# Biosolids-Derived Trace Metals in Soils and their Potential Bioavailability in New Zealand Pasture Soils

Susquehanna

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# Introduction

New Zealand has an international reputation as a leader in environmental awareness and its people strive to preserve that reputation by numerous commitments toward a sustainable society. The Ministry for the Environment (MfE) has set goals to reducing the percentage of sewage sludge that is landfilled by 95% from 320 publicly owned wastewater treatment plants from 2002-2007 (MfE, 2007). Beneficial use of biosolids as a soil amendment and source of plant nutrients is seen as an important step toward meeting this goal. Several challenges exist however. First, there is little cropland in the country where annual crops could easily accept biosolids applications where it could be incorporated to minimize nuisance and off-site impacts. Second, there is strong social resistance to allowing human wastes to come in contact with plants destined for human consumption. Finally, the Soils of New Zealand vary in their soil mineralogy and parent material over relatively short distances, and include materials. derived from very old sedimentary rocks, metamorphic rocks, and relatively recent volcanic materials. The variability of soil mineralogy makes it difficult to generalize a nation-wide policy for using this material appropriately.

As with all biosolids, the value of land application arises from the availability of nitrogen and phosphorous to plants, as well as the carbon that can build beneficial soil physical properties. Similarly, municipally-derived biosolids contain small amounts of trace elements, some of which can be toxic, so that when applications are made over a long period, metals can build up high concentrations in soil, become available to plants, and affect plant health or quality. Given the challenges stated above, receiving soils are often under tree plantations or in pasture, as much of New Zealand's agriculture is dominated by wool and mutton production and dairy products.

To help build a nationally relevant policy for the country, a multi-year evaluation was proposed that would examine the accumulation of trace metals on a range of potential pasture soils from around the country using a variety of municipally-derived biosolid materials. Bioavalibility of metals, impacts of biosolids on soil fertility and plant chemistry are also being evaluated. The objective of this paper is to report the trace element accumulation and bioavailability after the first five years of the study.

# **Experimental Method**

Soil monoliths were excavated from five soils that represent typical pasture lands around New Zealand and sealed in free draining lysimeters for this study (see Fig. 1) (Cameron et al, 1992). Biosolids that deliver 200 kg/ha N were incorporated each spring ryegrass was planted. At the end of five years, a subsample from each lysimeter was removed for a trace metal bioassay with wheat plants (see Fig 2).





Figure 1. Lysimeters growing ryegrass following biosolids treatment at Lincoln University. Figure 2. Soils removed from the lysimeters were used in a trace metal bioassay. Wheat seeds were planted and grown for 21 days.

Treatments consisted of biosolids to deliver 200 kg/ha N from Christchurch treatment works, (CCB), New Plymouth (pelletized, NPP), and a mix of green waste compost and biosolids from Wellington (Living Earth Compost, LEC). An 800 kg/ha N from Christchurch, as well as a control was used. Metal loads are shown in Table 1. Metals concentration were determined as "total" (31 HNO<sub>2</sub>-HCl), 0.04 M diethylentriaminepentaacetic acid (PDTA) and 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> extracts to assess recalcitrant and readily available concentrations. Trace metals were determined by ICP-OES.

A bioassay for trace metals was completed by growing wheat seeds from germination to 21 days and measuring plant shoot concentrations. Plant shoots were digested in hot, concentrated nitric acid. A diffusive gradients using thin films (DGT) technique was used to evaluate the availability of metals to plants from both soluble and potentially soluble pools. DGT was applied for 24 hours.

Five soils were used: Templeton fine sandy loam, Ashley Dene deep fine sandy loam, Foxton black sand, Egmont black loam, and Waihou silt loam.



Figure 3. Copper and zinc concentration in calcium nitrate extracts, soil solution, and wheat tissues after five annual application of biosolids. Error bars are S.E, and different letters indicated differences at p=0.05.

# Results

### **Macronutrients**

Following five annual application of biosolids to deliver 200 kg ha<sup>-1</sup> yr<sup>-1</sup> N, only 3 of the five soils had increases of total S in the soil, total Al, Ca, Mg, Na, P and Fe did not significantly increase. Biosolids applied at 800 kg ha<sup>-1</sup> N increased total soil S and P on all soils.

#### **Trace Elements in Soils and Plants**

Wheat grown from seed for 21 days in soils from the lysimeters had no statistical differences in germination or biomass, and had no visible symptoms of stress from the trace elements in soils. Plant concentrations remain within normal ranges.

- · Arsenic loads were very small and soil and plant concentrations were generally unaffected.
- Total cadmium did not increase except at the high application rate. However, several soils showed increased plant Cd concentrations from CCB and NPP. Increased Cd in soil solution, calcium nitrate, and DPTA extracts matched quite well with these instances. LEC, biosolids mixed with green-waste, reduced Cd concentration in calcium nitrate extracts.
- Chromium loads where larger from Christchurch than from other plants, and only this material
  produced increases in total Cr, DPTA and calcium nitrate extractable Cr. Although soil
  concentrations increased, Cr is immobile and did not increase in soil solution or in plant tissues.
   Cooper increased in total and extractable determinations for all soils and biosolid materials.
- Copper increased in total and extractable determinations for all soils and biosolid materia Plant Cu also increased on nearly all soil and treatment combinations (See Fig. 3).
- Nickel loads were small, but significant increase on most soils and treatments were observed in the total and extractable Ni, including soluble Ni in soil solution. Very small plant concentrations and high variability meant that very few treatments or soils were responsive to Ni in plant tissues.
- Lead increased in total and DPTA extractable fractions, but because of its general insolubility, only a few of the soils and treatment combination produced increased tissue lead concentrations, and only at the highest application rate (4xCCB).
- Zinc loads produced significantly higher total Zn and DPTA and calcium nitrate extractable concentrations. Despite rare increases in soil solution Zn, increased plant concentrations were observed for many treatments, notably CCB, and all high application rates (4xCCB)(See Fig. 3).

#### Table 1: Cumulative trace metal load following five years of biosolids applications

	N kg ha <sup>-1</sup>	C Mg ha <sup>.1</sup>	P kg ha <sup>.1</sup>	K kg ha <sup>.1</sup>	As g ha¹¹	Cd g ha <sup>.1</sup>	Cr g ha <sup>.1</sup>	Cu kg ha <sup>.1</sup>	Ni g ha <sup>.1</sup>	Pb g ha <sup>.1</sup>	Zn kg ha	
LEC	1000	17.9	307	253	409.4	57.1	3.3	10.1	500	2737	13.4	
NPP	1000	5.9	313	53	33.3	21.6	1.8	2.8	572	383	9.5	
CCB	1000	7.6	297	31	217.1	45.9	16	6.4	650	1621	24.6	
4xCCB	4000	30.2	1189	125	868.3	183.8	63.9	25.8	2600	6482	98.5	

#### **Diffusive Gradients in Thin Films**

DGT has been used to monitor metals and P concentrations in soils and sediments where the element is generally insoluble but as the soluble pool is depleted, dissolution from solid phases are expected to replenish the soluble fraction. The measured "effective concentration" (C\_E) is a function of both the soluble concentration and the re-supply from quickly soluble fractions. We believe the technique may be a useful proxy for plant uptake for metals concentrations below plant toxicity thresholds, such as soils treated with biosolids.



Figure 4. Effective Concentration (C\_E) from DGT measurements serves as an effective proxy for plant uptake of metals. Cu and Zn worked well because of a relatively wide range of plant concentrations. Cd, Cr, Ni, and Pb were not effectively predicted, in part because fissue concentrations had quite a narrow range of concentration.

## Predicting Trace Metal Bioavailability in Wheat

Total metal, extractable metals, soil solution concentration, soil pH, solution pH and C\_E were evaluated for their ability to predict plant concentrations in this experiment. We used  $R^2$  as the statistical mesare.

- Plant concentrations of Cd were small. The best predictor for plant concentration of Cd was soil pH
- · Cr in plants was best predicted by soil solution Cr
- The best predictor of plant Cu was soil solution, followed closely by DGT and calcium nitrate extracts (see Fig. 4)
- · Plant Ni was best predicted by soil solution
- Pb levels were too low in plants to evaluate effectively
- · Plant Zn was well predicted by calcium nitrate extracts and DGT (see Fig. 4).

On these soils from New Zealand, we found that total concentrations and DPTA extracts performed poorly compared to simple dilute salt extracts (calcium nitrate), soil solution concentrations, and DGT C\_E for predicting plant uptake of trace metals. DGT appears to be an effective proxy for metal bioavailability on New Zealand soils.

## Conclusions

After five years of consecutive biosolids applications from three New Zealand municipal areas, total soil and DPTA extractable Cu, Cr, Ni, and Zn increased in some soils, however these techniques were poor predictors of plant bioavailability. Most soils and biosolids treatment produced increased calcium nitrate extractable concentrations of Cd, Cr, Cu, Ni, and Zn, and this extraction performed well predicting most tissue responses. At high application rates, concentrations of Cu and Zn in plant tissues has doubled compared to control concentrations, and is approaching concentrations that generally produce phytotoxicity. For New Zealand, multiple sites will need to be selected to manage biosolids on a relatively short window to meet national goals for waste disposal without compromising soil productivity.

## References

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