

# Changes in Cd bioavailability in metal spiked soils amended with biosolids: results from a wheat seedling bioassay

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## Abstract

Three contrasting soils were collected from the Canterbury region in New Zealand and treated with a one-off application of Cd (1, 5 and 10 mg/kg applied as sulphate), in the presence and absence of biosolids applied at a rate equivalent to 400 kg N/ha. Soils were then incubated for two weeks and 24 weeks at a constant temperature of  $25 \pm 2$  °C in the absence of light. A seedling bioassay, using wheat (*Triticum aestivum*) was undertaken to assess changes in plant Cd concentrations and soil solution Cd chemistry during incubation. Six measurements of Cd availability were also employed to determine which test yielded the strongest correlation with plant Cd concentrations. Overall, Cd concentrations in shoots were significantly reduced on average by 30% in plants grown in Cd spiked soils amended with biosolids compared to unamended soils, even though no significant changes were detected in measures of Cd solubility. Of the six methods examined,  $\text{Ca}(\text{NO}_3)_2$  extraction yielded the strongest correlation with plant Cd, and a comparison between relationships determined for biosolids amended and unamended soils revealed no significant difference ( $p = 0.625$ ). Consequently, this result provides evidence that Cd bioavailability as measured by  $\text{Ca}(\text{NO}_3)_2$  is not altered in the presence of biosolids.

## Key Words

Plant uptake, Cd availability, soil amendments.

## Introduction

In New Zealand, biosolids are applied to land as an alternative means of waste disposal providing many benefits including increased soil fertility and productivity. Additionally, biosolids have been applied to metal-contaminated soils to assist in metal sequestration, rendering the metals less available to plants and other soil biota. For plants and soil biota, metal availability is controlled by numerous biogeochemical processes. These processes are strongly influenced by soil properties such as amounts of organic matter present, soil pH, clay and oxide content. For many soil biota the bioavailability of a metal depends on the concentration and chemical form (species) in the soil solution, particularly simple metal ion concentrations, (e.g.  $\text{Cd}^{2+}$ ). To be able to accurately assess metal bioavailability has been the focus of much research, although few studies have compared metal bioavailability across soils in presence and absence of biosolids amendments. This study attempts to compare the effects of soil amendments, such as biosolids has on the validity of potential measures of Cd bioavailability, using contrasting soil types spiked with increasing amounts of Cd salts.

## Methods

Three contrasting soils were collected from the Canterbury region in New Zealand and then treated with a one-off application of Cd (1, 5 and 10 mg/kg, applied as sulphate), in the presence and absence of biosolids applied at a rate equivalent to 400 kg N/ha. These treated samples were wetted to field capacity and then incubated for two weeks and 24 weeks at a constant temperature of  $25 \pm 2$  °C in the absence of light. A seedling bioassay, using bread wheat (*Triticum aestivum*) was undertaken to assess changes in plant Cd concentrations and soil solution Cd chemistry during the 24 weeks of incubation. Six measures of Cd solubility, total-Cd, EDTA and  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd, soil solution Cd, effective solution concentration (DGT-DIFS) and  $\text{Cd}^{2+}$  activity modelled using WHAM 6.0., were compared with plant Cd concentrations to determine which method gave the best predictive measure of Cd bioavailability. A linear regression with grouped data was also performed to determine the effects of biosolids amendment on the validity of these potential measures of bioavailability.

## Results and discussion

Comparisons between biosolids amended and unamended metal spiked soils revealed significant increases in concentrations of dissolved organic carbon (DOC), soil solution salinity, and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in soil solution as a result of the addition of biosolids, irrespective of metal treatment concentrations (Table 1). Overall, the increased length of soil incubation time resulted in a significant decrease in soil and soil solution pH, as well as an increase in salinity levels of the soil solution after 24 weeks (Table 1).

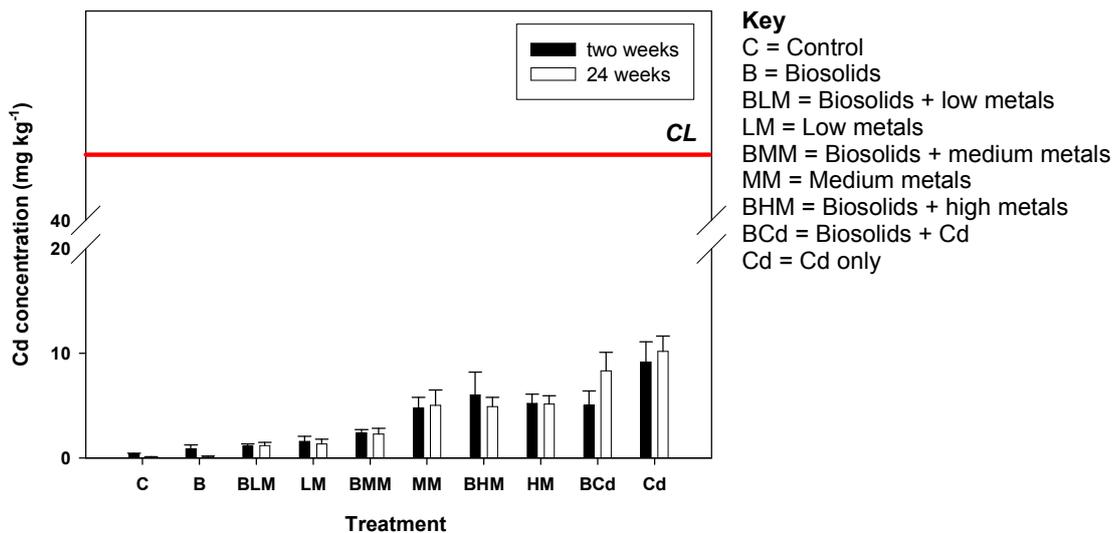
The presence of biosolids had no significant effect on total, EDTA,  $\text{Ca}(\text{NO}_3)_2$  extractable Cd or soil solution Cd, effective concentration of Cd, or  $\text{Cd}^{2+}$  activity (Table 2). In contrast, the longer soil incubation time of 24 weeks resulted in significant increases in the availability of Cd compared to an incubation period of two weeks (Table 2). These results showed that amending soils with biosolids did not affect the solubility of Cd, soil incubation time however, significantly increased the solubility of Cd.

**Table 1. Significance levels for comparisons of general soil parameters between biosolids amended and unamended metal spiked soils (n = 180), and between all treated soils sampled after two weeks and 24 weeks of incubation. Differences were considered significant at  $P < 0.05$  and significant differences are highlighted in bold in the table below.**

<i>Soil variable</i>	<b>Biosolids amended vs unamended Cd spiked soils</b>	<i>2 weeks vs 24 weeks incubation</i>
Soil pH	0.768	<b>&lt; 0.001</b>
Soil solution pH	0.196	<b>0.009</b>
DOC (mg/L)	<b>0.001</b>	0.24
Salinity of soil solution ( $\Sigma\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{Na}^+$ ) (mg/L)	<b>0.002</b>	<b>&lt; 0.001</b>
Soil solution Ca concentration (mg/L)	<b>0.027</b>	0.65
Soil solution Mg concentration (mg/L)	<b>0.001</b>	0.35

**Table 2. Significance values for comparisons of six potential measures of Cd bioavailability between biosolids amended and unamended metal spiked soils (log transformed data, n = 180). Differences were considered significant at  $P < 0.05$  and highlighted in bold in the table below.**

<i>Method</i>	<b>Biosolids amended vs unamended Cd spiked soils</b>	<i>2 weeks vs 24 weeks incubation</i>
Total metal	0.090	*
EDTA	0.190	0.98
$\text{Ca}(\text{NO}_3)_2$	0.760	0.28
Soil solution	0.320	<b>0.002</b>
DGT	0.320	<b>&lt; 0.001</b>
Free ion activity	0.320	<b>0.001</b>

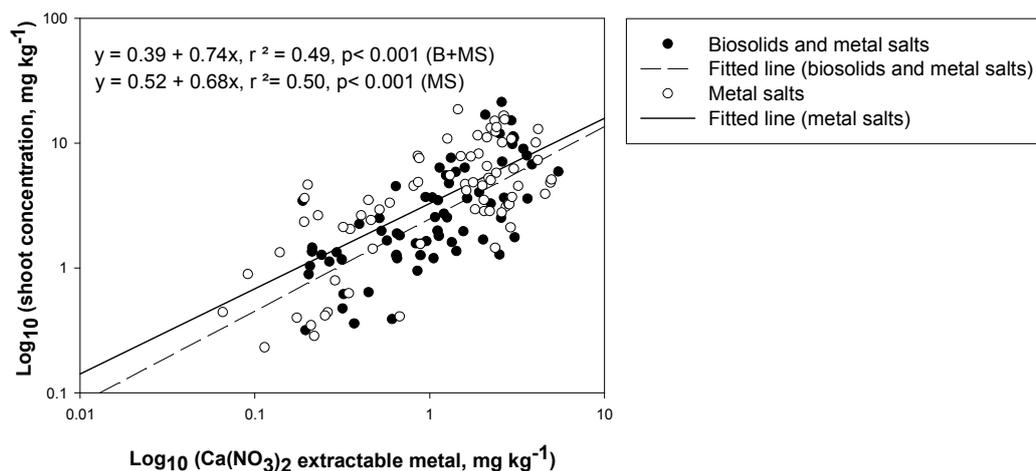


**Figure 1. Mean Cd concentrations in wheat shoot tissue (mg/kg dry weight) grown in biosolids amended and unamended metal spiked soils incubated for two weeks and 24 weeks. The critical level (CL) for Cd as depicted by the red line is 43 mg/kg. Bars denote the SEM, n = 89 for both trials.**

Comparisons of shoot Cd concentrations in plants grown in biosolids amended metal spiked soils with unamended metal spiked soils revealed a significant decrease in shoot concentrations in plants grown in biosolids amended soils compared to unamended soils for both soil incubation times ( $p = 0.003$  and  $p = 0.042$  for two and 24 weeks respectively). Additionally, this significant decrease ( $p < 0.001$ ) in shoot concentration in the presence of biosolids was observed across all levels of Cd soil concentrations (Figure 1), furthermore, a linear regression analysis of the grouped data revealed that for Cd, the addition of biosolids significantly reduced shoot concentration on average by 32% ( $p = 0.023$ ).

Calcium nitrate extractable Cd yielded the strongest correlation of the six bioavailability estimates ( $r^2 = 0.63$  for pooled soil and wheat data), while soil solution Cd yielded the poorest correlation ( $r^2 = 0.30$ ). There was no significance difference in relationships determined between available Cd and shoot Cd concentrations in the presence or absence of biosolids (Figure 2). Consequently this result provides evidence that Cd bioavailability as measured by  $\text{Ca}(\text{NO}_3)_2$  is not dependent on the presence or absence of biosolids and is a robust measure of bioavailability.

While the findings in this study appear to support the retention of Cd in biosolids amended soils, limitations in the experimental set-up and analyses make it difficult to accurately attribute the mechanism(s) by which Cd retention is occurring. Studies on the availability and uptake of Cd in plants have identified pH and DOC as the major influential factors controlling soil availability (McLaughlin *et al.* 2006; Collins *et al.* 2003; Gray 1999). However, pH did not significantly change with the addition of biosolids, and therefore can not be directly attributed to the reduction in Cd shoots concentrations in this study. From these results two possible mechanisms may be responsible for this effect: (1) DOC sourced from biosolids that is reducing the availability of Cd in soil solution to the plants via complexation of free  $\text{Cd}^{2+}$  and weakly sorbed Cd and, (2) addition of contaminants and salts in biosolids (i.e.  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ) which competitively inhibit the uptake of Cd by plants.



**Figure 2.** Effect of biosolids amendment on the relationship between shoot Cd concentration and Cd bioavailability as estimated by  $\text{Ca}(\text{NO}_3)_2$  extraction,  $n = 71$  (Biosolids + Cd salts) and  $n = 72$  (Cd salts).

## Conclusions

While, the addition of biosolids did not alter the solubility of these metals, soil incubation time did significantly increase the availability of Cd, which may be attributed to the decrease in soil and soil solution pH that was also observed. Overall, Cd concentrations in shoots were significantly reduced in plants grown in metal spiked soils amended with biosolids compared to unamended metal spiked soils. However, no strong relationship between measured soil variables (pH, DOC), and Cd concentrations in shoots were obtained. Statistical analyses also revealed that Cd bioavailability as measured by  $\text{Ca}(\text{NO}_3)_2$  is not dependent on the presence or absence of biosolids and is a robust measure of bioavailability.

## References

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