Pesticide sorption in fractured clayey tills varies substantially depending on soil domain and manure addition

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Background

• The observed unexpected leaching of strongly sorbing pesticides, especially in clayey areas

• Knowledge that water transport may be fast through macropores in such soils

• Our hypothesis that sorption behaviour is different in macropores

• Our hypothesis that dissolved and colloidal material from manure may influence sorption
The pesticides

**Tebuconazole**
Fungicide
Hydrophobic (Log $K_{ow}$ 3.7; 36 mg/L water)
No charge at neutral pH (pKa 5.0)

**Glyphosate**
Herbicide
Very hydrophilic (Log $K_{ow}$ -3.4)
Negatively charged at neutral pH
Excavation pits

To 4.5 m at site 1

To 6 m at site 2
Eight visible soil domains

- Plough layer
- Oxidized with brown macropores
- Oxidized with grey macropores and fractures
- Oxidized with reddish fractures
- Reduced with reddish fractures
- Reduced

[Diagram showing soil domains labeled 1 to 8, with descriptions of oxidation and reduction states]
Plough layer
Oxidized with brown macropores
Oxidized with grey macropores and fractures
Oxidized with reddish fractures
Reduced
Reduced with reddish fractures

1
5
2
4
7
6
8
3
Plough layer
- Oxidized with brown macropores
- Oxidized with grey macropores and fractures
- Oxidized with reddish fractures
- Reduced with reddish fractures

Reduced
Plough layer
Oxidized with brown macropores
Oxidized with grey macropores and fractures
Oxidized with reddish fractures
Reduced
Reduced with reddish fractures
Visible differences in samples

- Plough layer
  - Oxidized with brown macropores
  - Oxidized with grey macropores and fractures
  - Oxidized with reddish fractures
- Reduced with reddish fractures
- Reduced
Soil domain characteristics

Texture, pH, TOC, TIC, different fractions of Fe, Mn and Al, surface area, CEC, exchangable cations...

Site 2:

<table>
<thead>
<tr>
<th>TOC (%)</th>
<th>pH</th>
<th>Fe-oxides (g/kg)</th>
<th>Mn-oxides (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>0.05</td>
<td>5.9</td>
<td>201</td>
</tr>
<tr>
<td>0.37</td>
<td>0.12</td>
<td>1.1</td>
<td>21</td>
</tr>
<tr>
<td>0.67</td>
<td>0.17</td>
<td>3.9</td>
<td>153</td>
</tr>
<tr>
<td>0.06</td>
<td>0.05</td>
<td>6.4</td>
<td>261</td>
</tr>
<tr>
<td>0.12</td>
<td>0.37</td>
<td>12.6</td>
<td>910</td>
</tr>
<tr>
<td>0.05</td>
<td>0.37</td>
<td>7.2</td>
<td>97</td>
</tr>
<tr>
<td>0.06</td>
<td>0.05</td>
<td>8.3</td>
<td>44</td>
</tr>
<tr>
<td>0.17</td>
<td>0.37</td>
<td>8.3</td>
<td>201</td>
</tr>
</tbody>
</table>

Site 1 very similar
Tebuconazole sorption

\[ C_s = K_F \times C_w^n \]

\[ K_F: \]

\[ n = 0.77-0.87 \]
Glyphosate sorption

Data fit poorly to the Freundlich isotherm due to high concentration dependency:

\[ C_s = K_{FeX} \times C_w^n \times C_w^{-D} \]

[Sibbesen, 1981; De Jonge et al., 2001]

No single soil parameter influenced this distribution much

Also variation in \( n \) and \( D \)
Tebuconazole sorption with manure

- Less sorption as expected from hypothesis
- More sorption (reverse of hypothesis)
Glyphosate sorption with manure

Site 1, $K_{Fex}$

Control

0.1%

1%

10%

Generally same effect at site 2
Glyphosate sorption kinetics at low conc. (~1 µg/L)

Domains 2 and 7 show odd sorption kinetics – but not when manure is added.
Understanding the effect of pig manure

**Conductivity (µS/cm)**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>K_d (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>Manure, 1%</td>
<td>5</td>
</tr>
<tr>
<td>Manure, 1%</td>
<td>10</td>
</tr>
<tr>
<td>Manure, 0.1%</td>
<td>20</td>
</tr>
</tbody>
</table>

**Divalent metal ions**

- **Cu**
  - None: 4.9 mg/L
  - Manure: 7.5 mg/L

- **Zn**
  - None: 21900 mg/L
  - Manure: 4.9 mg/L

- **PO_4^{3-}**
  - None: 2648 mg/L
  - Manure: 182 mg/L

**Increasing K_d** - Likely candidates

**Minor effect** - Likely candidates

**DOC**

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<td>0</td>
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<tr>
<td>Manure, 1%</td>
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<td>Manure, 0.1%</td>
<td>20</td>
</tr>
</tbody>
</table>

**Phosphate**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>K_d (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>Manure, 1%</td>
<td>5</td>
</tr>
<tr>
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Conclusions

• Preferential flow channels differ geochemically from matrix soil

• Pesticide sorption influenced (Glyph. > Tebuc.)

• Pig manure has big influence on sorption (strength, conc. depend., kinetics) but differently in different soil domains

• In the case of glyphosate, the combined effect of DOC and phosphate

• So what is the effect on leaching (P-28, friday)?