

# Metal chemistry and bioavailability in a biosolids-amended forest soil following conversion of the land for agricultural usage

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## Abstract

Application of biosolids to forests as a method of disposal is currently being used by authorities around the world, including New Zealand. This practice can lead to a build up of metals (from the biosolids) within the forest litter layer. However, as long as the land remains under forest, the chance of these metals entering the human food chain is low. This may cease to be the case if the forest is cleared for conversion of the land back for agriculture. This study, using incubation and plant growth techniques, examines the fate of metals in a *Pinus radiata* plantation forest treated with metal-spiked biosolids, following simulated conversion of the land back for agricultural use. Mixing of the biosolids-treated forest litter into the underlying mineral soil resulted in high concentrations of metals (Cu, Ni and Zn) in easily extractable forms, and there was also very little change in these concentrations during a subsequent 2-year incubation of the samples. Soil solution concentrations of the metals were also enhanced substantially by the various original biosolids treatments. Chemical speciation of the soil solutions using WHAM 6 showed that whereas solution Cu was dominated by organic complexes, most Ni and Zn was present as  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ , with generally less than 5% of these elements present as organic complexes. Addition of lime to the soils substantially decreased both readily extractable and soil solution metal concentrations, however, even in their unlimed state there were no adverse effects due to the metals on plant growth as determined in a wheat germination and seedling growth test. Nevertheless, metal concentrations in the wheat seedlings were increased by the various original biosolids treatments. Plant metal concentrations showed strong correlations with either soil solution metal ion activities, or effective soil

solution concentrations as determined by diffusive gradients in thin films (DGT). The results from this study are discussed in relation to the possible consequences of growing agricultural crops on land converted from forest soils that have previously received applications of biosolids.

## 1. Introduction

Application of biosolids to forests as a method of disposal is currently being used by authorities around the world, including New Zealand (Magesan and Wang, 2003). The disposal of biosolids in this way is often considered to be a relatively safe option with regard to the chances of contaminants entering the food chain, and has been shown to have beneficial effects on tree growth (e.g. Brockway, 1983, Henry et al., 1993; Kimberley et al., 2004). However, since the biosolids are generally surface-applied under the trees, there is considerable potential for the accumulation of high concentrations of metals from the biosolids within the forest litter layer (McLaren et al., 2007). As long as the land remains under forest, these metals may not be of major concern. However, should the forests be cleared, and the land converted to some other form of land use, this may cease to be the case. For example, as a result of economic pressures, in the Canterbury Plains area of New Zealand, substantial areas of *Pinus radiata* plantation forests are being converted back to agricultural pasture. The completion of a biosolids field trial in a *Pinus radiata* forest (McLaren et al., 2007) presented an opportunity to simulate the conversion of the forest soil back for agricultural use and examine the fate and bioavailability of metals following conversion.

## 2. Methods

### 2.1 Soil sampling and preparation

The original field experiment was located in a *Pinus radiata* plantation on the Canterbury Plains, approximately 50 km west of Christchurch city. The soil at the site is a Lismore stony silt loam and consists of a silt loam mineral horizon ranging from 10 to 30 cm in depth containing many stones, overlain by a litter layer approximately 2-3 cm in depth, and underlain by coarse gravels. Properties of both the mineral soil (0-10 cm) and litter layers are shown in Table 1. Both layers are fairly acidic with low % base saturation. Total metal concentrations are within the range of typical background concentrations for New Zealand soils.

**Table 1. Initial soil properties at experimental site**

Property	Litter layer	Mineral soil (0-10 cm)
pH (H <sub>2</sub> O)	5.1	5.0
Base saturation (%)	40.1	19.5
Total C (%)	38.5	3.6
Total N (%)	1.1	0.1
Total Cu (mg/kg)	5.6	6.4
Total Ni (mg/kg)	8.6	10.1
Total Zn (mg/kg)	43.9	62.8

The original experiment consisted of a control plot (no biosolids), a plot receiving unspiked biosolids and 12 plots that received surface applications of biosolids spiked with increasing amounts of Cu (Cu-1, Cu-2, Cu-3, Cu-4) Ni (Ni-1, Ni-2, Ni-3, Ni-4) or Zn (Zn-1, Zn-2, Zn-3, Zn-4) (McLaren et al., 2007). Six years after the original biosolids application, material was sampled by spade from each plot from the surface (including litter) to a depth of 10 cm into the mineral soil. The combined litter and mineral soil in these samples was thoroughly mixed in a mechanical mixer to simulate the mixing that occurs during the conversion of the land from forest to pasture.

### 2.2 Experiment 1

Sub-samples of the soils (in triplicate) were incubated at 25°C and 80% field moisture capacity for a period of approximately two years. Moisture contents were maintained

by regular weighing and samples removed at intervals for the determination of total, EDTA-extractable and Ca(NO<sub>3</sub>)<sub>2</sub>-extractable soil metal concentrations. Soil solution samples were also taken using rhizon soil moisture samplers and analysed for metals, pH, major cations (Ca, Mg, K, Na) and anions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>), and dissolved organic carbon (DOC).

### 2.3 Experiment 2

At the end of Experiment 1, the replicate samples from each plot were combined, air-dried, and mixed thoroughly. Sub-samples (200 g) of these soils were then incubated with or without the addition of hydrated lime until the soil pH of the limed samples had stabilized. The soils were then used for a simple germination and seedling growth bioassay. The soils were placed in containers and moistened to 50% of the soil water holding capacity (SWHC) and then planted with 20 viable wheat seeds. The containers were placed in a constant environment room and seed germination after 5 days was recorded. The seedlings were then thinned to 10 per container and the plants grown for a further 15 days before harvesting. The seedlings were cut at soil level, dried in an oven, and the dry matter yields recorded. Concentrations of Cu, Ni and Zn in the plants were then determined.

Following harvesting of the seedlings, the soils were used to determine effective soil solution metal concentrations by the technique of diffusive gradients in thin films (DGT) (Zhang et al., 2001). Soil solutions were also extracted using rhizon soil moisture samplers and analysed for various constituents as described for Experiment 1.

### 2.4 Soil and soil solution analysis

Total metal concentrations in soil were determined using the acid digestion technique of Kovács et al., and EDTA-extractable metals were determined using the method of McLaren et al. (1984). Calcium nitrate-extractable metals were determined as described by McLaren et al. (2007). Metal concentrations in digests, extracts and soil solutions were determined by flame or graphite furnace atomic absorption spectrophotometry (FAAS or

GFAAS). Major cations in soil solutions were determined by FAAS and major anions by ion exchange chromatography. DOC was determined using a Shimadzu TOC 5000A analyser. Speciation of metals in soil solution was carried out using the WHAM 6 computer program (Tipping, 1998)

## 2.5 Plant analysis

Metal (Cu, Ni and Zn) concentrations in dried plant samples were determined by acid ( $\text{HNO}_3$ ) digestion followed by FAAS or GFAAS.

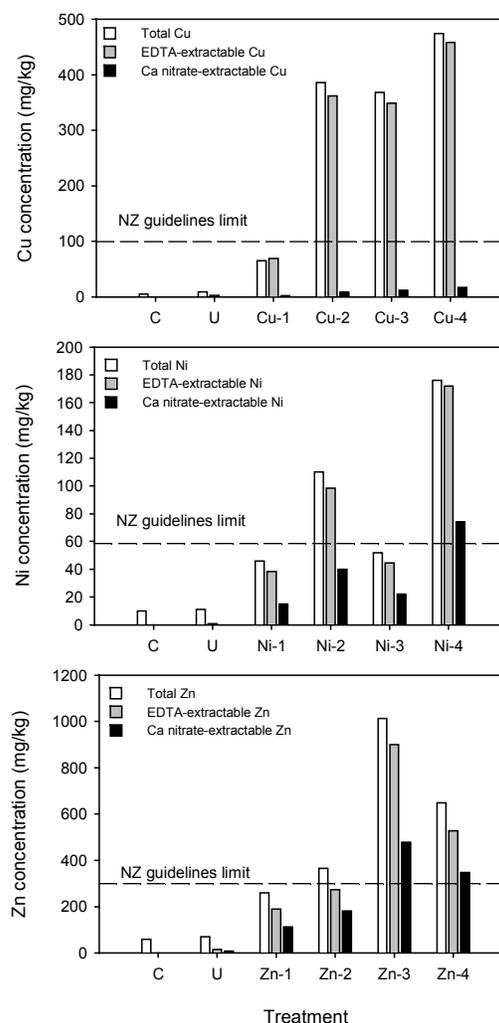
## 2.6 Effective soil solution metal concentrations

The new concept of “effective concentration”,  $C_E$  was introduced by Zhang et al, (2001) and includes both the soil solution concentration and an additional term, expressed as a concentration, which represents metal supplied from the soil solid phase.  $C_E$  was measured using DGT which, like a plant, locally lowers soil solution metal concentrations, inducing metal supply from the soil solid phase. In this study, following completion of the plant growth bioassay, the moisture content of the soil samples was raised to 80% of SWHC and, after a 24 h equilibration period, DGT devices were deployed on the soil surface. The devices were left in position for a further 24 h before removal, and analysis of the metals retained by the device.  $C_E$  was calculated from the resulting data as described by Zhang et al. (2001).

## 3. Results and Discussion

Initial analysis of the mixed litter/mineral soil samples showed extremely high Cu, Ni or Zn concentrations in the samples from plots that had originally received biosolids spiked with these metals (Figure 1). In the case of Cu and Zn, the three highest metal treatments were all above the current New Zealand guidelines for soils amended with biosolids (New Zealand Water and Wastes Association (2003). For Ni, only the Ni-2 and Ni-4 treatments were above the limit. The data in Figure 1 also shows that substantial proportions of the three metals were present in EDTA-extractable forms, and in the case of Ni, high concentrations

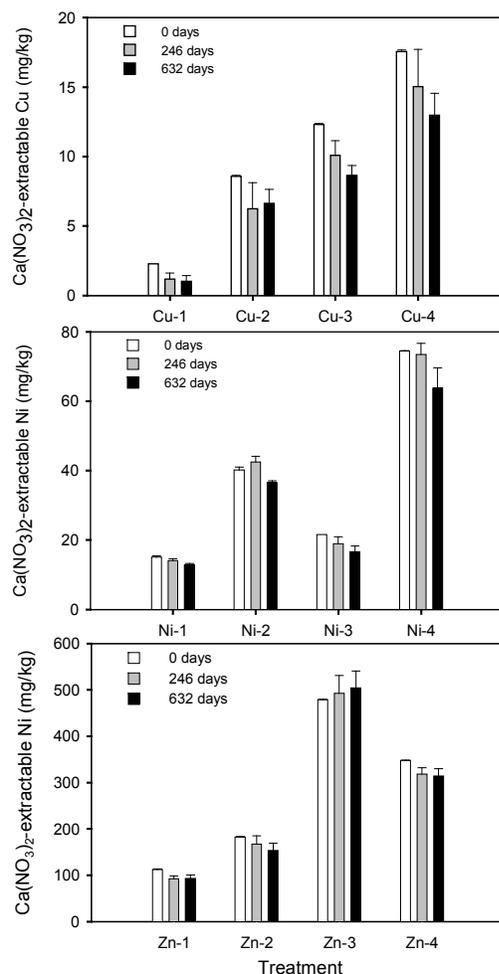
were also present in readily soluble forms extracted with  $\text{Ca}(\text{NO}_3)_2$ .



**Figure 1. Initial metal concentrations in mixed litter/mineral soil samples**

### 3.1 Experiment 1

During incubation of the samples over a period of nearly two years there was very little change in the solubility of Ni or Zn as determined by extraction with EDTA or  $\text{Ca}(\text{NO}_3)_2$  (Figures 2 and 3). Thus there appeared to be very little evidence of natural attenuation of solubility for these metals in this soil. However, there were some decreases in both EDTA-extractability and  $\text{Ca}(\text{NO}_3)_2$ -extractability of Cu with incubation period. Nevertheless, even after 632 days of incubation, extractable Cu concentrations in soils from the Cu-spiked biosolids plots were still considerably higher than those observed in the control and unspiked biosolids plots at the start of the experiment (Figure 1).

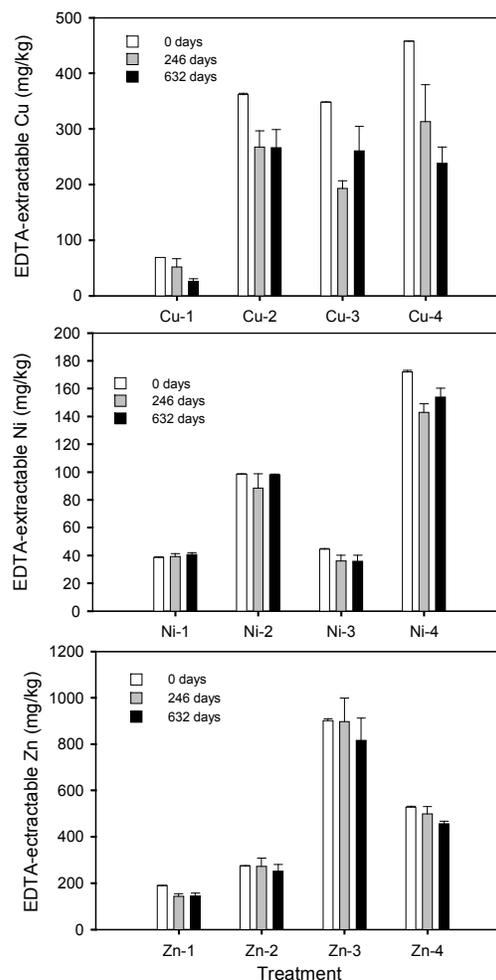


**Figure 2. Effect of incubation period on  $\text{Ca}(\text{NO}_3)_2$ -extractable metal concentrations**

The increasing concentrations of extractable metals with increasing level of metal spiking were also reflected in the metal concentrations observed in the soil solution at the end of the incubation period. Concentrations of Cu, Ni and Zn were all enhanced significantly by the original biosolids treatments (Tables 2, 3 and 4). In the case of Cu, concentrations increased from 0.003 mg/L in the control to 1.37 mg/L in the highest Cu treatment (Cu-4). For Ni, concentrations increased from 0.02 to 14.21 mg/L, and for Zn, from 0.25 to 116.9 mg/L.

**Table 2. Concentrations and speciation of Cu in soil solutions**

Plot	Cu (mg/L)	Cu speciation (%)			
		$\text{Cu}^{2+}$	$\text{CuSO}_4^0$	$\text{CuCl}^+$	Cu-org
C	0.003	0.7	0.0	0.0	99.3
U	0.07	4.7	0.1	0.0	95.2
Cu-1	0.17	10.6	0.1	0.1	89.2
Cu-2	0.67	19.4	0.5	0.0	80.0
Cu-3	0.77	38.5	0.7	0.1	60.8
Cu-4	1.37	39.4	0.8	0.1	59.7



**Figure 3. Effect of incubation period on EDTA-extractable metal concentrations**

**Table 3. Concentrations and speciation of Ni in soil solutions**

Plot	Ni (mg/L)	Ni speciation (%)			
		$\text{Ni}^{2+}$	$\text{NiSO}_4^0$	$\text{NiCl}^+$	Ni-org
C	0.02	93.1	0.3	0.4	6.1
U	0.05	94.6	1.3	0.5	3.6
Ni-1	2.31	95.1	1.6	0.3	3.0
Ni-2	8.12	95.2	2.0	0.2	2.6
Ni-3	3.53	94.4	0.9	1.0	3.7
Ni-4	14.21	94.1	2.5	0.3	3.0

**Table 4. Concentrations and speciation of Zn in soil solutions**

Plot	Zn (mg/L)	Zn speciation (%)			
		$\text{Zn}^{2+}$	$\text{ZnSO}_4^0$	$\text{ZnCl}^+$	Zn-org
C	0.25	92.5	0.4	0.4	6.7
U	3.05	93.3	1.4	0.5	4.8
Zn-1	31.00	94.1	2.3	0.4	3.2
Zn-2	47.80	88.8	3.2	1.5	6.5
Zn-3	155.10	93.1	3.5	0.3	3.1
Zn-4	116.90	93.1	3.6	0.7	2.6

Speciation of soil solution metals revealed that Ni and Zn were present predominantly (> 90%) as simple divalent ions,  $\text{Ni}^{2+}$  and

Zn<sup>2+</sup>, with generally less than 5% in the form of organic complexes, and even smaller proportions as complexes with sulphate or chloride (Tables 3 and 4). In contrast, Cu was present predominantly complexed with soluble organic matter (fulvic acids). In the control sample, more than 99% of the soil solution Cu was organically complexed, whereas this fell to approximately 60% in the Cu-3 and Cu-4 samples. The bulk of the Cu not complexed with organic matter was present at the Cu<sup>2+</sup> ion (Table 2).

### 3.2 Experiment 2

Conversion of forest soils to pasture is usually accompanied by liming to raise soil pH. Experiment 2 was undertaken to examine (a) the effect of liming on metal solubility in the soils and (b) any adverse effects on plant growth due to the high levels of soluble metals.

The unlimed soils had a mean pH of 4.66 ± 0.031. Liming increased the pH of the samples by approximately 1 pH unit to 5.61 ± 0.07.

The addition of lime had substantial effects on the concentrations of metals extracted by Ca(NO<sub>3</sub>)<sub>2</sub> (Table 5) and the concentrations of metals in the soil solution (Table 6). Copper, Ni and Zn solubilities as assessed by these methods were all decreased markedly by the addition of lime.

**Table 5. Effect of lime addition on Ca(NO<sub>3</sub>)<sub>2</sub>-extractable metals (mg/kg)**

Plot	No lime	+ lime
<b>Copper</b>		
Cu-1	0.6	0.3
Cu-2	4.4	1.0
Cu-3	7.7	0.8
Cu-4	11.4	1.4
<b>Nickel</b>		
Ni-1	13.0	4.1
Ni-2	34.5	10.2
Ni-3	15.1	2.6
Ni-4	59.3	23.7
<b>Zinc</b>		
Zn-1	75.5	19.1
Zn-2	114.0	23.2
Zn-3	387.0	146.4
Zn-4	232.8	90.6

**Table 6. Effect of lime addition on soil solution metal concentrations (mg/L)**

Plot	No lime	+ lime
<b>Copper</b>		
Cu-1	0.05	0.06
Cu-2	0.18	0.20
Cu-3	0.35	0.18
Cu-4	0.39	0.31
<b>Nickel</b>		
Ni-1	1.05	0.20
Ni-2	2.87	0.51
Ni-3	0.43	0.11
Ni-4	4.13	1.44
<b>Zinc</b>		
Zn-1	4.05	0.71
Zn-2	11.76	0.69
Zn-3	58.30	8.34
Zn-4	45.10	2.05

**Table 7. Effect of lime addition on metal speciation in soil solution (% metal present as M<sup>2+</sup>)**

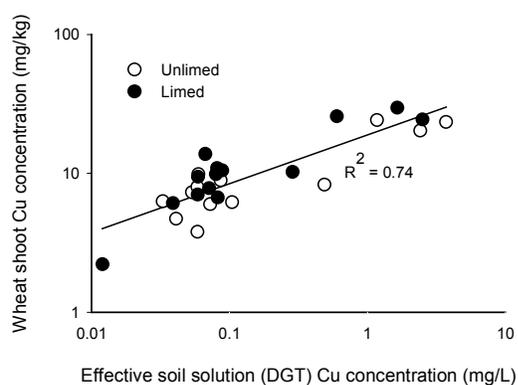
Plot	No lime	+ lime
<b>Copper</b>		
Cu-1	7.7	0.2
Cu-2	35.8	-
Cu-3	67.5	1.5
Cu-4	75.9	0.9
<b>Nickel</b>		
Ni-1	92.8	87.8
Ni-2	92.4	79.2
Ni-3	86.7	51.0
Ni-4	91.2	89.5
<b>Zinc</b>		
Zn-1	83.2	59.1
Zn-2	81.3	42.6
Zn-3	91.5	73.3
Zn-4	91.1	43.8

In addition, the addition of lime had substantial effects on metal speciation in the soil solution. Addition of lime resulted in large decreases in the proportions of Cu, Ni and Zn present in solution as simple divalent ions (Table 7). The decreases in the proportions of metals present as simple ions were matched by increases the proportions bound by dissolved organic matter (fulvic acids)

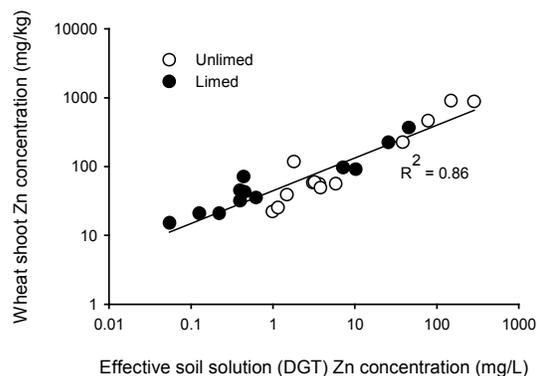
Although the Cu, Ni and Zn concentrations were very high in some of the soils used in this study there were no adverse effects on plant growth as assessed by the wheat seedling bioassay. The addition of lime also had no effect on plant growth. However concentrations of Cu, Ni and Zn in the

plants did generally increase with increasing concentration of metals in the soil. Wheat shoot Cu concentrations increased from 2.3 mg/kg in the unlimed control to over 20 mg/kg in the Cu-4 treatments. There was little difference in Cu concentrations between the corresponding limed and unlimed treatments. For Ni, wheat shoot concentrations increased from less than 1 mg/kg in the unlimed control to 22 mg/kg in the unlimed Ni-4 treatment. Nickel concentrations in plants from the limed treatments were generally lower than for the equivalent unlimed treatments (e.g., 6 mg/kg for the limed Ni-4 treatment). The largest increases in shoot metal concentrations were observed for Zn. Concentrations increased from 13 mg/kg in for unlimed control to just less than 900 mg/kg for the unlimed Zn-4 treatment. As for Ni, liming had a major effect on shoot Zn concentrations. For example, the Zn concentration for the limed Zn-4 treatment was only 224 mg/kg.

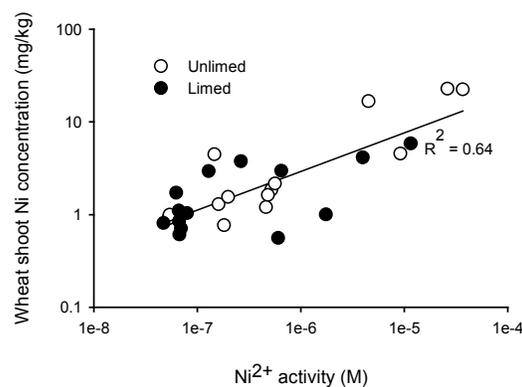
Various methods were examined for predicting plant metal concentrations, including total, EDTA-extractable and Ca(NO<sub>3</sub>)-extractable soil metal concentrations, soil solution metal concentrations and free ion activities (as predicted by WHAM 6), and effective soil solution metal concentrations as determined by DGT. With a few exceptions, all methods gave reasonable predictions of the metal concentrations in wheat shoots. However, the some of the best predictions were obtained with effective soil solution metal concentrations (Figures 4 and 5) or free ion activity (Figure 6).



**Figure 5. Relationship between Cu concentration in wheat shoots and effective soil solution Cu concentration**



**Figure 6. Relationship between Zn concentration in wheat shoots and effective soil solution Zn concentration**



**Figure 7. Relationship between Ni concentrations in wheat shoots and free Ni<sup>2+</sup> ion activity**

#### 4. Conclusions

In spite of the fact that the metal-spiked biosolids were applied to the forest soil six years prior to collection of the mixed litter/mineral soil used in this study, there were still substantial concentrations of Cu, Ni and Zn present in readily extractable and soluble forms. In the case of Ni and Zn in particular, such high concentrations of Ni<sup>2+</sup> and Zn<sup>2+</sup> in the soil solution might be expected to have adverse effects on plant growth and/or food chain implications. However, under the conditions of the bioassay used in this study no adverse effects on plant growth were observed. Nevertheless, plant Ni and Zn concentrations were increased well above those concentrations normally found in plants. Metal solubility in the soils was substantially reduced by liming, with associated reductions in Ni and Zn uptake by plants. Thus liming is clearly an

important management option when converting former biosolids-amended soils for agricultural purposes. In assessing potential problems associated with such conversions, the DGT technique shows considerable promise for assessing metal availability to plants.

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