Mobility and toxicity of heavy metal(loid)s arising from contaminated wood ash application to a pasture grassland soil.

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Experimental context:

Waste wood ash

- Generated with increasing frequency
- Good liming and soil fertiliser (Ca, Mg etc)
- Concentrated **heavy metals** (CCA wood)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr mg kg⁻¹</th>
<th>Cu mg kg⁻¹</th>
<th>Zn mg kg⁻¹</th>
<th>As mg kg⁻¹</th>
<th>Pb mg kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>23.9 ± 2.1</td>
<td>8.8 ± 0.6</td>
<td>23.2 ± 1.4</td>
<td>4.5 ± 0.2</td>
<td>15.5 ± 1.1</td>
</tr>
<tr>
<td>Ash</td>
<td>9914.1 ± 714.9</td>
<td>8793.4 ± 632.0</td>
<td>4666.7 ± 373.5</td>
<td>9259.4 ± 649.3</td>
<td>1988.4 ± 92.0</td>
</tr>
<tr>
<td><em>ICRCL trigger values</em></td>
<td>&lt; 1000</td>
<td>&lt; 130</td>
<td>&lt; 300</td>
<td>&lt; 40</td>
<td>&lt; 2000</td>
</tr>
</tbody>
</table>
Study aims:

- Examine mobility [leaching] of heavy metals from ash, when applied to soil with and without manure

- Determine toxic response to increasing doses of ash using bioassays

- Assess risk of heavy metals in the environment using plant uptake and modelling

**Heavy metals:** potentially toxic if mobile and bioavailable within the environment
Hypotheses:

1) Leaching of heavy metals from ash can be reduced by co-applying manure

2) Arsenic will be very soluble and bioavailable due to high pH

3) Co-applying manure can reduce phyto-toxicity and plant uptake of metals

**Organic amendment;** manure co-applied to bind metals and prevent plant uptake/toxicity
Experimental set-up:

Duration; 60 days
Materials and methods:

1) Pore water collected by rhizon sampler (picture), measured by ICP-MS for metals

2) Ryegrass germinated and harvested after 9 weeks, mass, digested and ICP-MS for metals

3) Toxicity bio-assays performed on pore water as ‘bioavailable’ fraction of metals (E.coli HB101 pUCD607)
Results-pore water:

- **Cr µg L⁻¹**
  - soil: a
  - soil + M: a
  - soil + 0.1% A: a
  - soil + 0.3% A: b
  - soil + 1.0% A: c
  - soil + 3.0% A: c

- **Cu µg L⁻¹**
  - soil: b
  - soil + M: c
  - soil + 0.1% A: b
  - soil + 0.3% A: c
  - soil + 1.0% A: b
  - soil + 3.0% A: c

- **Zn µg L⁻¹**
  - soil: a
  - soil + M: a
  - soil + 0.1% A: a
  - soil + 0.3% A: a
  - soil + 1.0% A: a
  - soil + 3.0% A: a

- **As µg L⁻¹**
  - soil: c
  - soil + M: c
  - soil + 0.1% A: b
  - soil + 0.3% A: b
  - soil + 1.0% A: b
  - soil + 3.0% A: a
Comparable with values from contaminated industrial and mine areas in Europe; from Moreno-Jimenez et al, 2011

<table>
<thead>
<tr>
<th>Site &amp; location</th>
<th>As (µg l⁻¹)</th>
<th>Cd (µg l⁻¹)</th>
<th>Cu (µg l⁻¹)</th>
<th>Pb (µg l⁻¹)</th>
<th>Zn (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United Kingdom</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Byrom Street, Liverpool</td>
<td>1–3</td>
<td>n.d.–2</td>
<td>2–10</td>
<td>n.d.–21</td>
<td>n.d.–360</td>
</tr>
<tr>
<td>Quaker Meeting House, St Helens</td>
<td>2–83</td>
<td>20–6120</td>
<td>4–55</td>
<td>1–22</td>
<td>6–93</td>
</tr>
<tr>
<td>Merton Bank, St Helens</td>
<td>15–52</td>
<td>n.d.</td>
<td>25–47</td>
<td>13–495</td>
<td>67–205</td>
</tr>
<tr>
<td>Kidsgrove, Staffordshire</td>
<td>1–2</td>
<td>n.d.–0.71</td>
<td>n.d.–8</td>
<td>63–6470</td>
<td></td>
</tr>
<tr>
<td>Prescot, Merseyside</td>
<td>1–108</td>
<td>5–1400</td>
<td>49–1190</td>
<td>2–72</td>
<td>72–3749</td>
</tr>
<tr>
<td>Spain</td>
<td></td>
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</table>

n.d., not detected.
Soil + M + 0.1% A, soil + M + 0.3% A, soil + M + 1.0% A, soil + M + 3.0% A

pH

Values with different letters (a, b, c) indicate significant differences among treatments.

Legend:
- a
- b
- c

Note: The image contains a bar chart showing pH levels for different soil treatments with annotations for significant differences.
Results - plant metals:

**Cr mg kg$^{-1}$**

- Soil
- Soil + M
- Soil + 0.1% A
- Soil + 0.3% A
- Soil + 1.0% A
- Soil + 3.0% A

**Cu mg kg$^{-1}$**

- Soil
- Soil + M
- Soil + 0.1% A
- Soil + 0.3% A
- Soil + 1.0% A
- Soil + 3.0% A

**Zn mg kg$^{-1}$**

- Soil
- Soil + M
- Soil + 0.1% A
- Soil + 0.3% A
- Soil + 1.0% A
- Soil + 3.0% A

**As mg kg$^{-1}$**

- Soil
- Soil + M
- Soil + 0.1% A
- Soil + 0.3% A
- Soil + 1.0% A
- Soil + 3.0% A
Results - plant mass:

- **soil only**
- **soil + manure 10% + ash 3%**
Results-toxicity assays:

Percentage luminescence compared to soil control

Phyto-toxicity limit

soil + ash 10%
Discussion & conclusions:

- High ash doses completely phyto-toxic, moderate doses improve plant biomass

- Manure application limits Cu and Cr mobility and uptake

- Arsenic bioavailability controlled by high pH, and P

- Ash has no effects on Zn in pore water or ryegrass; co-precipitated with Ca, Mg etc, or immobile at high pH?

“Moderate doses of ash, co-applied with manure would have minimal effect on heavy metal leaching and would improve plant biomass [short term] but continued application may lead to accumulation of toxic concentrations in soil. Risk of As entering food chain in grazed pasture areas”