Distribution of radionuclides in soils – dependence on soil parameters

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Contents

• modelling $K_d$
• model verification
• sensitivity study for Refesol 2 (variation of soil parameters)
• redox sensitivity
• discussion
Model description

Geochemical code: PHREEQC (Parkhurst and Appelo 1999)

Complexation models used with PHREEQC:
Dzombak and Morel (1990)
Bradbury and Baeyens (2009, 2009)
Tipping (Model VI, 2002)

Model components:
• soil solution
• oxalate extractable hydrous ferric oxides (HFO)  \textit{DM}
• clay (illite as representative material, including frayed edge sites)  \textit{BB}
• immobile organic matter  \textit{T}
• dissolved organic matter (DOM)  \textit{T}
• solid phases
Model Verification

Study of 18 different U-contaminated soils: Vandenhove et al. (2007)

Two Cs-contaminated soils: Nisbet (1995)

Figure 1. Comparison of measured and calculated U concentrations in soil solution

Figure 2. Activity of $^{134}$Cs in soil solution before and after treatment with 11.5 m potassium
### Reference soils (Refesols)

<table>
<thead>
<tr>
<th>Refesol</th>
<th>sand</th>
<th>silt</th>
<th>clay</th>
<th>pH</th>
<th>C&lt;sub&gt;org&lt;/sub&gt;</th>
<th>CEC&lt;sub&gt;eff&lt;/sub&gt;</th>
<th>Fe&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>Al&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>type</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-A</td>
<td>71</td>
<td>24</td>
<td>5</td>
<td>5.7</td>
<td>0.9</td>
<td>37.9</td>
<td>1.57</td>
<td>0.95</td>
<td>Cambisol</td>
</tr>
<tr>
<td>02-A</td>
<td>2</td>
<td>83</td>
<td>15</td>
<td>6.6</td>
<td>1.3</td>
<td>133.2</td>
<td>3.54</td>
<td>0.69</td>
<td>Stagnic luvisol</td>
</tr>
<tr>
<td>04-A</td>
<td>85</td>
<td>11</td>
<td>4</td>
<td>5.1</td>
<td>2.9</td>
<td>85.7</td>
<td>0.63</td>
<td>1.51</td>
<td>Gleyic podsol</td>
</tr>
<tr>
<td>06-A</td>
<td>9</td>
<td>55</td>
<td>36</td>
<td>6.8</td>
<td>2.5</td>
<td>236.6</td>
<td>5.03</td>
<td>1.57</td>
<td>Cambisol-Rendzina</td>
</tr>
<tr>
<td>08-A</td>
<td>69</td>
<td>21</td>
<td>10</td>
<td>5.3</td>
<td>1.04</td>
<td>51.2</td>
<td>3.50</td>
<td>0.35</td>
<td>Fluvisol</td>
</tr>
<tr>
<td>09-A</td>
<td>62</td>
<td>30</td>
<td>8</td>
<td>5.5</td>
<td>0.86</td>
<td>39.2</td>
<td>2.74</td>
<td>0.73</td>
<td>Luvisol</td>
</tr>
<tr>
<td>12-G</td>
<td>32</td>
<td>47</td>
<td>21</td>
<td>5.1</td>
<td>3.75</td>
<td>126.7</td>
<td>7.65</td>
<td>2.28</td>
<td>Cambisol</td>
</tr>
</tbody>
</table>

**Table 1**: characteristics of the reference soils, texture and C<sub>org</sub> in %, CEC<sub>eff</sub> (exchangeable Ca, Mg, H and Na) in mmolc/kg, oxalate-extractable oxides in g/kg.

source: K.H. Weinfurtner, Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany
Assumptions for the Refesol model

The composition of the soil solution of the Refesols is not yet known → use of a „standard“ soil solution for modeling:
(concentrations are geometric means of ranges of frequent values, Scheffer/Schachtschabel 2010):

<table>
<thead>
<tr>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>NH₄</th>
<th>Fe(3)</th>
<th>Al</th>
<th>Si</th>
<th>Cl</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>DOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>9.5</td>
<td>11</td>
<td>80</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>24.5</td>
<td>20</td>
<td>0.1</td>
<td>39</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 2: Composition of the „standard“ soil solution (values in mg/l)

• Fe and Al determined by equilibrium with ferrihydrite and gibbsite
• no phosphate fertilization → important for comparison with literature values
• DOC 27 mg/l, org. C 50% of org. matter
• concentration of contaminating nuclides: 1 Bq/kg DW
Calculated distribution coefficients – comparison with literature values

- calculation using „standard“ soil solution from Table 2
- equilibration of initial soil solution with surface assemblage \(\rightarrow\) equilibration with contaminated soil solution
- soil saturated with water

Fig. 3: Logarithmic distribution coefficient compared to literature values (IAEA Tecdoc 1616)
**Important soil parameters and processes**

- contaminant concentration
- dilution/evaporation
- clay (mineral) content
- Fe-/Al-oxides (oxalate extractable)
- immobile organic matter
- dissolved organic matter
- pH
- (redox state)

conditions for modelling: saturated soil, no oxygen in solution
Concentration dependence of $K_d$

$\rightarrow$ saturation effects
Dilution

dilution but constant activity: $\rightarrow$ less competition by major ions
Evaporation must not be confused with the case of unsaturated soil (relative concentrations constant, same chemistry).

Evaporation at constant activity: → more competition by major ions
Clay content

complexation on clay highly significant for Cs, moderate for Ni, negligible for U and Se (no clay sorption model for Se as yet)

$K_d$ Ni:
150 l/kg (0 % clay)
200 l/kg (55 % clay)

note linear scale!
Content of Fe/Al oxides

strong influence of Fe/Al oxides for U and Se

red: values for Luvisol (Refesol 2)
**Immobile organic matter**

Soil density effects and blocking of mineral surface sites by org. matter not included

*strong influence on Ni, moderate on U, no model for Se binding as yet*
Dissolved organic matter

65% of DOM is active

average content of active DOM: 35.6 mg/l

moderate to strong influence on Ni and U, none on Cs, no model for Se binding as yet
CO$_2$ pressure (organic activity)

red: values for Luvisol (Refesol 2)

formation of carbonate complexes that keep U in solution, competition effects by carbonate sorption on Fe/Al oxides
Variation of pH

pH (equilibrium with Calcite)
SI Gibbsite (pH > 6) = 2

K\text{d} in l/kg

no precipitation reactions

pe = 13.5…4.5

pH dependence of K\text{d}(U) in batch experiments
(Vandenhove et al. 2007)
Comparison of ranges

$K_d$ ranges

- Cs
- Ni
- U
- Se

- Concentration
- Evaporation
- Dilution
- Clay
- Feox
- pCO2
- pH/pe
- DOM
- Org. C
Conclusions – sensitivity study

• in many cases the distribution of radionuclides strongly depends on soil parameters
• the variation of a single parameter may change the $K_d$ by more than an order of magnitude
• the $K_d$ variations can reasonably be modelled by PHREEQC
• $K_d$ variability is important for predicting the influence of environmental conditions on radionuclide distributions in soils
Redox states of soils

In soil solutions, a couple of elements (O, C, N, S, Fe ....) may occur in various oxidation states e.g. iron as Fe$^{2+}$ or Fe$^{3+}$

→ electron transfer

example: reduction of ferric hydroxide

$$4 \text{Fe(OH)}_3 + 12 \text{H}^+ + 4\text{e}^- \rightarrow 4 \text{Fe}^{2+} + 12 \text{H}_2\text{O}$$

the redox potential $E_h$ is given by the Nernst equation:

$$E_h = E_h^0 - \frac{0.059}{n} \cdot \log \frac{[\text{Red}]}{[\text{Ox}]} \quad \text{(at 25°C)}$$

$E_h^0$: standard potential
Against hydrogen electrode
n: number of transferred electrons
{…}: chemical activity
**Redox states of soils**

lower pe: reducing conditions, high electron activity  
higher pe: oxidizing conditions, low electron activity

from Sposito 1989

from Appelo/Postma 2005
Modelling redox zonation

decomposition of organic matter
soil: RefeSol 2 (Luvisol)

Assumptions:
• Decomposition causes no significant changes in the number of organic binding sites
• Stepwise decomposition of org.matter starting at pe ~ 13 – 14 (soil solution saturated with oxygen)
• Reductive decomposition of hydrous ferric oxide (decreasing number of Hfo binding sites)
• Se precipitated as elemental Se or as FeSe, Ni as Ni(OH)$_2$, U as Uraninite (UO$_2$)
• In the $K_d$ calculations the precipitated material is assigned to the solid phase (may still be present in the solution as a colloid, e.g. Se !)
Redox behaviour of characteristic solutes

behaviour as described in the literature (e.g. Appelo & Postma 2005)
Redox behaviour of uranium

Below pe 3:
Decomposition of Hfo

→ Release of ions bound by complexation

Below pe 0:
Precipitation of uraninite (UO$_2$)

White circles: Hfo content
Black diamonds: distribution coefficient

$pCO_2 = 3.5$

$pCO_2 = 1.75$

More carbonate complexes
Redox behaviour of nickel

Precipitation of Ni(OH)_2 at low pe

Formation of mixed Al-hydroxides discussed in the literature
**Redox behaviour of Caesium**

Ionic strength effect due to ion release (Hfo decomposition!)

Precipitation of minerals at low pe, e.g. FeS

black diamonds: distribution coefficient
white circles: ionic strength
Redox behaviour of selenium

pe 9 (531 mV): transformation of selenate to selenite in solution
pe 2.5 (150 mV): precipitation of elemental Se
pe -0.4 (-25 mV): precipitation of FeSe

No modelling of Se binding to org. matter!

from Ashworth et al. 2008
(sandy loam, column experiment, Hfo content not specified)

Colloidal Se in solution?
Conclusions – redox study

- Redox behaviour dominated by Hfo dissolution and precipitation of nuclide
- $K_d$ for U und Se degrees of magnitude higher in the anoxic region
- $K_d$ definition: how to deal with finely dispersed or colloid material?
- Need for studies that provide all parameters necessary for modelling


