5)	86 (2.2)	59 (0.9)
Bordeaux, France	6.1	5.8	74 (1.8)	41.3 (0.6)	38.4 (7.6)	1289 (83)	873 (392)	138 (6.2)	67 (1.8)
Felton, UK	7.5	6.9	14 (1.1)	87.3 (2.3)	81.3 (2.5)	1087 (36)	875 (32)	34 (4.4)	55 (1.1)
Sala, Sweden	6.6	7.4[a]	154[a]	36.3 (3.5)	36.3 (14.8)	448 (20)	186 (55)	69 (2.0)	52 (0.7)
Woburn, UK	6.4	6.1	24 (1.1)	38 (1.0)	31.9 (4.6)	287 (7.6)	202 (10)	106 (3.6)	88 (1.8)

DOC, dissolved organic carbon; W, indicates Woburn soil used in the metal salt amendment experiment; < DL, metal concentration below the detection limit.
Bulk soil pH determinations with SEM < 0.2.
Figures in brackets are SEM.
[a] Determination made from two replicates only.

amended soil with a total concentration of 350 mg Zn kg^{-1} had around 7800 μg Zn^{2+} litre^{-1} in soil solution at pH 6.3. The same soil amended with sewage sludge, and
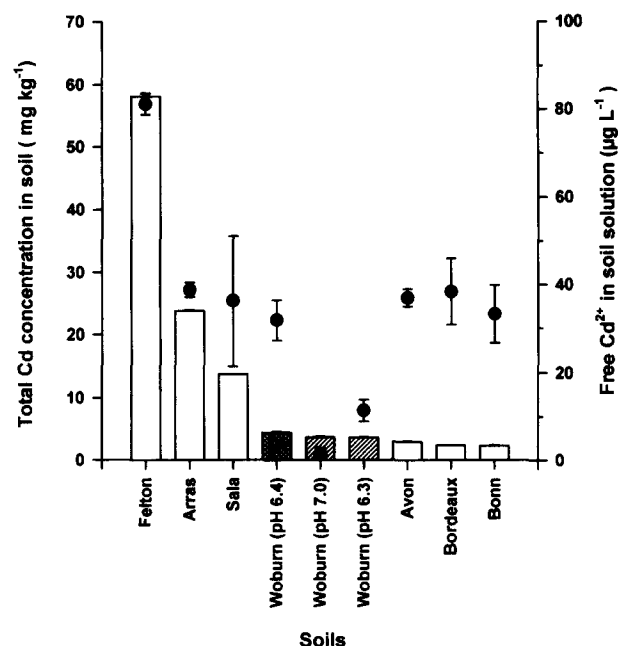

Fig. 2. Relationship between total soil Cd and free Cd^{2+} in soil solution from a range of polluted soils from Europe. Bars represent total Cd concentration in soil (mg kg^{-1}). □ Industrially polluted soils; ▨ Woburn soils amended with CdSO$_4$; ▩ Woburn soil amended with sewage sludge; ● free Cd^{2+} ion concentrations in soil solution (μg Cd^{2+} litre^{-1}). Error bars represent SEM.
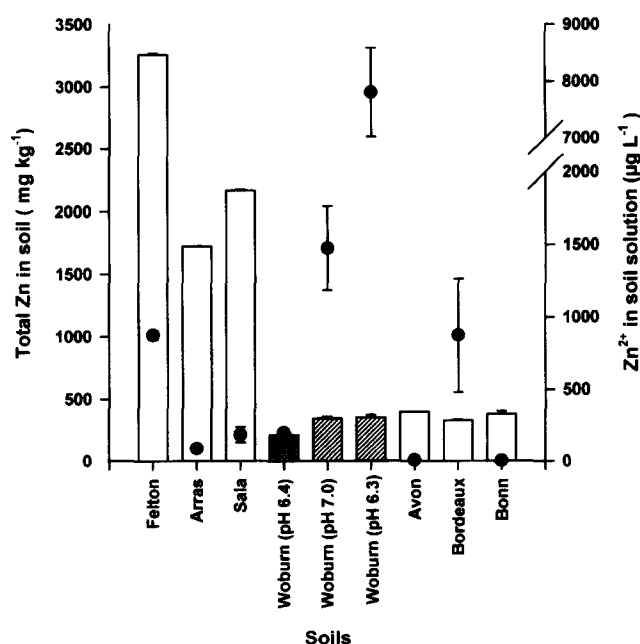

Fig. 3. Relationship between total soil Zn and free Zn^{2+} in soil solution from a range of polluted soils from Europe. Bars represent total Zn concentration in soil (mg kg^{-1}). □ Industrially polluted soils; ▨ Woburn soils amended with ZnSO$_4$; ▩ Woburn soil amended with sewage sludge; ● free Zn^{2+} ion concentrations in soil solution (μg Zn^{2+} litre^{-1}). Error bars represent SEM.

containing a total soil Zn concentration of 210 mg kg^{-1}, only had 200 μg Zn^{2+} litre^{-1} in soil solution (Table 3; Fig. 2). Surprisingly, total soluble and free ion concentrations of Cd were much higher in soils to which metal-contaminated sewage sludge had been added some 36 years previously, compared with 'one-off' CdSO$_4$ additions. However, the opposite was the case with Zn, where total soluble and free ion concentrations were much higher in the ZnSO$_4$ amended soils compared with long-term sewage sludge additions. Hence, Cd availability in soil solution as Cd^{2+} was less in artificially spiked soils compared with soils contaminated by long-term additions of sewage sludge. In contrast, Zn availability in soil solution as Zn^{2+} was much higher in artificially spiked soils compared with long-term sewage sludge treated soils. Our Cd data are in contrast to the work of Korcak and Fanning (1985), who found both greater uptake by corn and extractability with DTPA of Cd and Zn from metal salt amended soils compared with soils receiving the same amounts of metals via sewage sludge additions. Our results are also contrary to those of Ham and Dowdy (1978) who found no difference in Cd and Zn availability between soils treated with metal salts and sewage sludge.

It is somewhat surprising to find Cd availability as Cd^{2+} in soil solution to be greater in soil amended with sewage sludge compared with soils amended with a single addition of the metal salt. McBride (1994) discussed the potential for increased metal toxicity in soils treated with sewage sludge, as a consequence of added organic matter mineralizing and releasing more free metal ions into soil solution. In the case of the sludge amended soil used in this study, the last addition was over 36 years ago. Therefore, the effect of organic matter addition on availability of Cd would be negligible as oxidation and mineralization processes have reduced the organic carbon content of the sludge amended soil close to levels found in the unamended soils.

The pH of the soils from the contaminated sites ranged from 6.1 to 7.5. As pH is a primary factor affecting metal solubility, a direct comparison of the metal concentrations found in soil solutions collected from these soils was only made with soils amended with metal salts in the same pH range.

Soil solution extracted from the other contaminated sites had between 35 and 87 μg Cd litre^{-1} (Table 3; Fig. 2). Cd solubility was greatest in soil from Felton, which had a total soil Cd concentration of 58 mg kg^{-1}, and over 80 μg Cd^{2+} litre^{-1} in soil solution. The other soils from contaminated sites all had similar Cd^{2+} concentrations in soil solution (32–39 μg Cd^{2+} litre^{-1}), despite total soil concentrations ranging from 2.2 (Bonn) to 23.8 (Arras) mg kg^{-1} (Table 2). The proportion of free Cd^{2+} as a percentage of total soluble Cd present in soil solution from industrially contaminated soils was similar to that found in the sulphate amended soils

(Table 3; Fig. 3). However, for soils of similar pH, the total concentration of Cd found in soil solution was much smaller in the metal sulphate amended soils compared with industrially contaminated soils. Hence, amendment of soil with $CdSO_4$ may result in a smaller exposure of organisms to potentially toxic free Cd^{2+}.

The largest concentration of Zn^{2+} in soil solution extracted from a contaminated site was $875\,\mu g$ Zn^{2+} litre^{-1} (Felton) compared with $1475\,\mu g$ Zn^{2+} litre^{-1} in solution from the pH 7.0 soil amended with $ZnSO_4$. Soil solution extracted from Woburn soil amended with sewage sludge had about 70% of the total Zn present as free Zn^{2+}. In the other contaminated sites studied, the proportion of free Zn^{2+} to total Zn in solution ranged from 8 to 80%. This variation did not correspond with changes in any one factor, such as pH, dissolved organic carbon concentration, cation exchange capacity, or total metal content of the different soils (Table 3). The variability in both solubility and chemical form of Zn in soil solution from industrially contaminated soils demonstrates the need to determine both the quantity and chemical species present before drawing conclusions on availability or toxicity of heavy metals.

Clearly, the comparison of heavy metal availability across different soil types and sources of heavy metal input is difficult. In general, artificially contaminated soils with Cd and Zn sulphates did not match the availability of these metals in soils from the contaminated sites because Zn solubility was too large and that of Cd too small. In addition, it is clear that considering simply the total soil solution concentrations may not be sufficient to distinguish between the different exposure concentrations of free metal ions in different soils. However, differences in Cd and Zn availability were apparent in the same Woburn soil amended with sewage sludge and metal sulphates. Therefore, extrapolation from artificially contaminated soils may lead to erroneous conclusions about heavy metal availability and hence their long-term impact.

Acknowledgements

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