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Distribution of radionuclides in soils – modelling the dependence on soil parameters

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- model description
- model verification
- sensitivity study (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:

- **Ni,U,Se:** oxalate extractable hydrous ferric oxides (HFO) DM
- **Cs,Ni,U:** clay minerals (illite as representative material, including frayed edge sites) BB
- **Ni,U:** immobile organic matter T
- **Ni,U:** dissolved organic matter (DOM) T
- soil solution
- solid phases

Model Verification

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

Two Cs-contaminated soils: Nisbet (1995)

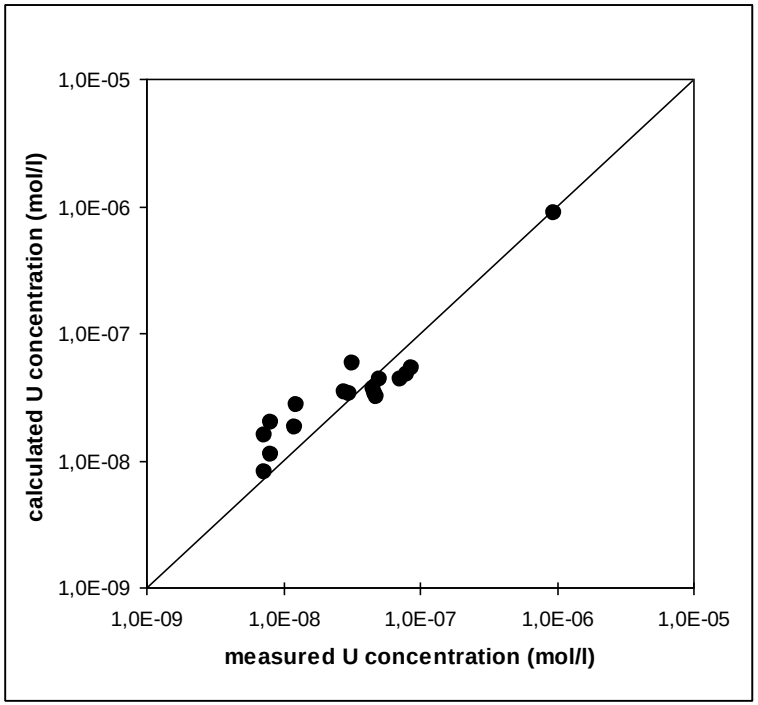


***Figure 1**. Comparison of measured and calculated U concentrations in soil solution*

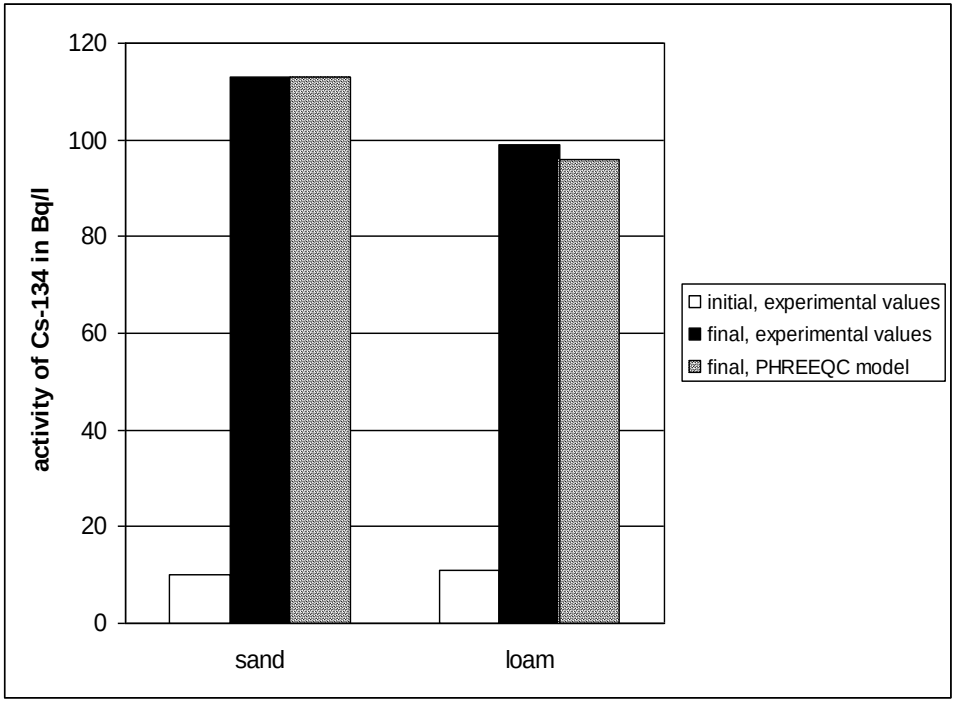


***Figure 2**. Activity of ^{134}Cs in soil solution before and after treatment with 11.5 m potassium*

Reference soils (RefeSols)

Refesol	sand	silt	clay	pH	C_{org}	CEC_{eff}	Fe_{ox}	Al_{ox}	type
02-A	2	83	15	6.6	1.3	133.2	3.54	0.69	**Stagnic luvisol (loam)**
04-A	85	11	4	5.1	2.9	85.7	0.63	1.51	**Gleyic podsol (sand)**

Table 1: characteristics of the reference soils, texture and C_{org} in %, CEC_{eff} (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

used in the Reference Biosphere Project in collaboration with BfS, HelmholtzZentrum Munich and GRS

background: long-term radioecological risk assessment of nuclear waste disposal

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):

Na	K	Mg	Ca	NH_4	Fe	Al	Si	Cl	N	P	S	DOM
6.3	9.5	11	80	0.9	-	-	10	24.5	20	0.01	39	54

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 (^{135}Cs,^{63}Ni, ^{238}U and ^{79}Se)

Calculated distribution coefficients – comparison with literature values

- calculation using „standard“ soil solution from **Table 2**
- equilibration of initial soil solution with surface assemblage → equilibration with contaminated soil solution

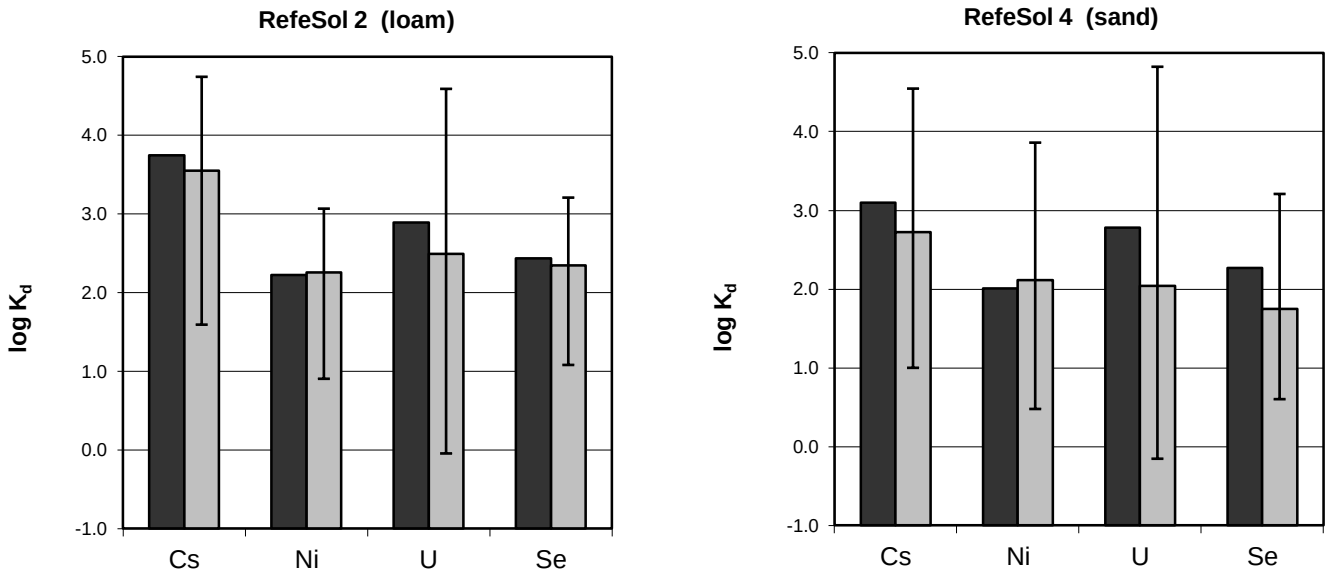


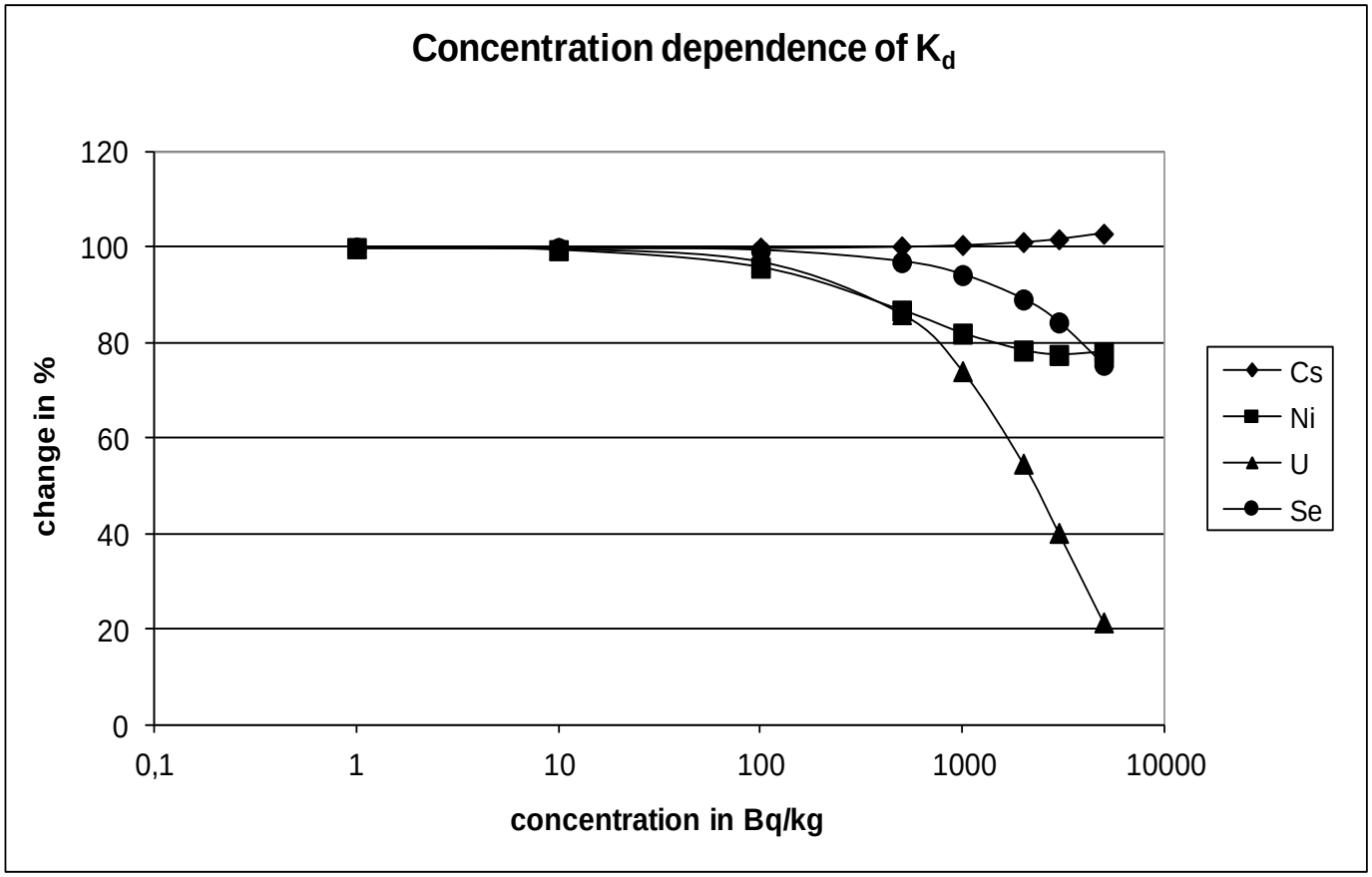
***Fig. 3**: Logarithmic distribution coefficient compared to literature values (IAEA Tecdoc 1616)*

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)

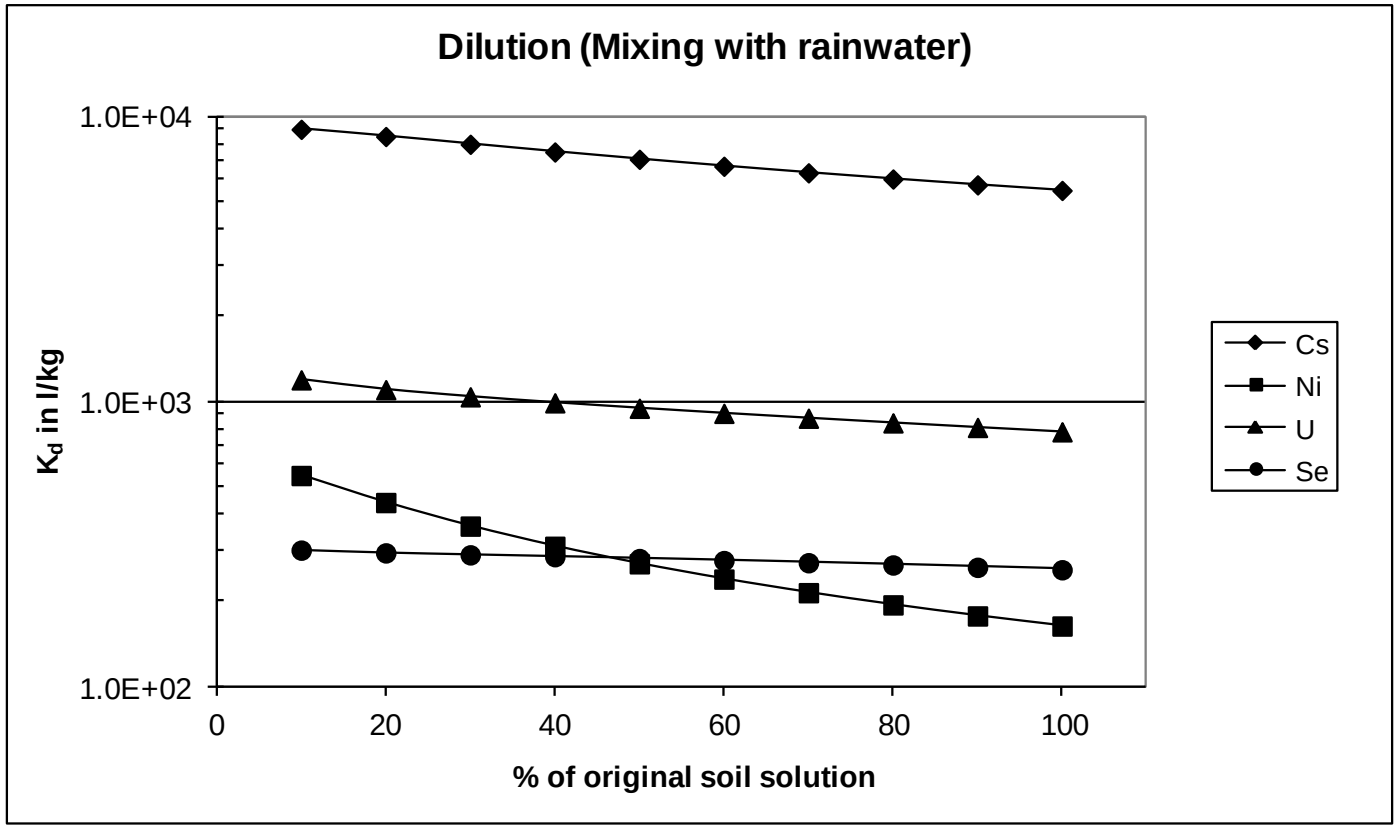
conditions for modelling: saturated soil, no oxygen in solution

Concentration



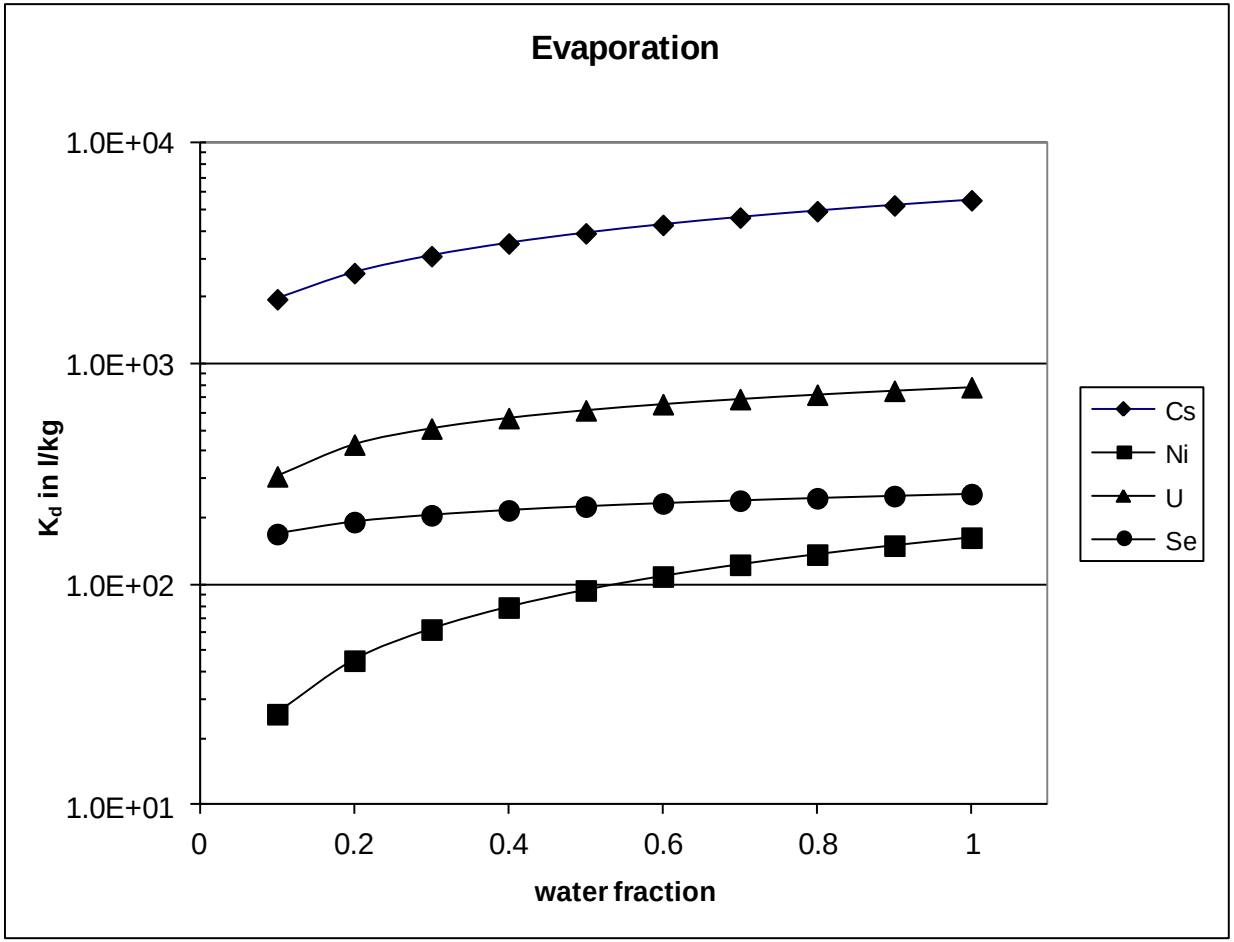
→ saturation effects

Dilution



dilution but constant activity: → less competition by major ions

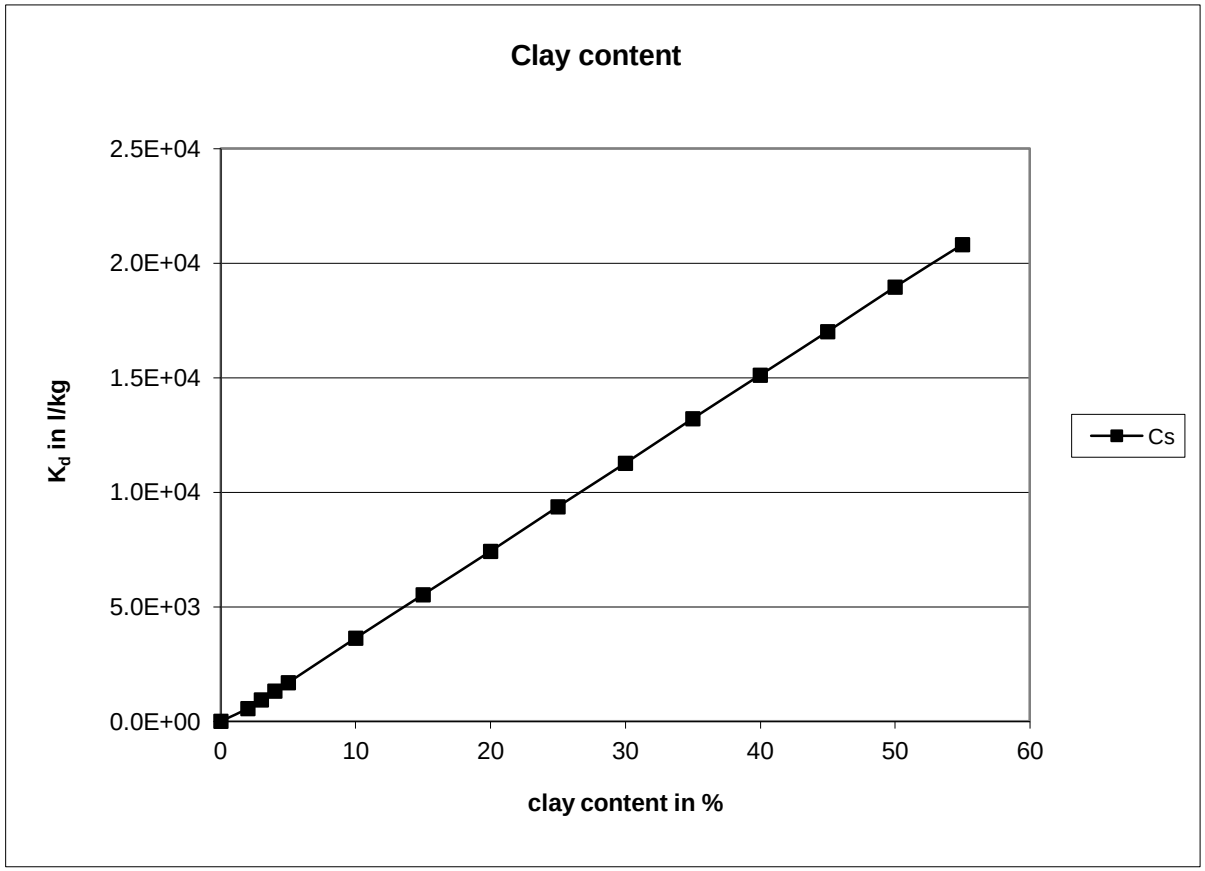
Evaporation



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



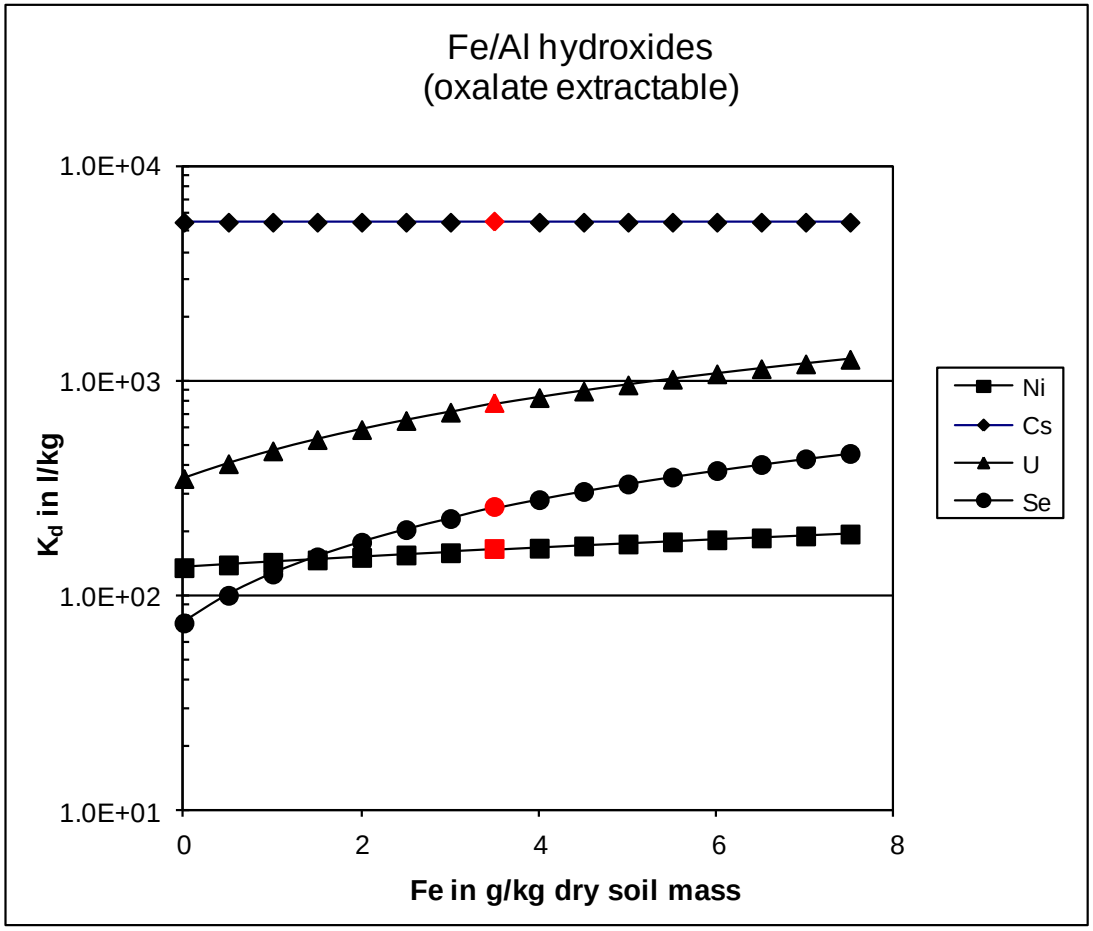
note linear scale!

K_d Ni:

150 l/kg (0 % clay)
200 l/kg (55 % clay)

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

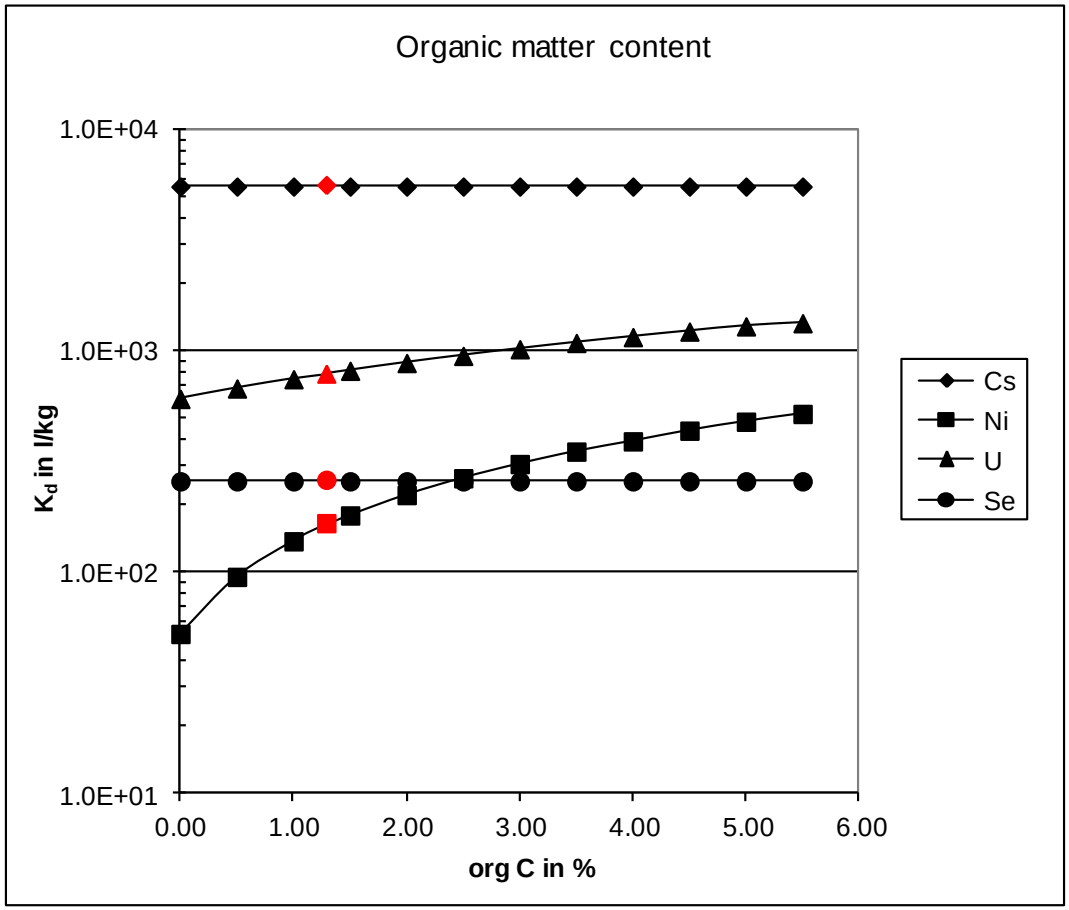
Content of Fe/Al oxides



red: values for Luvisol (Refesol 2)

strong influence of Fe/Al oxides for U and Se

Immobile organic matter

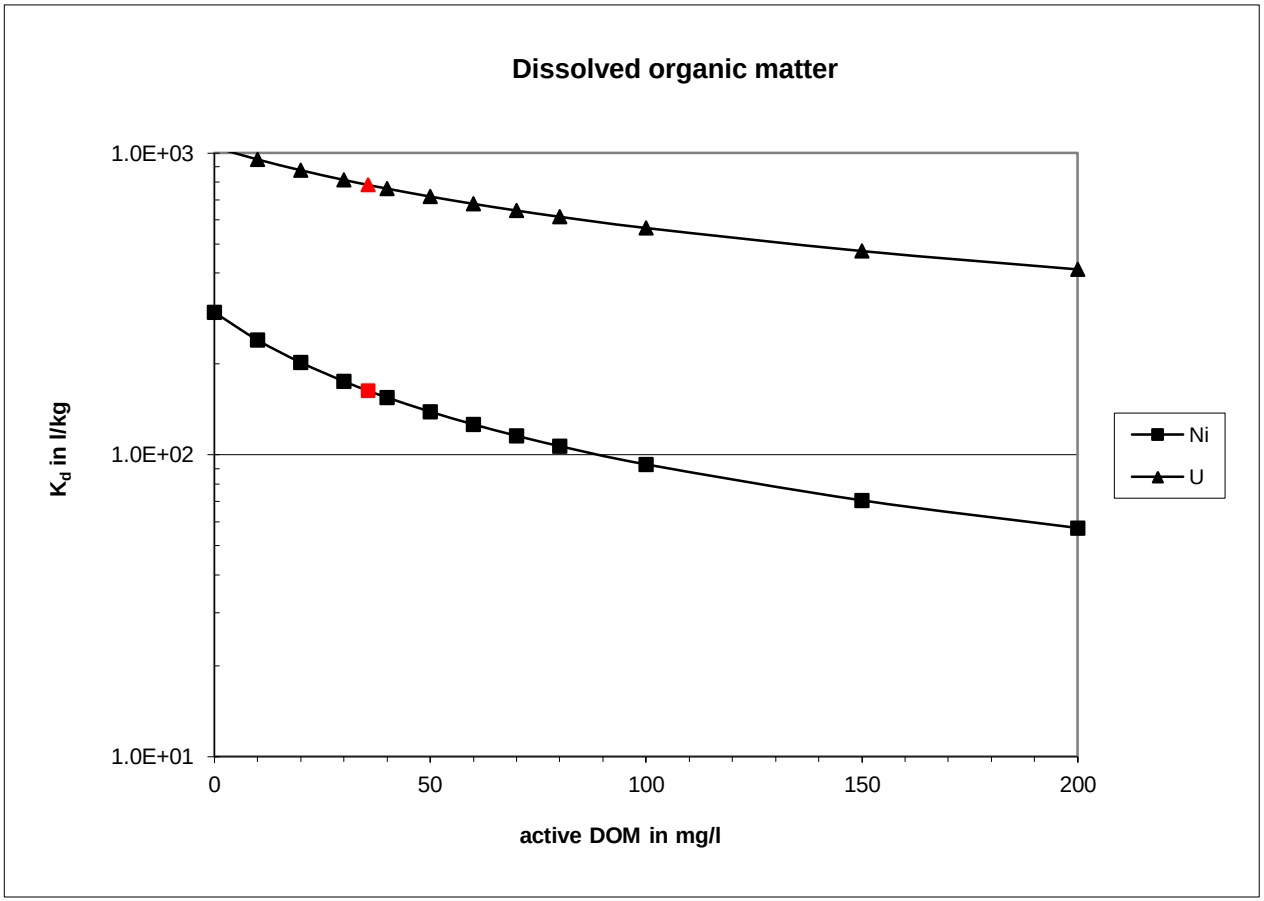


red: values for Luvisol (Refesol 2)

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

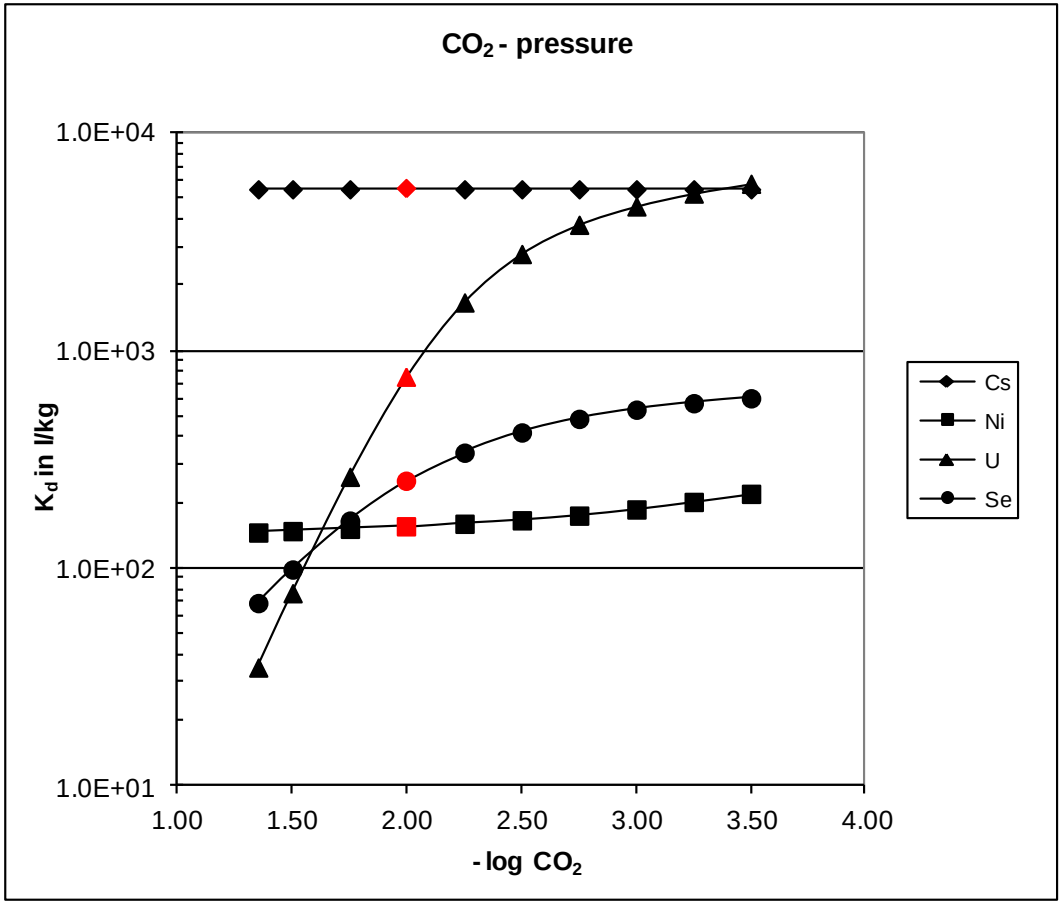


65 % of DOM is active

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

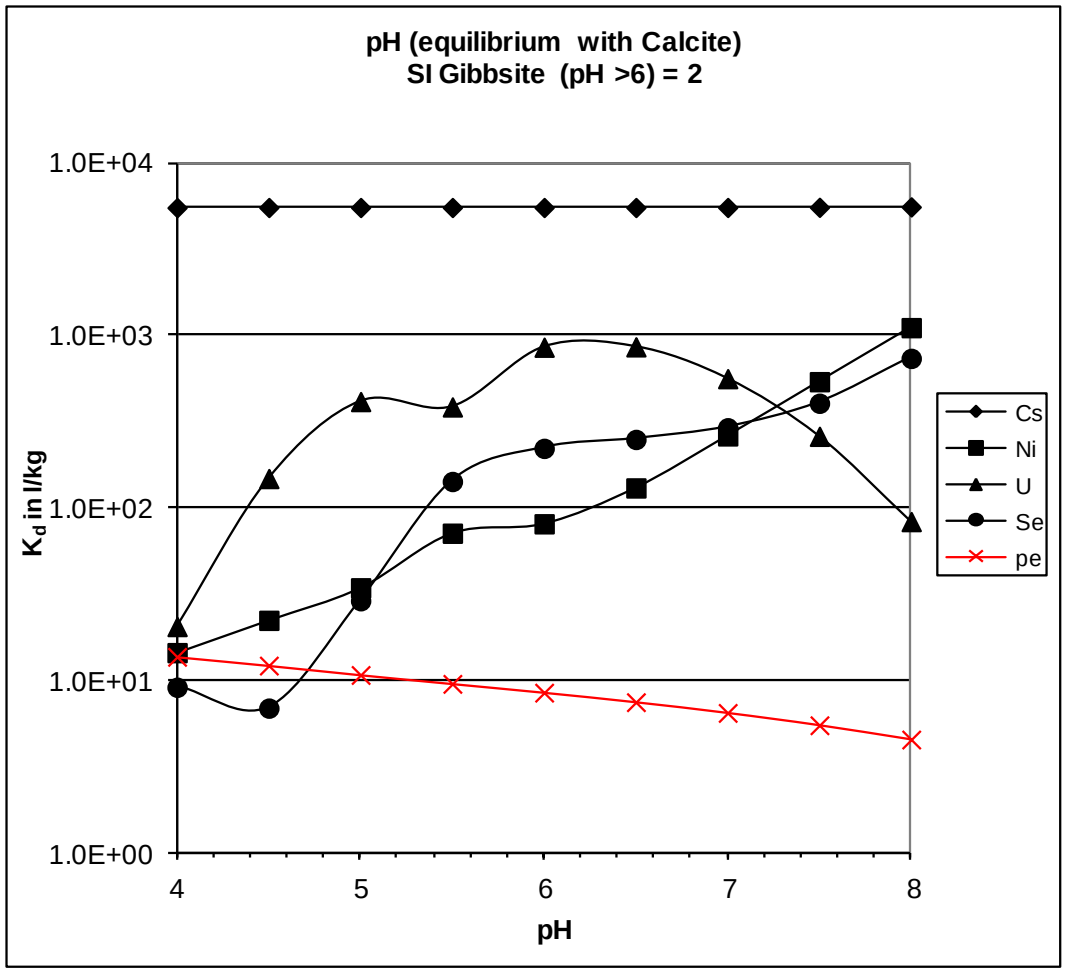
CO_2 pressure (organic activity)



red: values for Luvisol (Refesol 2)

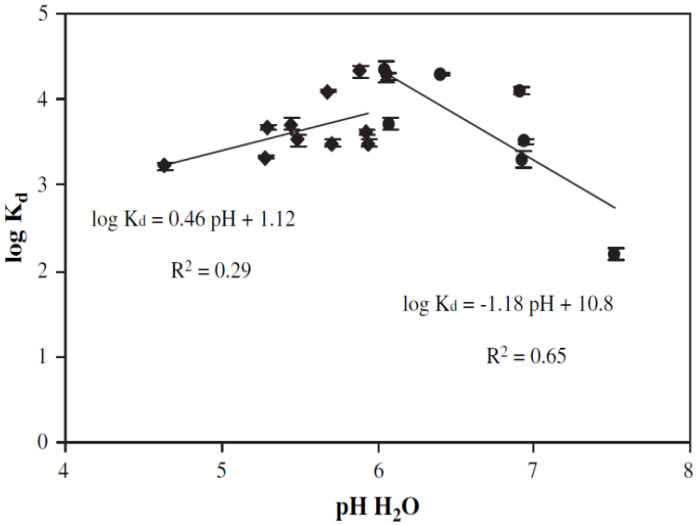
formation of carbonate complexes that keep U in solution, competition effects by carbonate sorption on Fe/Al oxides

Variation of pH



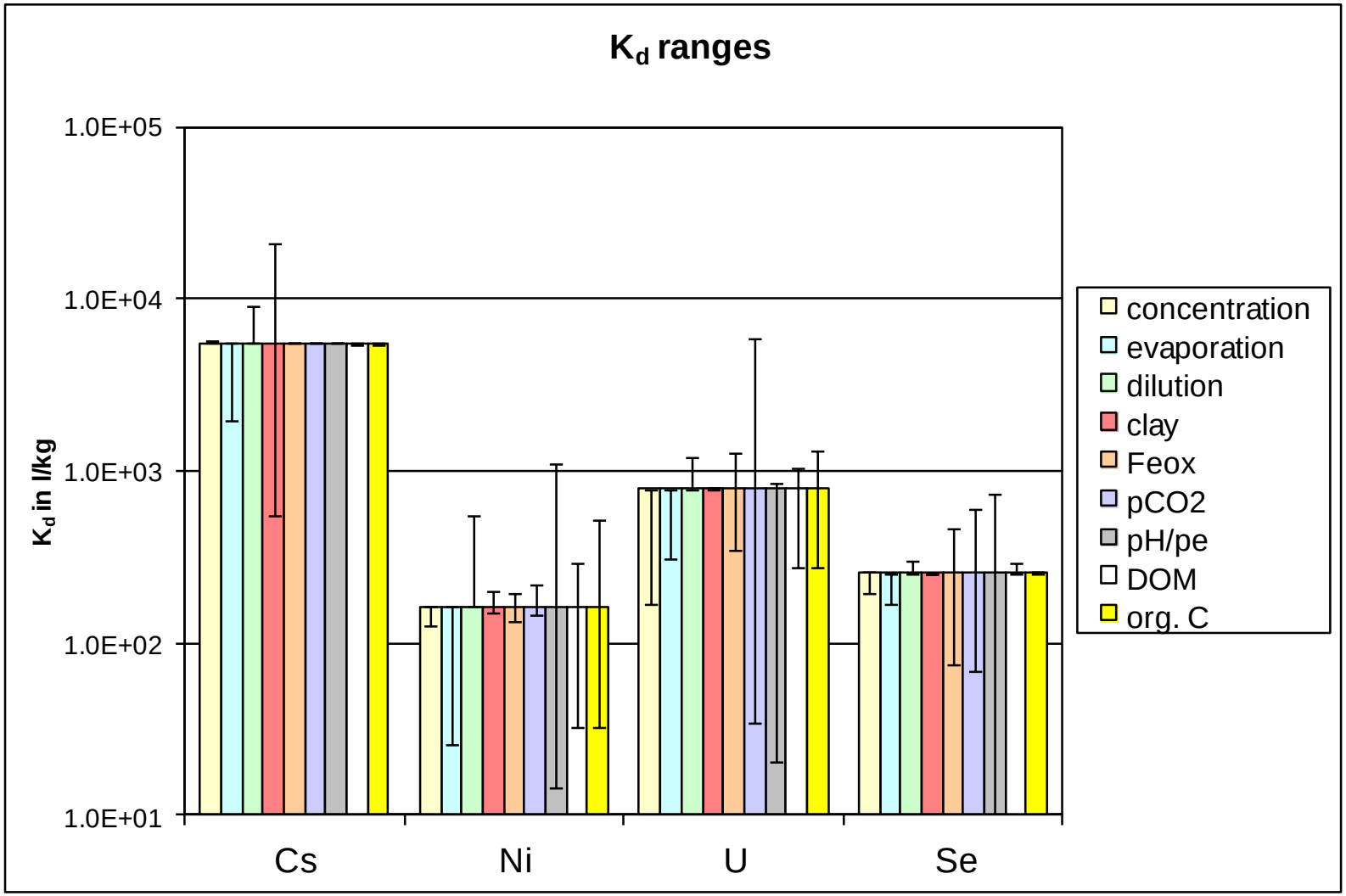
no precipitation reactions

pe = 13.5….4.5



pH dependence of K_d(U) in batch experiments (Vandenhove et al. 2007)

Comparison of ranges



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

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Thank you!

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