Evaluating the use of DGT-DIFS to measure Cd, Cu, Ni and Zn plant availability in soils treated with biosolids and metal salts

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Abstract

The application of biosolids to land is increasing because it provides an alternative means of waste disposal and benefits the soil via improved .soil fertility and productivity. However, the metals present in biosolids are potential concerns for environmental and public health, arising from the possibility of metal accumulation in soils and their introduction into the food chain via plant uptake. The success of environmental risk assessments of metal contaminated soils depends on the accuracy with which they estimate metal bioavailability. Diffusive gradients in thin-films (DGT) combined with 2D-DIFS (DGT-induced fluxes in soils) is a relatively new technique for measuring labile metals in soils and is characteristically expressed as the effective solution metal concentrations (C_E). This technique has shown to be a promising surrogate for predicting metal uptake in plants and is being extensively examined using three soil types collected from the Canterbury region. Lysimeters (containing soil monoliths) were treated with a one-off application of increasing levels of Cd (1, 5, 10 mg/kg), Cu (50, 200, 750 mg/kg), Ni (30, 150, 300 mg/kg) and Zn (70, 300, 1000 mg/kg) in the presence and absence of biosolids (400 kg N ha/yr). Ryegrass (*Lolium perenne*) seeds were sown in each lysimeter immediately after treatment application. Harvests were made at six monthly intervals Ryegrass was analysed for total plant metal content and the soil (0-10 cm) was sampled and assessed using the DGT and 2D-DIFS method. Metal concentrations in plants generally increased as treatment levels increased. Cadmium concentrations were higher in treatments without biosolids, and highest in the combination high metal treatments. Copper, Ni and Zn concentrations in plants were higher in soils treated with metal salts in the presence of biosolids. However, for Cu and Zn these differences were less than for Ni. The linear relationship between plant metal uptake and C_E was strongest with Cu ($r^2=0.87$), followed by Zn ($r^2=0.64$) and Ni ($r^2=0.44$). The weakest linear relationship was found for Cd ($r^2=0.17$).

1. Introduction

Trace metals (e.g. Cd, Cu, Ni and Zn) are naturally present in various concentrations in soils, with several being essential for plant growth (e.g., Cu, Ni and Zn) and animal health (e.g. Cr and Se).. However, the accumulation of metals in soil, particularly Cd, Cu, Ni and Zn, arising from anthropogenic activities is of concern, particularly in agricultural production systems due to the potential threat of adversely affecting food quality (safety and marketability), crop growth (phytotoxicity), and/or environmental health (soil flora and fauna) (McLaughlin et al., 2000; McLaren et al., 2003; Speir et al., 2003).

Biosolids is the residual product of sewage wastewater treatment and has been used widely in the agriculture industry for several years valuable source of organic matter and macronutrients, and an alternative method of waste disposal (Antoniadis and Alloway, 2000; Speir et al., 2003; McLaren et al., 2005; Oliver et al., 2005). However, biosolids also contain microbial contaminants and trace metals and for these reasons, its agricultural use in New Zealand is regulated (McLaren et al., 2004; 2005).

Risk assessments acknowledge that total metal concentrations are not the best indicators of metal bioavailability, and therefore estimating metal bioavailability in soils has been the focus of many recent studies (Gray & McLaren, 2006; Meers, et al., 2006; Rooney et al., 2006; Menzies et al., 2007). However, the success of measuring metal bioavailability differs according to element, plant species and soil type. For example the bioavailable fraction is often quantified as the fraction of contaminant extractable in a chemical reagent based on correlation with the total contaminant uptake

by plants. In these cases bioavailability is largely a measure of metal solubility. These solubility assessments and other chemical extraction methods (e.g. EDTA, and calcium nitrate) have had limited successful applications as bioavailability measurement tools (McLaughlin et al., 2000; Menzies et al., 2007).

The difficulty in assessing metal bioavailability across soil types results from the combination of abiotic and biotic processes and soil properties, such as soil pH, soil texture, organic matter content, metal adsorption and desorption from mineral surfaces and metal release through mineral dissolution, and interactions with plant and soil micro-organisms (McLaughlin et al., 2000; Speir et al., 2003; Basta et al., 2005; Chojnacka et al., 2005).

Diffusive gradients in thin film (DGT) is a relatively new method of assessing metal bioavailability in soils and has shown promising results in the estimation of plant metal uptake from soils (Ernstberger et al., 2002; Degryse et al., 2003; Nolan et al., 2005; Zhang et al., 2001; 2004). Metal fluxes measured by DGT are affected by concentrations of metal ions in the soil solution and the re-supply of metal ions from the soil solid phase. This re-supply of metal ions is dependent on the amount of labile metal sorbed onto the solid phase and the rate of exchange between the solid and the solution phase. The DGT technique works in combination with the 2D-DIFS model (Harper et al., 2000; Sochaczewski et al., 2007) to give C_E (effective concentration). Effective concentration isa theoretical concentration derived from the time-averaged flux of accumulated metals on the resin gel and the kinetic resupply rate of labile metals into solution from the solid phase of the soil (Zhang et al., 2001).

A major aim of this research is to extensively test the effectiveness of the DGT technique in estimating plant bioavailability across a range of soil types over a 24 month period. This research forms part of an ongoing project assessing the bioavailability and mobility of Cd, Cu, Ni and Zn in biosolids and metal salt treated soils.

2. Methods

2.1 Lysimeter collection and soil treatment

Lysimeters containing three contrasting soil types (Halkett sandy loam, Summit Hill-Rapaki complex and Wakanui silt loam) were collected from the Canterbury region. These are currently housed in-ground, outside at the Lincoln University field laboratory to provide thermal insulation and natural environmental exposure.

The top ten centimetres of each lysimeter were thoroughly mixed with the treatments listed in Table 1. Biosolids were obtained from the Christchurch City Council treatment works at Bromley and were applied at a rate of 400 kg N/ha/yr. Metals applied directly to the soil were in the form of metal sulphates. Cadmium and Ni concentrations chosen were based on current biosolids guideline levels (NZWWA, 2003). Copper and Zn concentrations chosen were based on work to date by ESR and the Centre for Soil and Environmental Quality. Ryegrass (*Lolium perenne)* seeds were then sown into each lysimeter immediately after treatment application.

Table 1. Soil treatments.

Treatment	Cd added (mg/kg)	Cu added (mg/kg)	Ni added (mg/kg)	Zn added (mg/kg)
Control	-	-	-	-
Biosolids	-	-	-	-
Biosolids + low metals	1	30	50	70
Low metals	1	30	50	70
Medium metals	5	200	150	300
High metals	10	750	300	1000
Cd only	10	-	-	-

2.2 Plant harvest and analysis

Ryegrass is harvested at six-monthly intervals immediately prior to soil collection for DGT analysis. After harvest, plants were dried (at 50°C) for 3 days, milled and then digested on a heating block using 10 ml of concentrated HNO_3. Samples were analysed for total Cd, Cu, Ni and Zn using GFAAS, FAAS and ICP-OES.

2.3 Soil collection, DGT deployment and 2D-DIFS calculations

Soil samples from lysimeters were obtained by coring a sub-sample (2.5 cm diameter by 10 cm depth). Samples were air-dried, sieved (2 mm) and the maximum water-holding capacity (MWHC) determined. Soil samples are raised to 80% of MWHC and left to equilibrate 24-hours prior to DGT placement.

2.4 DGT measurements and the calculation of effective concentration (C_E) using 2D-DIFS

The DGT device consists of a backing plate, chelating resin gel (Chelex-100 resin), a defined diffusion gel layer and a membrane filter held in place by a cap with a 17 mm window. Soil paste is smeared on the filter window of the DGT device before placement onto the soils. DGT devices are left in the saturated soil for 24 hours. The resin gel layer is then removed from the DGT device and metals extracted into 10 ml of 1M of HNO_3 prior to analysis using ICP-OES.

The mass of the metals accumulated by the resin gel is obtained using the following equation

$$M = C_e(VHNO_3 + Vgel)/fe$$

where, C_e is the metal concentration in the 1M HNO_3, $VHNO_3$ is the volume of HNO_3, Vgel is the volume of gel and fe is the elution factor for metals. The time averaged concentration at the soil-diffusive layer interface (C_{DGT}) can be calculated from

$$C_{DGT} = M\Delta g/DtA$$

where, Δg is the diffusion layer thickness, D is the diffusion coefficient of the metal in the diffusion layer at a given temperature, t is the deployment time (s) and A is the area in membrane exposed to the soil.

Effective concentration, C_E, is calculated from

$$C_E = C_{DGT}/R_{DIFF}$$

where R_{DIFF} is calculated using the 2D-DIFS modeling programme from soil density, porosity, and the diffusion coefficients for each of the metals in water and soil. R_{DIFF} represents the ratio of the mean interfacial concentration due to resupply by diffusion only to the initial or bulk solution concentration.

3. Results and Discussion

3.1 Metal accumulation in ryegrass

Total metal concentration results for ryegrass are presented in Tables 2 and 3. At six months, Cd across all treatments varied from 0.001 mg/kg (Wakanui soil) to 2.8 mg/kg (Halkett soil), and at 12 months ranged from 0.04 mg/kg (Halkett and Wakanui soils) to 5.9 mg/kg (Wakanui soil). At six months, Cu concentrations across all treatments ranged from 1.7 mg/kg (Halkett soil) to 3.0 mg/kg (Summit soil), and at 12 months from 6.1 mg/kg (Halkett soil) to 64.8 mg/kg (Wakanui soil).

Table 2. Cd levels in ryegrass harvested 6-months after treatment application. Levels of metals are reported as the mean plant concentration ± se (n = 3).

Soil and treatment	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
Halkettl				
Control	0.03±0.01	1.7±0.24	0.1±0.01	7.1±0.58
Biosolids	0.06±0.01	1.5±0.04	0.2±0.04	10.9±1.4
Biosolids + low metals	0.2±0.05	2.1±0.12	12.3±1.9	33.7±9.5
Low metals	0.8±0.44	2.7±0.21	12.0±1.7	36.1±5.5
Medium metals	NG	NG	NG	NG
High metals	NG	NG	NG	NG
Cd only	2.8±0.27	NM	NM	NM
Summit				
Control	0.01±0.00	1.7±0.12	0.1±0.00	6.0±0.51
Biosolids	0.01±0.00	2.0±0.15	0.2±0.03	8.0±1.06
Biosolids + low metals	0.03±0.00	2.3±0.13	12.6±2.4	34.4±12.3
Low metals	0.03±0.01	3.0±0.52	8.7±3.66	18.5±4.9
Medium metals	NG	NG	NG	NG
High metals	NG	NG	NG	NG
Cd only	0.9±0.02	NM	NM	NM
Wakanui				
Control	0.0001	2.1±0.03	0.1±0.04	6.7±0.22
Biosolids	0.0001	1.7±0.06	0.2±0.02	7.1±0.14
Biosolids + low metals	0.0005	2.1±0.14	12.0±1.2	24.1±3.5
Low metals	0.0003	2.2±0.07	8.2±1.24	16.7±1.4
Medium metals	NG	NG	NG	NG
High metals	NG	NG	NG	NG
Cd only	0.52±0.02	NM	NM	NM

NG = no growth; NM = not measured

Table 3. Cd levels in ryegrass harvested 12-months after treatment application. Levels of metals are reported as the mean plant concentration ± se (n = 3)

Soil and treatment	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
Halkett				
Control	0.04±0.0	6.1±0.27	1.7±0.25	25.7±0.62
Biosolids	0.1±0.02	6.2±0.8	1.8±0.21	25.6±1.80
Biosolids + low metals	0.2±0.04	6.4±0.61	38.0±9.8	57.8±12.2
Low metals	0.3±0.04	6.1±0.36	46.5±1.3	56.2±9.6
Medium metals	NG	NG	NG	NG
High metals	2.8±0.81	42.8±6.7	164±28	200±20.3
Cd only	1.2±0.23	4.8±0.42	1.8±0.29	19.6±1.60
Summit				
Control	0.1±0.01	7.1±0.26	1.4±0.09	33.8±6.02
Biosolids	0.04±0.0	7.0±0.35	2.2±0.66	32.6±3.45
Biosolids + low metals	0.2±0.05	7.4±0.56	29.2±3.3	56.4±5.47
Low metals	0.5±0.23	8.0±0.73	38.3±7.4	72±14.52
Medium metals	3.40	15.0	175.7	180.3
High metals	NG	NG	NG	NG
Cd only	2.1±0.94	6.0±0.97	3.7±1.46	22.9±3.95
Wakanui				
Control	0.04±0.0	6.5±0.26	1.5±0.07	24.0±1.24
Biosolids	0.04±0.0	6.8±0.46	1.8±0.24	27.0±1.03
Biosolids + low metals	0.2±0.05	6.7±0.41	39.0±2.4	62.8±11.40
Low metals	0.1±0.02	6.4±0.13	31.2±6.6	44.0±5.90
Medium metals	0.6±0.10	6.9±1.9	77.0±13	94.2±24.02
High metals	5.9±2.08	64.8±12	131±4.9	312±74.70
Cd only	0.6±0.03	5.9±0.37	2.9±0.77	23.2±2.25

NG = no growth; NM = not measured

At six months, Ni concentrations across all treatments ranged from 0.1 mg/kg (Halkett soil) to 3.0 mg/kg (Summit soil), and at 12 months ranged from 1.4 mg/kg (Summit soil) to 175.7 mg/kg (Summit soil). At six months, Zn concentrations across all treatments ranged from 7.1 mg/kg (Halkett soil) to 36.1 mg/kg (Halkett soil), and at 12 months ranged from 33.8 mg/kg (Summit soil) to 311.8 mg/kg (Wakanui soil).

Nearly all observed plant metal concentrations were higher than in the corresponding controls, with the exception of Cu, which had lower concentrations in lysimeters treated with biosolids. Generally, ryegrass from the Halkett soil had the widest ranging metal concentrations, with Summit soil having the smallest range. For all soils, ryegrass Cd concentrations were higher in the combination high metal treatments than the Cd-only treatments.

3.2 Effective concentration (C_E) of Cd, Cu, Ni and Zn as measured by DGT

The results of C_E measurements for each of the metals are shown in Figures 1 and 2. Effective concentration was related to the total metal content of ryegrass for all four metals for both the six and 12 month harvest. All data was fitted using simple linear regression.

For Cu and Zn, good fits to the plant content were obtained (r^2 = 0.87 and 0.64 respectively). For Ni the r^2 value was lower (0.44), and Cd had the lowest r^2 value (0.17).
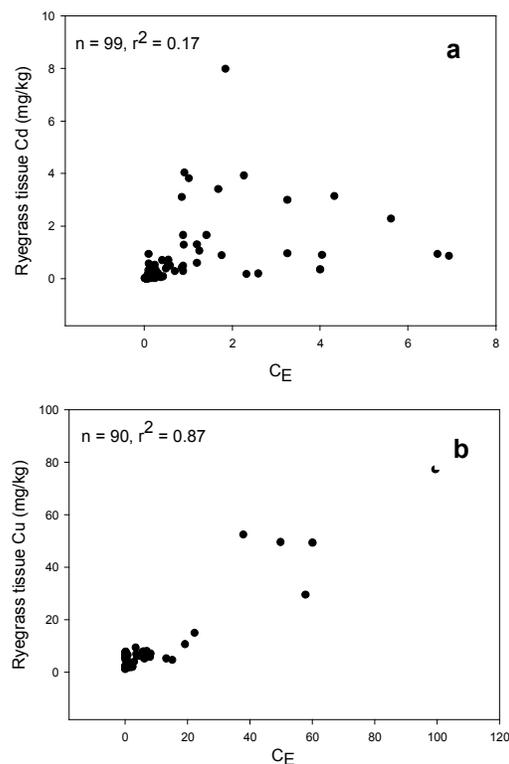
Figure 1. Plots of (a) Cd and (b) Cu in ryegrass tissue plotted against Cd and Cu measured by DGT in soils (C_E measured in mg/l).

Of all the metals, Cu and Zn provided the strongest relationship with C_E, followed by Ni then Cd. Although weaker relationships were observed for Cd and Ni, it is worth noting that results for the 12 month harvest alone produced higher r^2 values (0.4 and 0.6 respectively).

The use of DGT as a predictor of metal concentrations in plants has shown promising results in recent studies (Zhang et al., 2001; Zhang et al., 2004; Almas et al., 2006) for Cd, Cu and Zn. However, Almas et al., (2006) noted that the linear relation between Cd as measured by DGT and ryegrass uptake was weak ($r^2 = 0.53$, p=0.18), concluding that the success of DGT as a predictor of plant uptake was affected by plant health and species.
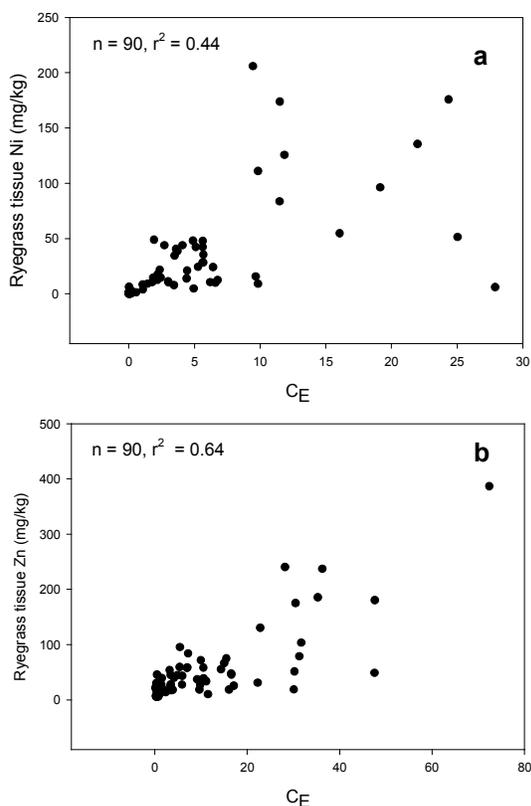
Figure 3. Plots of (a) Ni and (b) Zn in ryegrass tissue plotted against Ni and Zn measured by DGT in soils (C_E measured in mg/l).

4. Summary

Soil properties strongly influence Cd, Cu, Ni and Zn uptake in ryegrass. The addition of biosolids influences the availability of Cu and Ni, which also varies in response depending on soil type. From these preliminary results the DGT technique has shown to be promising for Cu, Ni and Zn, however, the linear relationship with Cd and plant uptake was weak. These results form part of a much larger dataset that includes soil and plant samples from Hamilton, Nelson and Wellington as well as additional soils from around the Canterbury region.

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