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

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Outline

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- Methods
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  - Treatments
  - Plant analysis and DGT-DIFS
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Research Aims

- To extensively test the effectiveness of the Diffusive gradient in thinfilms (DGT) technique in estimating plant bioavailability across a range of soil types.

- To measure the longer term changes in metal bioavailability in soils treated with biosolids and metal salts.
Background – Biosolids use

• Advantages
  – Good source of nitrogen and phosphate – improves soil fertility
  – Alternative means of waste disposal

• Disadvantages
  – Public health (pathogens) and cultural concerns
  – Environmental concerns
    • Metals, organic contaminants
Background – metal bioavailability

- Total concentrations not good indicators of bioavailability in contaminated soils

- Soil properties and processes (e.g. CEC, pH, org matter) affect bioavailability

- Plant bioavailability largely a measure of solubility (e.g. chemical extraction methods)
Soil locality

Halkett soil: Sandy loam, sourced from West Melton area

Summit Soil: Silt loam (basalt and loess), sourced from Port Hills area

Wakanui Soil: Silt loam, sourced from Lincoln University area
## Treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cd added (mg/kg)</th>
<th>Cu added (mg/kg)</th>
<th>Ni added (mg/kg)</th>
<th>Zn added (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Biosolids*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Biosolids* and low metals</td>
<td>1</td>
<td>30</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>Low metals</td>
<td>1</td>
<td>30</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>Medium</td>
<td>5</td>
<td>200</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>High metals</td>
<td>10</td>
<td>750</td>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>Cd only</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Biosolids were added at a rate of 400 kg N/ha/yr

-Cd and Ni levels were chosen based on current biosolids guidelines

-Cu and Zn levels were chosen based on work to date by ESR and Lincoln University

-each treatment had three replicates per soil
Field Lysimeter Trials, Lincoln University

Lysimeter trench

November, 2006

Cd-only treatment, Wakanui soil

April, 2007

Medium metal treatment, Summit soil
Methods

• Ryegrass harvested at 6-monthly intervals is analysed for total Cd, Cu, Ni and Zn
• Soil sub-samples from the lysimeters are taken immediately after harvest
• Soils are analysed using the in DGT method
• Total soil concentration, EDTA, CaNO$_3$ and soil solution extraction are also carried out
DGT

- DGT device consists of a backing plate, cation resin gel and a polyacrylamide diffusive gel with a membrane filter and cap to hold layers in place
- DGT mimics the response of a plant root – removes metals from soil solution - induces resupply from the solid phase
Calculating effective concentration, $C_E$

- Effective concentration, $C_E$, is the theoretical soil solution concentration that includes the resupply rate of metals from the solid phase to solution phase ($R_{\text{diff}}$)
- Metals accumulated on the resin gel = $f$ area exposed, pore size, thickness of diffusive gel and temperature ($C_{\text{DGT}}$)
- The DIFS (DGT induced fluxes in sediments) model calculates $R_{\text{diff}}$ (resupply rate) from physical properties of the soil (e.g. soil porosity and tortuosity)
Cadmium concentrations in ryegrass

- Cd 6-months
- Cd 12-months

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals

Cadmium tissue Cd concentrations (mg/kg)

Treatments

Halkett soil
Summit soil
Wakanui soil

C          B          BLM      LM      MM      HM      Cd-only

Treatments

Halkett soil
Summit soil
Wakanui soil

Cadmium tissue Cd concentrations (mg/kg)

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals
Copper concentrations in ryegrass

- Cu 6-months
- Cu 12-months

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals

Copper tissue Cu concentrations (mg/kg)

Halkett soil
Summit soil
Wakanui soil

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals
Nickel concentrations in ryegrass

- Ni 6-months

- Ni 12-months

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals
Metal concentrations in ryegrass

- Zn 6-months
- Zn 12-months

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals

C = control; B = biosolids; BLM = biosolids + low metals; LM = low metals; MM = medium metals; HM = high metals
Changes in plant uptake

- Absence in plant growth on the MM and HM treatments at 6 and 12 months as a result of metal toxicity
- Cd, Ni and Zn levels increase as treatment concentrations increase – these metals are more available than Cu
- Cd and Zn levels not considered phytotoxic
- The addition of biosolids to the LM had some effect on the availability of Cd, Cu, Ni and Zn
- Cd and Zn levels drop between 6 and 12 months – metals becoming less available
- Control on Cd and Zn availability different from Cu and Ni
- Soils responded differently to treatments – MM and HM treatments growth poor and uneven
- Changes were also detected in soil solution pH and dissolved organic carbon
Cd and Cu DGT-DIFS results

Plots include all soil data from the 6 and 12 month harvests
Ni and Zn DGT-DIFS results

Plots include all soil data from the 6 and 12 month harvests
DGT-DIFS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Equation of the line</th>
<th>$r^2$</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>$Y = 0.58 + 0.32(x)$</td>
<td>0.19</td>
<td>$&lt;0.0001$</td>
</tr>
<tr>
<td>Cu</td>
<td>$Y = 5.6 + 0.69(x)$</td>
<td>0.86</td>
<td>$&lt;0.0001$</td>
</tr>
<tr>
<td>Ni</td>
<td>$Y = 11.23 + 4.86(x)$</td>
<td>0.49</td>
<td>$&lt;0.0001$</td>
</tr>
<tr>
<td>Zn</td>
<td>$Y = 22.7 + 3.87(x)$</td>
<td>0.73</td>
<td>$&lt;0.0001$</td>
</tr>
</tbody>
</table>

- Strongest linear relationship with Cu and Zn
- Weakest linear relationship with Cd – however this had the smallest range of concentrations
- Ni shows potential for stronger linear relationship
• Dataset is in its infancy and will include samples yet to be collected from this project as well as data from ESR and Lincoln University trials

• Potential dataset of 500 samples from 10 New Zealand soils and two plant species (ryegrass and wheat)
Conclusions

- Concentrations of metals were still too toxic for germination in MM and HM at 6 and 12 months.
- Concentrations of Cd and Zn were lower in the 12 month harvest. Cu and Ni concentrations were even between treatments and harvests.
- Cd and Zn availability is controlled by factors different from Ni and especially Cu.
- DGT-DIFS appears to be a reasonable measure of bioavailability for Cu and Zn and has potential to be a reasonable.