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ARBEITSBERICHT NAB 23-14

An Updated Sorption Database for Use in Swiss Biosphere Modelling

August 2023

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An Updated Sorption Database for Use in Swiss Biosphere Modelling

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

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List of Acronyms

CEC	Cation Exchange Capacity
DOC	Dissolved Organic Carbon
FOA	Food and Agriculture Organisation of the United Nations
GM	Geometric mean
GSD	Geometric Standard Deviation
HLW	High-Level Radioactive Waste
ILW	Intermediate-Level Radioactive Waste
LLW	Low-Level Radioactive Waste
NABO	Swiss Soil Monitoring Network (in German: “Nationale Bodenbeobachtung”)
NABODAT	National Soil Information System (in German: “Nationale Bodeninformations-system”)
NTB	Nagra Technical Report
OM	Organic Matter
OMM	Upper Seawater Molasse
OSM	Upper Freshwater Molasse
PSI	Paul Scherrer Institute
RBG	General Licence Application (In German: “Rahmenbewilligungsgesuch”)
SDB	Sorption Database
SFR	Final repository for short-lived radioactive waste (in Swedish: “Slutförvaret för kortlivat radioaktivt avfall”)
SGT	Sectoral Plan for Deep Geological Repositories (in German: “Sachplan geologische Tiefenlager”)
SRS	Savannah River Site
SwiBAC	Swiss Biosphere Assessment Code
TDS	Total Dissolved Solid
TIC	Total Inorganic Carbon
USDA	United States Department of Agriculture
USM	Lower Freshwater Molasse

1 Introduction

1.1 Purpose of the database compilation

At the time of writing, Nagra is in Stage 3 (SGT E3) of the Swiss process to select a site or sites for deep geological disposal of HLW and ILW/LLW. At the commencement of the project reported here, three siting regions were being considered with potential for hosting a deep geological repository (or repositories). However, in September 2022, near the end of the project, Nördlich Lägern in Northern Switzerland was recommended for repository siting. In 2024, Nagra anticipates submitting documents justifying site selection and for the general licence application (RBG) for a proposed repository site. Safety assessments for potential repositories in the three siting regions will form part of the site selection process.

Post-closure safety assessment includes modelling the behaviour of radionuclides potentially released from deep geological disposal to the biosphere. Nagra's biosphere modelling is reflected in the SwiBAC code (Walke & Keesman 2013). It is intended that biosphere modelling for the RBG application will divide the biosphere into compartments, representing:

- top soil
- deep soil
- an unsaturated zone
- a local shallow aquifer
- river bed sediments; and
- surface water (including suspended sediment)

For the RBG application, SwiBAC will be used to assess a reference biosphere based on an agricultural area within a Northern Swiss valley, with a river, underlying Quaternary aquifer, and a present-day climate. In addition to the reference biosphere, based on a river valley, the same compartment structure can be adapted to represent alternative biosphere systems, including, for example:

- the same system, but with a warmer, drier climate, and
- a wetland area drained for agriculture

The aim of this report is to provide a sorption database for use in SwiBAC in SGT E3. The database updates Nagra's biosphere sorption database documented in (Tits & van Dorp 1999). Like this earlier database, the updated database provides sorption coefficients ("K_d" values) describing linear sorption isotherms for radioelements that may be important in the waste inventory. However, whereas the previous database focussed on sites being considered in the late 1990's, in central and Northern Switzerland, the updated database is targeted at the conditions (compositions of sediments, soils, shallow groundwaters, and surface waters) found in the three siting regions being considered in SGT E3. The revised database also incorporates new information that has become available since (Tits & van Dorp 1999) was produced.

1.2 Nature of the distribution coefficient, K_d

Consistent with common practice for safety assessments, as was done in the previous version of the database (Tits & van Dorp 1999), sorption is represented using linear isotherms described by:

$$K_d = \frac{C}{S}$$

Where: C is the concentration of a chemical constituent, such as a radionuclide, (the sorbate) that is sorbed on the surfaces of a solid phase (the sorbent) and S is the concentration of the same chemical constituent in the water. When the units of C are mol/kg, the units of S are mol/m^3 and the units of K_d are $m^{3/}$kg.

Assumptions underpinning the use of a K_d value to model sorption are that:

- Partitioning of a chemical constituent between the aqueous phase and a co-existing solid surface is a linear function of the chemical constituent's aqueous concentration.
- The solid surface has many more sites where sorption may occur than the number of sites required.
- Reversible equilibrium occurs between the dissolved and sorbed forms of the chemical constituent (i.e. the reaction is fast compared to the duration of the experiment).

The use of a K_d value does not imply anything about the mechanism of sorption, but encompasses the effects of all mechanisms by which a solute can be taken up from an aqueous solution by solid surfaces. Such mechanisms may include physical adsorption caused by non-specific intermolecular forces (e.g. hydrogen bonding and van der Waals forces); or chemical adsorption, involving chemical bond formation between a solute and a solid surface (e.g. ion exchange or surface complexation). However, the definition of K_d excludes processes such as precipitation/dissolution reactions and physical filtration of small particles.

Sorption of any constituent to a solid surface depends strongly on the characteristics of the solid surfaces, and the chemical conditions of the environment (depending on the aqueous constituent, this might include pH, redox state, concentrations of ligands). K_d values measured for a given aqueous constituent for different solid phases and chemical conditions may vary by many orders of magnitude. Accordingly, experimental K_d values should be used in assessment models only for the solids and chemical conditions for which they were obtained.

Published values of K_d were typically obtained by batch experiments in which a quantity of solid is placed in a volume of solution containing a chemical constituent of interest. After a period of time, the solid and solution are separated and the concentrations of the constituent on the solid and remaining in solution are measured and used to calculate K_d.

1.3 Approach

1.3.1 Overall approach

An "ideal" approach to selecting K_d values would use experimentally determined sorption isotherms for each considered radionuclide under well-defined relevant chemical conditions (water composition, pH, Eh etc.), on well-characterised relevant solid materials (soils and sediments of known solid-phase compositions). Each experiment would be well-controlled and element concentrations in aqueous and solid-phases would be measured after chemical equilibrium between aqueous and solid-phases had been demonstrated. However, the very long timescales relevant to post-closure safety assessment for geological disposal mean that the system being modelled is not the biosphere as it exists at the present-day. Rather, present-day conditions are taken to be analogous to conditions in the long term when radionuclide releases might occur and during timeframes when potential radiological consequences may be maximised. Given that biosphere conditions cannot be tightly constrained, assessments are undertaken on the basis of a reference system and the robustness of that system is explored through alternative cases and sensitivity calculations. For each radionuclide of interest (i.e. the radionuclides considered in the present report) a reference

K_d and a plausible range of K_d values is therefore needed for each combination of considered soil/sediment types and coexisting water conditions (notably pH and Eh). The plausible range takes account of:

- uncertainties in the chemical conditions under which sorption occurs, reflecting in part spatial variability in these conditions, and
- uncertainties in the characteristics of soils/sediments in which sorption takes place, again reflecting in part spatial variability in these characteristics

It is only if safety assessments were to identify potential for uncertainty concerning sorption of a particular radionuclide to affect calculated doses to a degree that might affect the conclusions of the assessment, that more detailed investigations of sorption, targeted at that nuclide, might be considered. Commensurate with this context, the overall approach to the work reported here aimed to recommend K_d values that are consistent with:

- published K_d values for sorption on similar materials, and under similar chemical conditions, to those of northern Swiss shallow groundwaters, surface waters and soil porewaters
- fundamental theoretical understanding of sorption
- the chemical speciation of the considered elements over the ranges of conditions in northern Swiss shallow groundwater, surface waters and soils, as calculated using the latest PSI/Nagra Chemical Thermodynamic Database 2020, Version 1-1, and
- the variations in sediment in soils, lake beds and rivers

The approach had three strands:

1. a review of post-1999 literature on sorption of radionuclides that potentially could be released from a Swiss repository for HLW and LLW/ILW
2. a review of the spatial distributions and characteristics of sediments, soils, shallow groundwaters, lake waters and river waters in Northern Switzerland, and
3. compilation of relevant sorption data (K_d values) and development of an approach for assigning K_d values to different compartments in the SwiBAC biosphere model

The compilation of relevant sorption data in (3) draws on (1) and (2).

The report is structured as follows:

- Chapter 2 describes the chemical environments for which K_d values are recommended.
- Chapter 3 provides an overview of the literature on sorption that was reviewed.
- Chapter 4 describes the chemical characteristics and recommended K_d values for each considered element.
- Chapter 5 overviews the recommended K_d values and highlights limitations in their application.
- Appendix A gives the ranges of K_d values for each considered element in the reviewed literature.
- Appendix B compares the K_d values recommended for use in the biosphere modelling of SGT E3 with those in Nagra's earlier compilation, given in (Tits & van Dorp 1999).

1.3.2 Selection of K_d values

When selecting K_d values, it is assumed that the biosphere in Northern Switzerland in the future will be similar to the present biosphere, so that a description of the present chemical conditions in the biosphere is also similar to future chemical conditions. This assumption is justified because:

- The present biosphere is a product of processes operating in previous glacial and interglacial episodes and these processes are expected to operate in future glacial/interglacial cycles.
- No major rock units chemically different to those presently at/near the ground surface may in future approach the ground surface due to erosion, resulting in soils and lake/river bed sediments with significantly different chemical characteristics to those presently within the considered area of Northern Switzerland.

There are no published K_d values for radioelements that could be released from a Swiss repository for HLW and LLW/ILW, on the soils and lake/river sediments of Northern Switzerland, under chemical conditions in shallow groundwater, surface water and soil porewaters. Furthermore, K_d values reported for these radioelements in published literature for similar solids and waters to those found in the biosphere of Northern Switzerland are often not accompanied by:

- Full details of the conditions under which they were obtained.
- Evidence that equilibrium was attained between the element in solution and on the solid when the element's concentrations in the aqueous phase and on solid phase were measured.
- Evidence that sorption is in fact controlling the uptake of the element by the solid and not precipitation and/or co-precipitation of the element, such that aqueous concentration is solubility limited.

For these reasons, published K_d values are not recommended directly for use in Nagra's SGT E3 biosphere modelling. Instead, the approach is to specify K_d values for each element based on:

1. published K_d values obtained for solids and aqueous chemical conditions as close as possible to those present in the biosphere of Northern Switzerland
2. the calculated aqueous chemical speciation of each element of interest across the range of chemical conditions in shallow groundwaters, lake waters and river waters and soil porewaters in Northern Switzerland

3. theoretical considerations that point to the relative magnitudes of sorption within groups of chemically similar elements and between groups of chemically different elements, and
4. theoretical considerations that point to differences in sorption between different sediment types

Recommendations, and associated justifications, for K_d values are provided in Chapter 4.

1.3.3 Achieving consistency among selected K_d values

Many factors affect sorption and, therefore, there is inevitably uncertainty about the relative variations in sorption between different elements under any given set of physical and chemical conditions. However, several general principles suggest relative variations in sorption.

- Elements that form differently charged aqueous species under a given set of conditions will tend to sorb differently (e.g. a metal that forms a negatively charged species will sorb differently to another element that forms a positively charged species under the same conditions).
- Hydroxo-complexes of metal ions tend to sorb strongly by surface complexation.
- Hydrated metal ions with similar first hydration constants and similar sizes tend to sorb similarly.
- As pH increases from very acidic values to very alkaline values the charges on solid surfaces tend to change from being positively charged to being negatively charged. Therefore, an element that forms a negatively charged aqueous species at low pH will tend to sorb more strongly than an element that forms a positively charge aqueous species at the same pH; the former will be attracted to the surface, while the latter will be repulsed. The reverse relationship holds at high pH.
- Sorption by ion exchange is sensitive to the composition and salinity of the solution. Higher salinities and/or concentrations of elements that may compete for exchange sites with an element that sorbs by ion exchange will reduce sorption.
- Sorption by surface complexation will generally be insensitive to the salinity of the solution.

Based on these principles and published sorption data, similarities and differences between different elements considered by this report are summarised in Tab. 1-1. The characteristics of each element that influence sorption, and the resulting recommended K_d values are described in detail in Chapter 4.

Tab. 1-1: Summary of similarities and differences in likely sorption characteristics within and between groups of elements that have similar chemical characteristics, or between individual elements

Elements	Relevant redox states	Similarities/differences in/ between element groups	Justification/caveats
Na, K, Cs	+I	• Cs > K > Na	• All sorb by cation exchange. • Relative order follows the Hoffmeister series. • Published measurements of cation exchange on sediments (e.g. Liu et al. 2004, Kaplan 2016).
Ca, Sr, Ra	+II	• All > K and Na • Ca < Cs • Ra > Sr ≥ Ca	• All sorb by cation exchange. • Higher charge than alkali metals. • Experimental data suggest sorption order. • Some ambiguity in order of sorption for Sr and Ca – some data shows greater sorption for Sr, other data suggests similar sorption for both elements.
Sm, Ho, Ac, Am, Cm, Cf	+III	• All sorb similarly • Expect sorb > alkali/alkaline earth metals	• All sorb by surface complexation. • All are trivalent and readily hydrolyse. • There are differences in speciation as a function of pH, which are expected to be reflected in differences in K_d.
Al	+III	• Expect sorb > alkali/alkaline earth metals • Sorption unlikely to control aqueous concentrations – likely dissolution/precipitation reactions	• Sorbs by surface complexation. • Trivalent and readily hydrolyses.
Zr, Th, Ti	+IV	• Similar sorption to Group IIIa elements • Similar sorption within the group over most of the pH range, Th likely sorbs less strongly than Zr at low pH • Oxides/hydroxides of these elements may also limit dissolved concentrations	• Th and Zr sorb by surface complexation. • All are tetravalent and tend to hydrolyse. • Over most of the relevant pH and Eh ranges all form neutral aqueous species. • At pH < 6, Th could be cationic species, but Zr would form a neutral species; cationic Th species would be repulsed by +ve solid surfaces. • No sorption data exist for Ti, and the similarity to Zr and Th is uncertain, but based on similar oxidation state and occurrence in together in some minerals.

Tab. 1-1: Cont.

Elements	Relevant redox states	Similarities/differences in/ between element groups	Justification/caveats
Fe, Ni, Co	+II, +III (Fe), +II(Ni) +II(Co)	• Sorption of Fe, Ni likely similar under reducing condition s (both +II) • Ni likely < Fe under oxidising conditions (Fe +III) at pH << 7, but at higher pH Fe will likely be solubility-limited • Ni likely ≤ Co, but material dependent	• Ni and Fe(II) sorb by a combination of cation exchange and surface complexation, the latter becoming more important at higher pH. • Ni and Fe speciate similarly across the relevant pH range under reducing conditions (both +II). • The aqueous chemistry of Fe(III) is very different to that of Fe(II) and Ni(II), with Fe(III) being much less soluble than Fe(II) and more readily hydrolysed. • Co and Ni both likely uncomplexed divalent cations in solution under relevant conditions, both 1st row transition elements (next to each other in the Periodic Table). • Limited experimental data for Co and Ni.
C	-IV	• Sorption unlikely to control aqueous concentrations – likely dissolution/precipitation reactions of carbonate phases	• Notional K_d calculated assuming 1% of soil carbon available for isotopic exchange, dividing this by the aqueous concentration of inorganic carbon. • Such a K_d is only a means of representing C partitioning between solid and aqueous phases by an assessment model.
Si	+IV	• Sorption unlikely to control aqueous concentrations – likely dissolution/precipitation reactions	• Notional K_d calculated assuming 1% of soil silica is soluble and dividing this by the aqueous concentration of silica. • Such a K_d is only a means of representing Si partitioning between solid and aqueous phases by an assessment model.
Sn	+II, +IV	• May sorb more strongly than Pb	• Sorbs by surface complexation. • Likely in the Sn(IV) form over the relevant range of pH and Eh, and strongly hydrolysed. • Sn has a smaller covalent radius and larger first hydration energy than Pb, so Sn may sorb more strongly, which is supported by the limited available data (e.g. Bradbury & Baeyens 2009 and references therein).
Pb	+II	• May sorb less strongly than Sn.	• Sorbs by surface complexation. • Pb has a larger covalent radius and smaller first hydration energy than Sn, so Pb may sorb more strongly, which is supported by the limited available data (e.g. Bradbury & Baeyens 2009 and references therein).
Nb	+V	• Similar to Zr at pH < 5 • Likely Nb < Zr at higher pH	• Sorbs by surface complexation. • Very strong tendency to hydrolyse. • At pH < 5 both Zr and Nb form neutral hydroxo species. As pH rises Zr remains in neutral form, Nb forms increasingly -ve species.

Tab. 1-1: Cont.

Elements	Relevant redox states	Similarities/differences in/ between element groups	Justification/caveats
Tc, Mo	+IV, +VII (Tc) +VI (Mo)	• Tc and Mo likely to sorb similarly under oxidising conditions (Tc +VII, Mo +VI) • Under reducing conditions (Tc +IV) and alkaline pH, Tc > Mo • Under reducing conditions (Tc(IV) and acidic pH, Mo > Tc	• Sorb by surface complexation. • Under oxidising conditions, the Tc and Mo speciate similarly (pertechnate anion (TcO_4^-) and molybdate ion (MoO_4^{2-}) respectively). • Published data suggest both sorb weakly over relevant pH and Eh conditions, but reduced Tc sorbs more strongly.
Hg, Pd	0, +II	• Hg and Pd likely to sorb similarly in oxidising and reducing conditions in the absence of organics • Potentially Hg sorbs more in organic-rich systems, though little data are available for Pd	• Over relevant ranges of pH and Eh, Pd will speciate similarly to Hg. Pd and Hg also have similar covalent radii and first hydration constants. • Hg forms complexes with organic ligands. • There are few data for Pd complexing with organic ligands.
Ag	0, +I	• Similar to Na under oxidising conditions (Eh > 0.45 V) • Under reducing conditions Ag < Na	• Under oxidising conditions (Eh > 0.45 V) Ag and Na have similar speciation (both dominantly uncomplexed +1 cations). Under more reducing conditions Ag possibly in neutral solid form (redox 0).
Se	-II, 0, +IV, +VI	• Under oxidising conditions (+VI states stable) or moderately reducing (+IV state) and pH > 8 may be like Mo • Se > I^- • Se(IV) > Se(VI)	• Sorbs by surface complexation. • Complex chemistry reflecting several redox states being possible. • Similarity with other elements uncertain. • Selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are similarly charged to molybdate (MoO_4^{2-}). • Experimental data suggest sorption of Se(IV) > Se(VI). • Experimental data suggest sorption Se > I.
Po	0, +II, +IV	• Oxidising conditions (+IV state stable) similar sorption to U (+VI) • Reducing conditions (0 state stable) Po < U	• Po sorbs by surface complexation. • Under oxidising conditions (+IV state stable) Po progressively hydrolyses with increasing pH, like U. • Under reducing conditions (0 state) solid Po may be stable (but does not occur naturally in isolation, being found in U-ores), but U likely forms species that are cations (lower pH) neutral and hydrolysed (near-neutral pH) or anions (higher pH).

Tab. 1-1: Cont.

Elements	Relevant redox states	Similarities/differences in/ between element groups	Justification/caveats
Pa	+V (possibly +IV, but unlikely)	• At 4.5 < pH > 5.5 sorbs similarly to Zr • At pH < 4.5 likely Pa < Zr • At pH > 5.5 sorbs similarly to Th • At pH < 5.5 likely Pa > Zr	• Sorbs by surface complexation. • Pa, Th and Zr strongly tend to hydrolyse. • At pH > 4.5 both Pa and Zr are predicted to form neutral hydroxo species ($PaO(OH)_3$, and $Zr(OH)_4$ respectively). • Similarly at pH > 5.5 both Pa and Th are predicted to form neutral hydroxo species (Th forms $Th(OH)_4$). • At pH < 4.5, Pa is predicted to cationic (successively $PaO(OH)_2^+$, $Pa(OH)^{2+}$ and PaO^{3+} with decreasing pH), but Zr will remain in a neutral species ($Zr(OH)_4$). • At pH < 5.5 Th will be in the form of cations with higher positive charge than Pa species (successively $Th(OH)_2^{2+}$, $ThOH^{3+}$ and Th^{4+} with decreasing pH).
U	+IV, +VI	• U sorbs similarly to Np *except* • In carbonate-free, moderately reducing water (U(VI)dominated) at pH > 7, U(VI) < Np(V) or U(VI) < Np(IV)	• U sorbs by surface complexation. • Experimental data show U(IV) sorption > U(VI). • For relevant Eh and pH, U and Np speciate similarly, except: (1) Np(V) remains cationic at pH > 7, but U(VI) is neutral at pH 7 and as pH increases forms increasingly negative anionic species; and (2) under moderately reducing conditions (U(VI) and Np(IV) dominate) Np forms neutral $Np(OH)_4$, but U(VI) forms anionic species. As pH increases above neutral, charged solid surfaces become increasingly -ve.
Np	+IV, +V	• Np sorbs similarly to U *except* • In carbonate-free, moderately reducing water (U(VI) dominate) at pH > 7, Np(V) > U(VI) or Np(IV) > U(VI) • Np(IV) sorbs more strongly than Np(V)	• Np sorbs by surface complexation. • Experimental data show Np(IV) sorption > Np(VI) sorption. • See justification for U above.
Pu	III, IV, V	• Pu (III) and Pu(IV) > Pu(V)	• Pu sorbs by surface complexation. • Experimental data show Pu(III) or Pu(IV) sorb more strongly than Pu(V).
Cl	-I	• Weakly to non-sorbing	• Cl is mostly Cl^- and likely sorbs only weakly at low pH when metals show little hydrolysis and solid surfaces are +ve. • Experimental data support only week sorption at most.

Tab. 1-1: Cont.

Elements	Relevant redox states	Similarities/differences in/ between element groups	Justification/caveats
I	-I, +V	• Weakly sorbing, but I > Cl • I(-I) < I(+V)	• I^- behaves like Cl^-. • Experimental data show sorption of iodate (IO_3^-) > iodide (I^-). • I binds to organic compounds, but maybe not by sorption. Maybe sorption onto Fe-oxides/oxyhydroxides.

Some of the considered elements may have dissolved concentrations that reflect the solubility of solid phases (i.e. they are "solubility-limited") in the considered environments. This is particularly likely in the cases of Ca and Si, which could be solubility-limited by a solid carbonate phase (most likely calcite) and a silica phase (most likely quartz), respectively. In such cases, the experimentally determined equilibrium ratio between concentration of the element in the solid phase and the concentration of the element in the coexisting aqueous phase can be treated as a K_d in an assessment model ***provided*** that the solid and aqueous materials are the same, and under the same conditions, as in the experiment. This approach was adopted in Tits & van Dorp (1999).

This report considers only sorption parameters for the element in solution and does not distinguish between different isotopes of each element. Most of the considered elements will be present naturally in the soils and sediments considered, but the isotopes or ratios of isotopes comprising these natural occurrences will be different to those of the elements originating in the waste repository. The naturally occurring element may consist of higher proportions of stable isotopes or be entirely composed of stable isotopes. Thus, isotopic exchange between an element in the aqueous phase that originates in the wastes, and the same naturally occurring element in the solid phase, may dilute the aqueous phase concentration of a radioisotope considered by the biosphere assessment. If it occurs, isotope dilution is likely to be of most significance for Cl-36, I-129, C- 14, Ca-41, U-235. However, it is outside the scope of the work described in this report to consider this process.

2 Chemical environment description

2.1 Purpose of chemical environment descriptions

This Chapter briefly summarises the chemical conditions present in soils, river, lake and shallow groundwater in Northern Switzerland (Fig. 2-1). The purpose is not to give an in-depth interpretation of the compiled data, but instead to provide a basis for determining the plausible variations in chemical speciation of elements in the different environments. Knowledge of these variations can be used to estimate generally how sorption of each element will vary in the different environments. The most important chemical characteristics of the environment that will influence sorption are:

- variations in pH of soil porewaters, river waters, lake waters and shallow groundwaters, which will influence the chemical speciation of most elements
- variations in Eh in the soil porewaters, river waters, lake waters and shallow groundwaters of the different compartments, which will influence the chemical speciation of redox-sensitive elements
- variations in the concentrations of ligands that might potentially form complexes with certain elements, especially Cl^-, HCO_3^-, and SO_4
- variations in the contents of sorbents in the different soils, river and lake sediments of the area

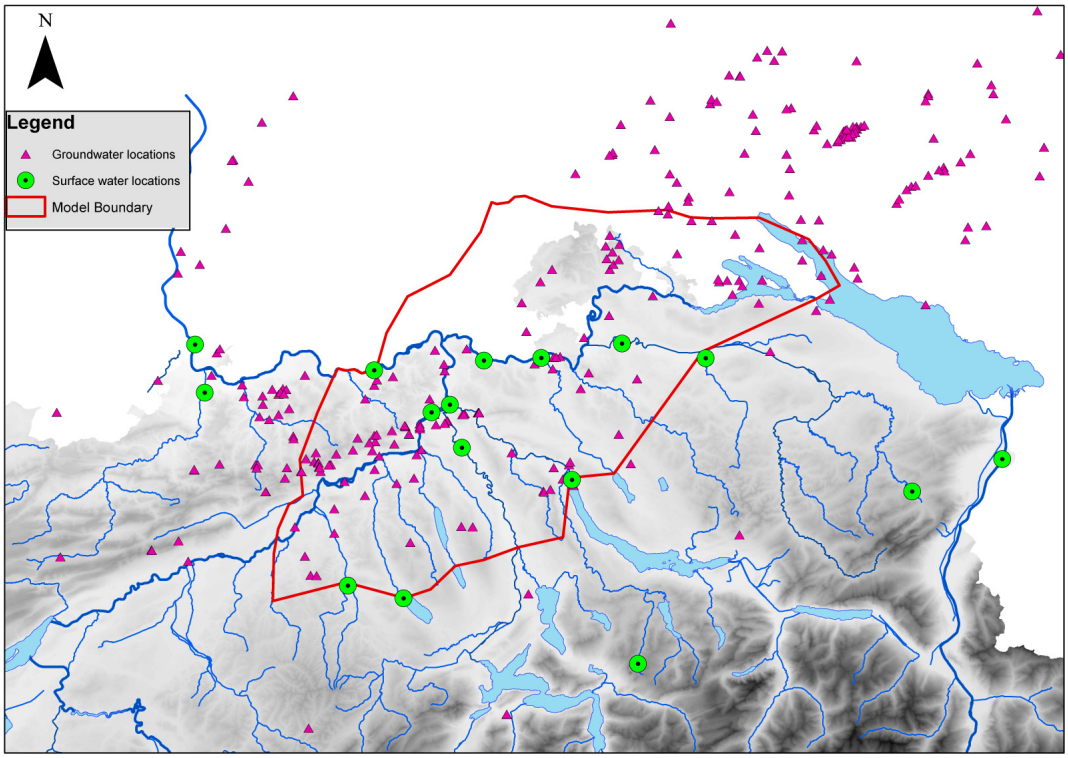

Fig. 2-1: Defined boundary for Northern Switzerland for the data compilation

Note, that some groundwater locations are situated in southern Germany to enable observations made along relevant groundwater flow-paths to be taken into account. Moreover, some lake data are also from lakes located outside the defined boundary. This was done to obtain a larger data set, representing a larger range of environmental conditions.

2.2 Soils

Soil data are compiled from different sources. A compilation has been made of properties (pH, organic matter etc.) of agricultural soil (grassland, arable land, fruit/wine/vegetables production) at 64 standard locations in Northern Switzerland. The compiled data were obtained from the Swiss Soil Monitoring Network (NABO). NABO records the temporal development of the quality of Swiss soils based on chemical, physical and biological soil properties. A long-term monitoring system of around 110 sites spread across Switzerland is used to monitor soils undergoing normal management.

An important module of NABO is the National Soil Information System NABODAT, which brings together soil data from different sources, harmonises them and makes them available for further needs. Currently, around 25.000 locations are included. These data are combined with information from gridded soil information that uses state-of-the-art machine learning methods to map the spatial distribution of soil properties (e.g., Hengl et al. 2017). Data for seven different soil depths (0 cm (surface), 5 cm, 15 cm, 30 cm, 60 cm, 100 cm, 200 cm) exist. However, based on a first pre-processing analysis, the first depth (0 cm; surface) is excluded from the compilation made in this work because it seems to be too strongly impacted by artificial processes and would not represent natural soils conditions. Data were extracted only for Northern Switzerland.

Based on the data compilation, soil characteristics are summarised in Tab. 2-1.

Tab. 2-1: Summary of soil characteristics in Northern Switzerland

Bottom depth (cm)	**Available soil water capacity (volumetric fraction) until wilting point**			**Proportion of clay particles (< 0.002 mm)** (%)			**Proportion of silt particles (≥ 0.002 mm and ≤ 0.05 mm)** (%)			**Proportion of sand particles (> 0.05 mm)** (%)			**pH**		
Interval	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
15	19	27	37	5	19	32	25	40	53	22	41	65	3.9	5.7	7.1
30	18	24	34	3	20	35	24	40	54	18	40	67	4.2	5.9	7.1
60	17	23	32	3	21	37	24	39	53	18	40	67	4.6	5.8	7.2
100	14	22	31	0	22	41	18	34	47	21	44	77	4.7	5.9	7.4
200	13	21	28	0	22	41	18	33	46	23	45	76	4.7	6	7.4

The spatial distributions of soils with different textures across Northern Switzerland are shown in Fig. 2-2.

The 64 agricultural soils show widely varying clay contents in the ploughed layer (upper 20 cm). About 72% of these soils have a clay content of > 15%, of which 44% have more than 25% clay (mean clay content: 22%). At 42 standard locations where animal fodder is grown, the shallowest soils have clay contents between 6 and 59%, with an average of 21% (not shown in Tab. 2-1).

None of the soils in the considered area of Northern Switzerland would be classified as “organic rich soils” according to the classification of the Food and Agriculture Organisation of the United Nations (FOA 2015). According to this classification, organic soils have > 12 wt.-% organic carbon and 20 wt.-% organic matter. In contrast, in Northern Switzerland, the average organic matter content of the 64 soils is 6.4 wt.-%, when the most organic-rich soils are included. In general, the organic matter content lies between 1.7 and 10 wt.-%, with a tendency towards lower soil organic matter content in arable land.

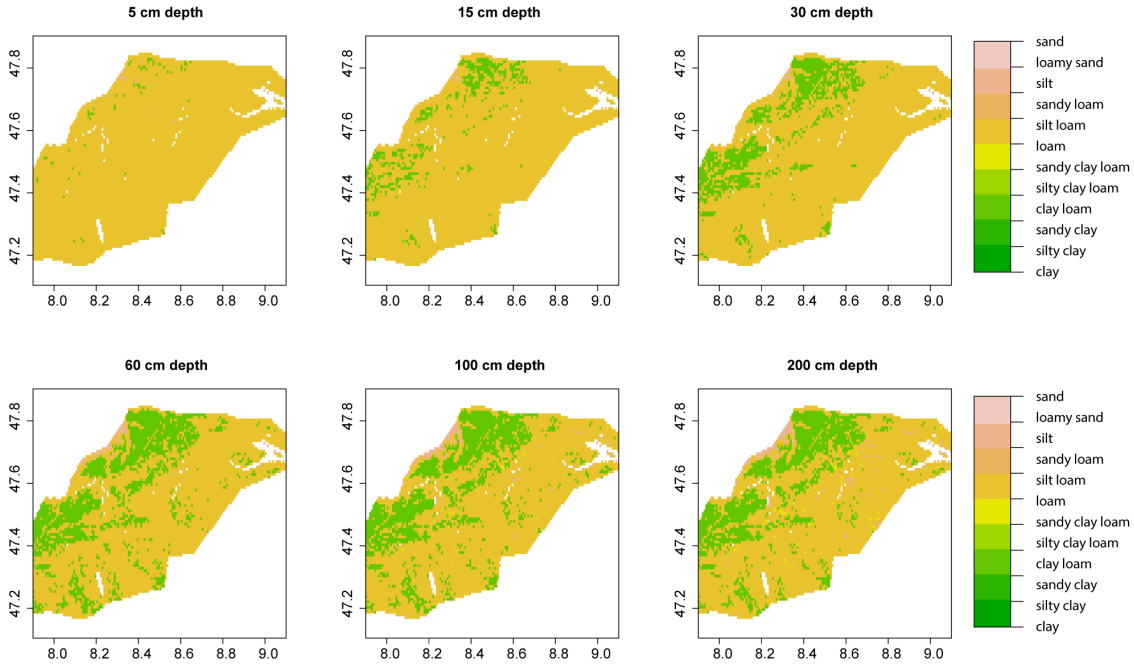

Fig. 2-2: Soil texture classes for six different soil depths

Soil texture classification is based on the United States Department of Agriculture (USDA) system. Soil textural class names are determined by the relative mass percentages of sand, silt, and clay-sized particles in the soil.

It is estimated that soils with organic matter > 10 wt.-% cover ca. 0.7% of the country's land surface, and only ~ 5% for Northern Switzerland. The extensive areas of these relatively organic-rich soils that were previously identified in wide valley bottoms are now recognised to be more fragmented.

The pH of the soils ranges from 3.9–7.4 (mean pH 5.7). Of the 64 soils included:

- 20% are very acid to acid (pH < 4.3, 4.3 – 5.0).
- 47% are slightly acid (pH 5.1 – 6.1).
- 20% are neutral (pH 6.2 – 6.7).
- 13% show a slightly alkali pH (6.8 – 7.6).

Excluding the grass soils, the mean pH is 6.0 (range 4.5 – 7.2).

Soils in the Jura region may have relatively high pH's (up to 7.2 on agricultural soils), due to chalky rocks of the Jura hills.

Most cultivated soils have a pH between 4 and 9, but a pH below 3 and above 10 can be measured in acid sulphate soils or sodic soils, respectively (Brady & Weil 2009). Generally, pH and Eh are negatively correlated in soils (Bohrerova et al. 2004, van Breemen 1987), but both Eh and pH can greatly vary over very short distances (Hinsinger et al. 2009, Yang et al. 2006).

Soil Eh fluctuates normally between −300 and +900 mV. Waterlogged soils have an Eh below +350 to +250 mV and dry soils above +380 to +400 mV.

2.3 Rivers

The river waters in Northern Switzerland are all fresh and their compositions vary relatively little, with all waters showing generally similar proportions of major cations and anions (Fig. 2-3). Data for dissolved inorganic carbonate, alkalinity or dissolved carbonate are not available. However, balancing charge using only dissolved carbonate species (and taking into account of reported pH), the waters are all deduced to be Ca-HCO_3 dominated.

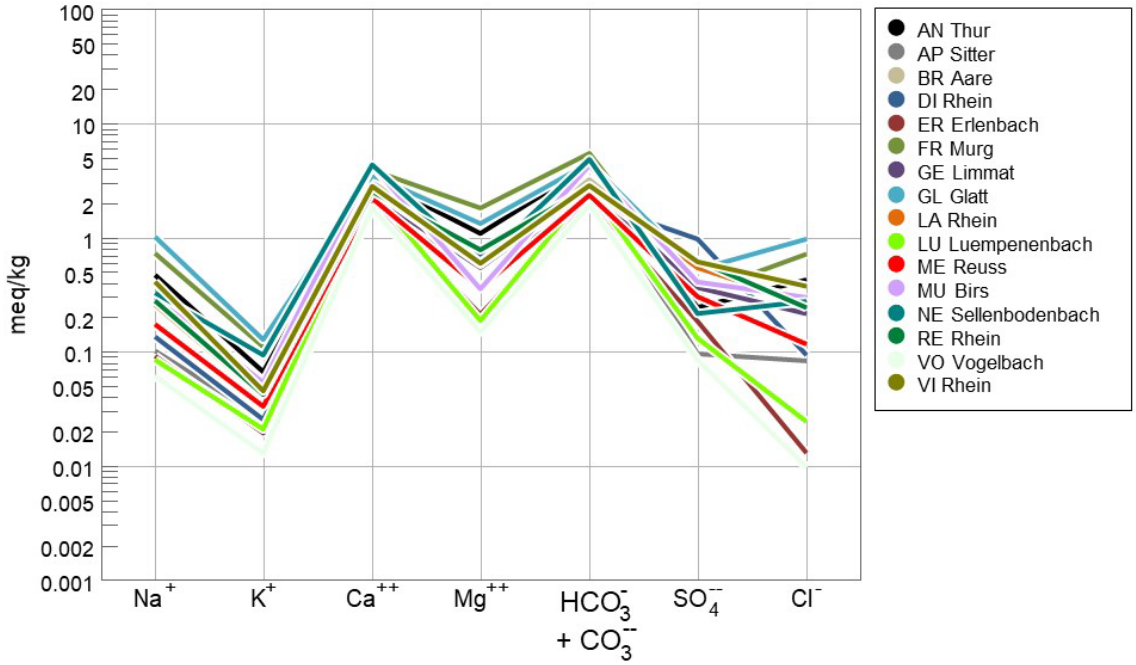

Fig. 2-3: Schoeller plot showing the concentrations of major constituents in Northern Swiss river waters

The total carbonate concentration (HCO_3 + CO_3^{2-}) is calculated assuming that the charge imbalance in the reported water composition is entirely due to carbonate.

The overall pH range of these river waters is from slightly acid (pH = 6.25) to slightly alkaline (pH = 8.73), with the averages of pH values for waters in each river all being slightly alkaline (pH = 7.63 to 8.35). The waters are all in contact with the atmosphere and, therefore, will have redox states buffered by the atmosphere.

The composition of river bed sediments in Northern Switzerland is variable, both spatially and temporally, reflecting, for example, seasonal variations in water flows and organic productivity. The main characteristics are summarised in Tab. 2-2.

Compared to soils, the river bed sediments tend to have higher clay contents, and organic contents.

Tab. 2-2: Summary of river bed sediments in Northern Switzerland

Parameter	**Mean**	**St.dev**
Organic C (wt.-%)	5.6	1.59
Clay content (vol.-%)	35.7	5.9
Sand content (vol.-%)	56	15
Silt content (vol.-%)	8	6
Na^+ (mg/kg)	534	106
K^+ (mg/kg)	81'116	1'133
Mg^{2+} (mg/kg)	10'256	1'232
Ca^{2+} (mg/kg)	649'020	17'100
Redox potential (Eh, mV)	Always positive, but value depends on the discharge rates (+5 - +260 mV)	
pH	8.4	0.6

2.4 Lakes

Like the river waters described in Chapter 2.3, the lake waters of Northern Switzerland are all fresh and have Ca-HCO_3 dominated chemistry, with relatively small variations in the proportions of major constituents between different lake waters (Fig. 2-4).

The reported pH spans a narrower range than the river waters, varying between pH = 7.8 and pH = 9. Like the river waters, the lake waters are all in contact with the atmosphere and, therefore, will have redox states buffered by the atmosphere.

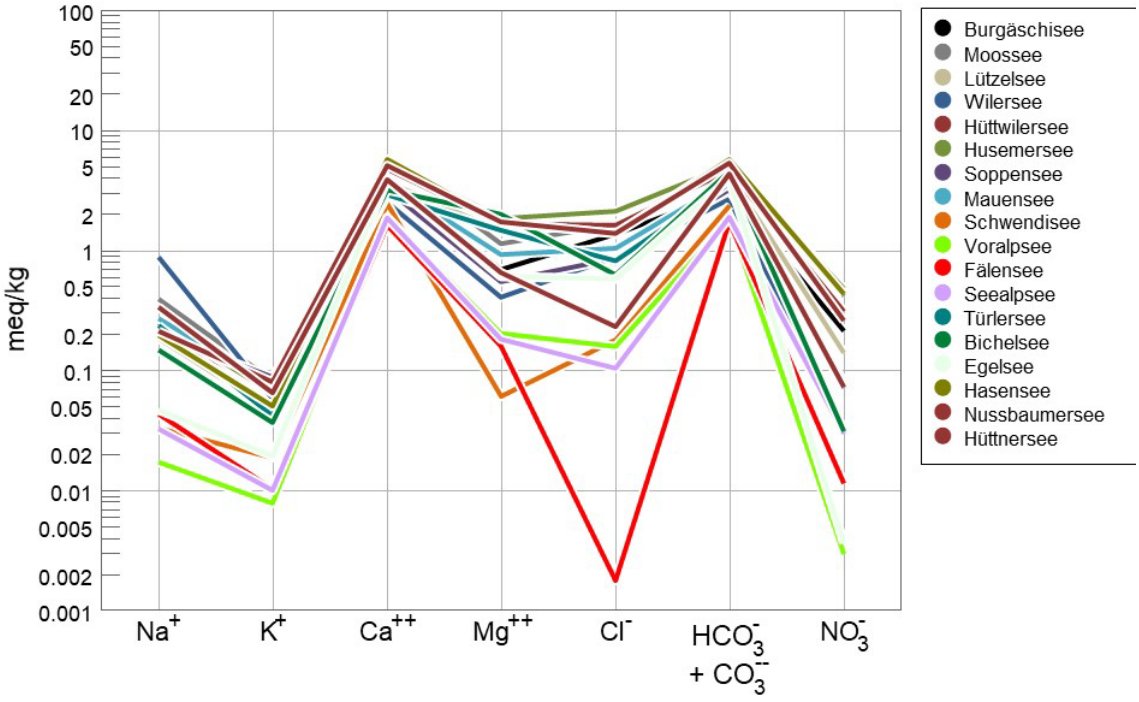

Fig. 2-4: Schoeller plot showing the concentrations of major constituents in selected Swiss lake waters

Note, some lakes are located outside the defined boundary for Northern Switzerland leading to a higher variability in hydrochemistry data. The dissolved carbonate (HCO_3^- + CO_3^{2-}) is calculated from the reported alkalinity and the Cl^- content is calculated to achieve charge balance.

The lake bed sediments have variable compositions (Fig. 2-5), presumably reflecting predominantly geological differences between the river catchments that drain into them. The concentrations of Ca and total inorganic carbon (TIC) vary in concert, and the molar ratio Ca/TIC is close to unity in all lake bed sediments. These observations suggest that variations in concentrations of Ca and TIC are caused to a large degree by different concentrations of calcite in sediments from different lakes.

The total organic carbon content of the lake bed sediments is a potentially significant influence on sorption and varies between 3 wt.-% and 18 wt.-%, with a mean of 6.6 wt.-%, similar to that observed in river bed sediments (Chapter 2.3).

The lake sediments are reducing, being oxygen-poor or even anoxic.

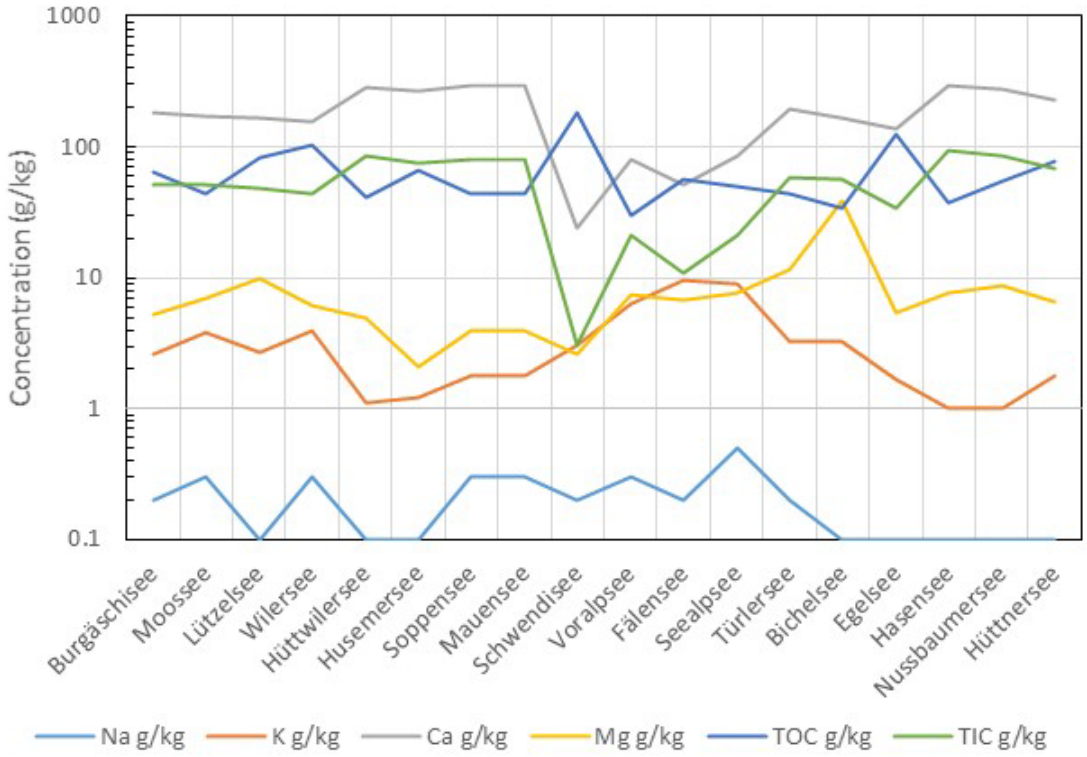

Fig. 2-5: Chemistry of lake bed sediments

2.5 Shallow aquifers

Groundwater characteristics are relevant to the present study because the shallow aquifer is represented by a compartment in the SwiBAC model; it receives potentially contaminated groundwater discharging from depth and may itself discharge into rivers or lakes and interact with the overlying soil compartments. Such shallow groundwater discharges would influence the chemical conditions within soils and river bed/lake bed sediments and thereby sorption within them.

In the considered area of Northern Switzerland, shallow aquifers range in age from Triassic to Quaternary (Tab. 2-3). These aquifers have widely varying lithological characteristics. Unconsolidated and lithified clastic aquifers, and carbonate aquifers (including ones that are karstified) occur in the area. However, consistent with the conceptual model for SwiBAC, only the unconsolidated Quaternary aquifers are relevant to the "local aquifer" compartment of the biosphere model; the other aquifers are relevant only if they contribute groundwater to the Quaternary aquifers, rivers, lakes or soils. Therefore, only the chemistries of shallow groundwaters in the various aquifers relevant to the biosphere modelling are considered, and groundwater compositions at depths > 150 m are not considered.

This report only concerns sorption in unconsolidated sediments that may compose unconsolidated shallow aquifers. Details of the shallow aquifers and the maximum depth for which water compositions were obtained are given in Tab. 2-3.

Tab. 2-3: Summary of rock formations penetrated by boreholes from which the compiled shallow groundwater compositions were obtained

For the OSM, OMM, USM as well as Deep karst in the Malm a further separation into shallow (s) or deeper (d) aquifer was carried out.

Unit	**Sub-unit**	**Max. depth of water considered** (m)
Quaternary aquifer	Clastic rocks, mainly molasses	60
	Gravel outside the valley floors, fluvioglacial deposits	60
	Gravel in the valley floors, recent river gravel	60
Tertiary aquifer	Upper freshwater molasse (OSM)	60 (s)
		103 (d)
	Upper seawater molasse (OMM)	70 (s)
		129 (d)
	Lower freshwater molasse (USM)	50 (s)
		100 (d)
Malm	Open karst	85
	Deep karst	Unknown (s)
		135 (d)
	Malm-sRhBo	Unknown
	Effingen Member	63
	Hauptrogengestein Formation/Birmenstorfer	Unknown
Lias		Unknown
Keuper	Region Rhine graben	59
Muschelkalk	Region Folded Jura	102
	Region Tabular Jurassic	119
	Rhine valley	100

Compared to the river waters (Chapter 2.3) and lake waters (Chapter 2.4) the aquifer waters show greater variability in both salinity and composition (Fig. 2-6, Fig. 2-7). Most waters are Ca-HCO_3 type, but Na-HCO_3 type, Na-Cl type, Na-SO_4 and Ca-SO_4 type also occur. The deepest Tertiary and Muschelkalk groundwaters are Na-Cl dominated. All the waters in the Keuper and Muschelkalk, except for the deepest Muschelkalk water, are SO_4-dominated.

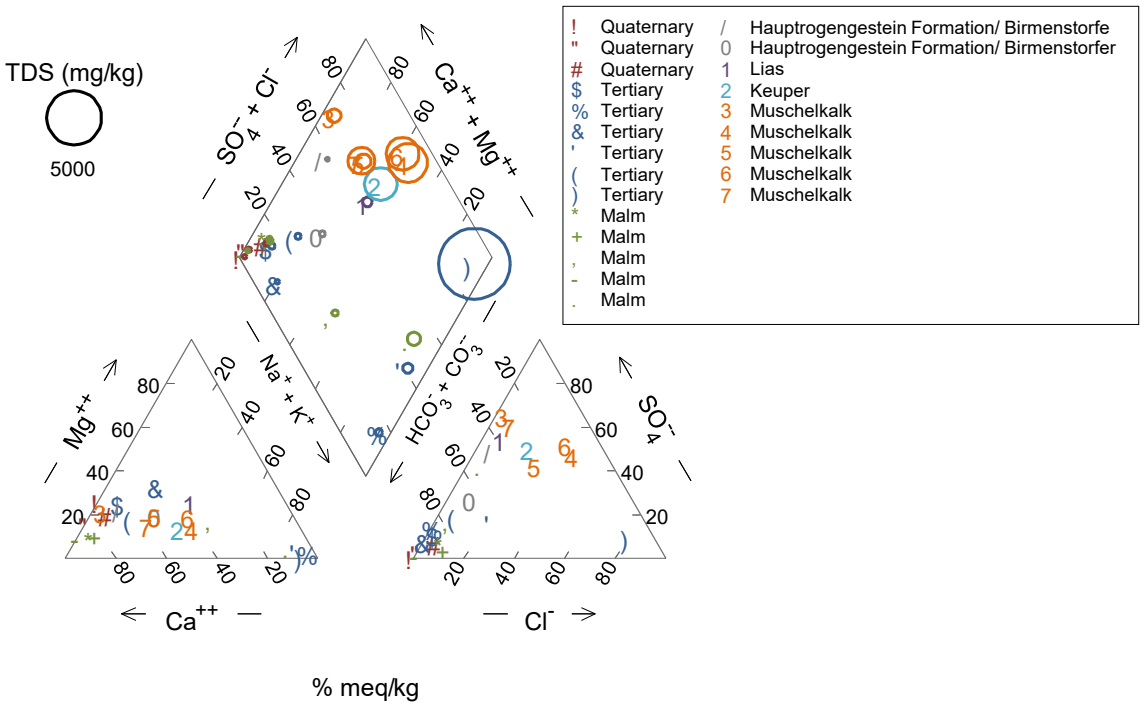

Fig. 2-6: Piper diagram showing the variation in major constituents of shallow groundwaters in Northern Switzerland

Carbonate content (HCO_3^- + CO_3^{2-}) was calculated to achieve charge balance.

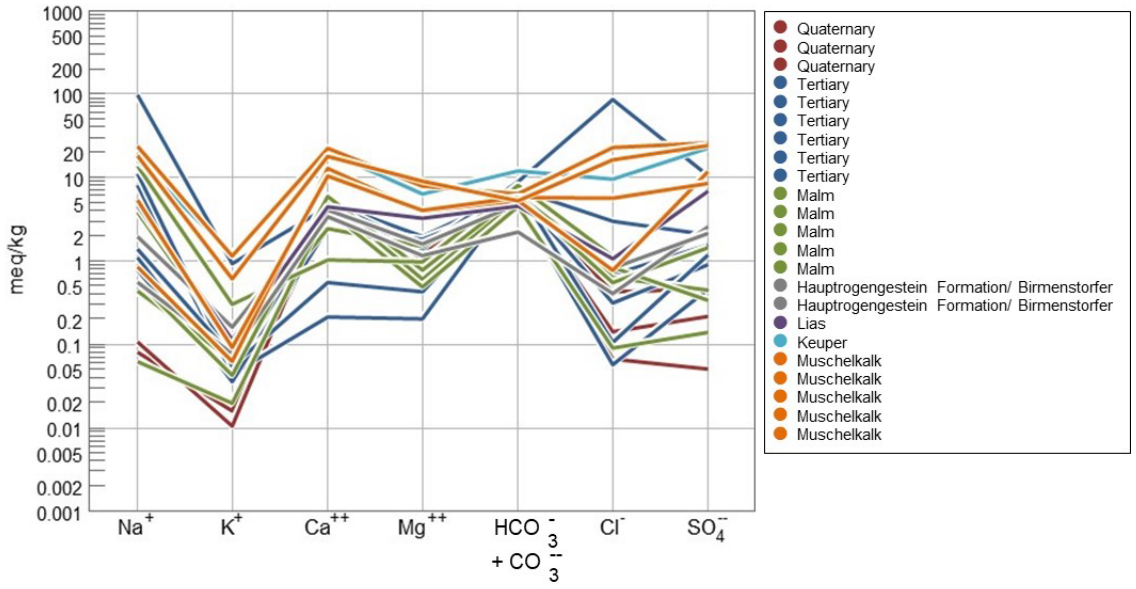

Fig. 2-7: Schoeller plot showing the concentrations of major constituents in Northern Swiss shallow groundwaters

The carbonate concentration (HCO_3^- + CO_3^{2-}) is calculated to achieve charge balance.

The reported pH of the shallow aquifer waters is mostly between 7 and 7.5 but varies between 6.5 and 8.9 (Fig. 2-8).

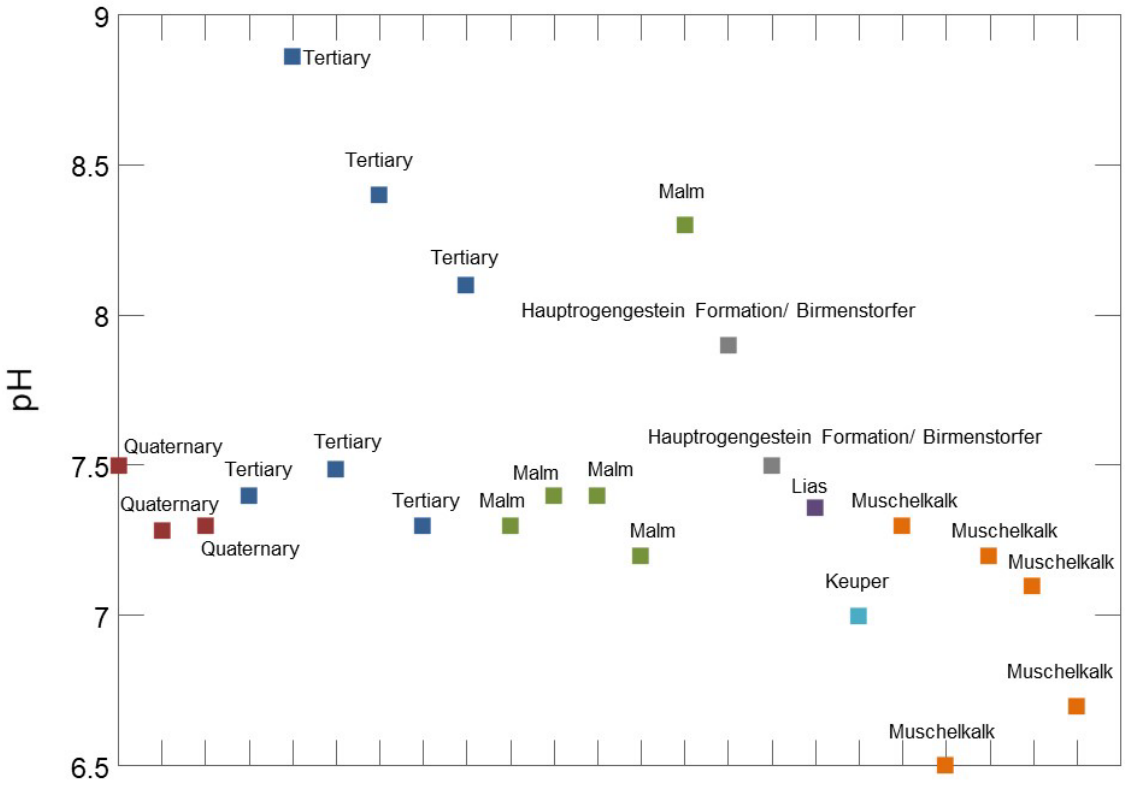

Fig. 2-8: Aquifer pH. Note, most relevant are the shallow Quaternary aquifer properties

However, other aquifers can contribute water to these Quaternary aquifers and also may discharge into rivers and lakes. Different aquifers are spaced equally along the X-axis.

The redox state of the shallow aquifer waters, as indicated by reported Eh, is oxidising to slightly reducing (Fig. 2-9). The redox potential of water is notoriously subject to perturbation during sampling and analysis, and it is unclear to what extent the reported Eh values represent *in-situ* conditions. Sampling- or analysis-related contamination with air would tend to result in analysed Eh being more positive (oxidising) than natural, in-situ, Eh.

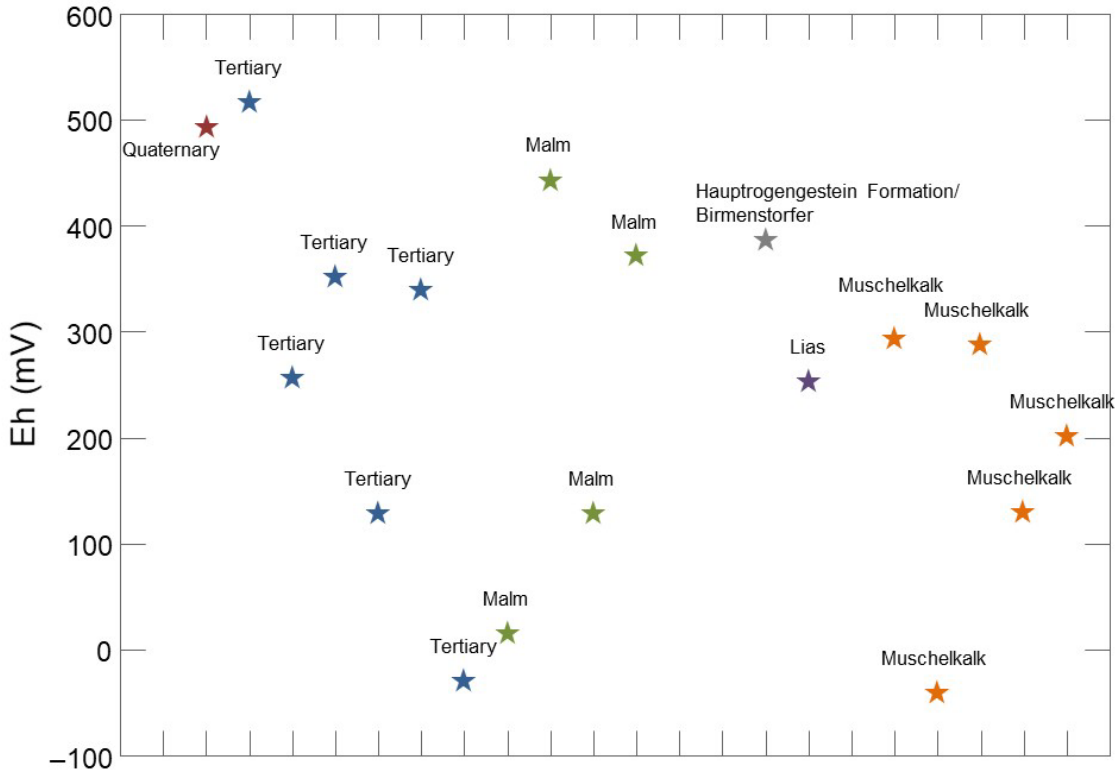

Fig. 2-9: Aquifer Eh. Note, most relevant are the shallow Quarternary aquifer properties

However, other aquifers can contribute water to these Quaternary aquifers and also may discharge into rivers and lakes. Different aquifers are spaced equally along the X-axis.

2.6 Summary of the environmental conditions

All the waters in the soils, and lake and river sediments are fresh, the dominant ions being Ca and HCO_3. Shallow groundwaters may be substantially more saline than the soil, lake and river waters, and have more variable compositions. River waters have total dissolved solid contents (TDS) of 161 mg/L to 774 mg/L, whereas lake waters have TDS ranging from 152 mg/L to 572 mg/L. In contrast shallow groundwaters have TDS in the range 360 mg/L to ~ 1'700 mg/L. Most shallow groundwaters are Ca-HCO_3 type, but Na-HCO_3 type, Na-Cl type, Na-SO_4 and Ca-SO_4 type also occur. The deepest Tertiary and Muschelkalk groundwaters are Na-Cl dominated. All the waters in the Keuper and Muschelkalk, except for the deepest Muschelkalk water, are SO_4-dominated.

The lake and river waters are oxidising as they are in contact with the air. However, the porewaters in the lake and river bed sediments are likely to be reducing, at least locally where they contain organic matter. The reported pH range for porewaters in river bed sediments is narrower than the pH range reported for river water.

The ranges of pH and redox conditions in the considered waters of Northern Switzerland relevant to the compartments included in SwiBAC are shown in Fig. 2-10. This figure also shows combinations of Eh and pH for each kind of compartment included in SwiBAC.

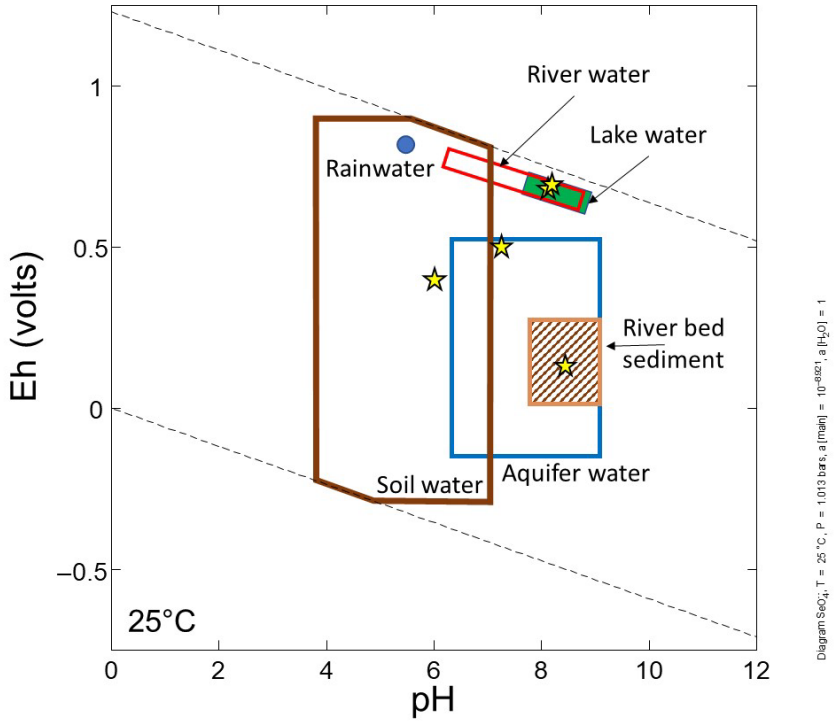

Fig. 2-10: Summary of ranges of reported pH and Eh for soil and sediment porewaters, river water, lake water and shallow aquifer water in Northern Switzerland

Yellow stars represent reference pH-Eh values for which K_d values are recommended for use in the biosphere model (see Chapter 4). These values and their rationale are given also in Tab. 2-4.

Tab. 2-4: Values of Eh and pH in different compartments of the biosphere model (also plotted as yellow stars in Fig. 2-10)

Compartment	**pH**	**Eh(V)**	**Reason**
River water	8.11	0.68	Typical values for the river Rhine (as a reference system) in Northern Switzerland
Lake water	8.2	0.7	Typical river lake water characteristics for Lake Zurich
River bed sediment (River bed water)	8.4	0.13	Typical river bed sediment characteristics for Lake Zurich
Aquifer	7.25	0.5	Typical values from Quaternary aquifers in Northern Switzerland (see also Fig. 2-8 and Fig. 2-9). Shallow aquifer in Northern Switzerland represent typically Quaternary aquifers and these aquifers are represented by a compartment in the SwiBAC model and may discharge into rivers or lakes and interact with the soil compartments. Such shallow groundwater discharges would influence the chemical conditions within soils and river bed/lake bed sediments and thereby sorption within them.
Soil water	6	0.4	Typical values for agricultural soils (excluding grass soils) obtained from the Swiss Soil Monitoring Network (NABO). These reference data fit very well with the mean values of gridded soil information, which use state-of-the-art machine learning methods to map the spatial distribution of soil properties (see also Tab. 2-1).

3 Overview of reviewed literature

The review covered both peer-reviewed papers and public-domain reports produced by organisations such as radioactive waste management organisations and research agencies. The focus was on literature published since 1999, when Nagra's previous biosphere sorption database in (Tits & van Dorp 1999) was developed. However, some literature sources from before this date have been consulted where they:

- contain the only available data for a particular element
- can be used to support recommendations of K_d values under conditions different to those considered in Nagra's previous sorption database, in (Tits & van Dorp 1999)
- where they have been used as a basis for a post-1999 compilation of sorption data and need to be consulted to understand the relevance of the compilation

When undertaking the literature review, care was taken to access only sources that contain data likely to be relevant to the chemical conditions of interest to the present study (i.e. those associated with soils, sediments, lakes and streams in Northern Switzerland). However, it proved challenging to determine confidently that reported data were obtained under the relevant conditions. Published references commonly do not report full details of the water chemistry, solid phases and experimental conditions (notably pH and redox conditions) under which data were obtained. Additionally, in practice, most published experimental studies of sorption do not distinguish between the various sorption mechanisms, or even between sorption and co-precipitation or precipitation. Instead, such studies often report distribution coefficients for species of interest, usually based on measuring aqueous concentrations of the species in the absence and presence of a solid of interest (either a single phase or an assemblage of phases such as a soil or a rock). There is commonly some uncertainty about whether a reported experimental study has actually investigated sorption or some other solid-liquid partitioning mechanism. Furthermore, there is often no good evidence provided that equilibrium between an element in the aqueous and solid phases had been achieved in the reported experiments.

For these reasons, reliance has not been placed on any single literature source. Instead, multiple sources have been considered for sorption of each element, and reported K_d values that appear anomalous (see also discussion in Chapter 1.3.3) have been disregarded when recommending K_d values.

The consulted literature sources and the ranges of K_d values reported in them are given in Appendix A.

4 Selection of sorption parameter (K_d) values

4.1 Assigning K_d values to sediment types

The SwiBAC biosphere model to be used in SGT E3 subdivides the biosphere into several compartments, between which transfers of radionuclides are calculated (generally consistent with Walke & Keesman 2013). Each compartment contains a single kind of solid material (soil, unconsolidated aquifer sediment, river bed sediment or lake bed sediment) to which it is necessary to assign a K_d value.

In practice, there will be a continuous variation in sorption characteristics between different sediment types, reflecting the fact that textural and solid-phase characteristics do not change sharply between different types of material. The following pragmatic approach has been adopted for assigning K_d values for each element to each compartment, taking this variability into account.

1. Based on the review of soil and sediment characteristics described above, the soils and lake/river bed sediments and unconsolidated aquifers of Northern Switzerland are divided into three groups, the smallest number judged to be commensurate with representing differences in the main variables that represent sorption:
   a. fine grained, lower organic content (clay content ≥ 30 wt.-%, organic matter content < 5 wt.-%)
   b. fine grained, higher organic content (clay content ≥ 30 wt.-%, organic matter content ≥ 5 wt.-%)
   c. coarse low-organic content (clay content < 30 wt.-% and organic matter content < 5 wt.-%)

2. For each soil/sediment type, in the presence of each kind of reference water (Tab. 2-4), three K_d values are given:
   a. “Reference” value
   b. “Lower Guide” value
   c. “Upper Guide” value

The above tripartite classification of sediment types differs from that in the earlier K_d compilation of Tits & van Dorp (1999), where they defined three groups of soil/sediment as follows:

1. coarse-grained soils, which contain few particles with large surface areas per unit mass which contribute to sorption, i.e. the material is mainly sand and gravel; clay and silt content is less than 5%
2. fine-grained soils, which contain significant amounts of particles with large surface areas which are available for sorption, i.e. the material is more than 30% silt and clay, and
3. organic soils have an organic matter content of between 10 wt.-% and 30 wt.-% as well as a major proportion of fine-grained material

Thus, the coarse-grained soils defined by Tits & van Dorp (1999) contain much less clay than the coarse-grained low-organic content soil/sediment defined in the present work. On the other hand, the fine, organic-rich soils/sediments defined in the present work may contain much less organic matter than the organic soils defined by Tits & van Dorp (1999). These differences reflect the

different areas being considered by Tits & van Dorp (1999) (the Rhine Valley and Engelbergertal), and in the present work (Northern Switzerland around the three siting regions being considered in SGT E3).

Here, the "Reference" K_d value is one that is considered most appropriate for the reference conditions in Northern Swiss sediments and soils, in the presence of Northern Swiss shallow groundwater (aquifer water), lake water and river water and soil water (i.e. under the pH and redox conditions indicated by yellow stars in Fig. 2-10 and listed in Tab. 2-4).

The "Reference K_d" is suitable for use in "base case" biosphere calculations in SwiBAC. The "Lower Guide" and "Upper Guide" values, in contrast, are likely to lie towards the lower end and upper end, respectively, of the natural ranges of K_d values in these predominantly Northern Swiss environments. These "Lower Guide" and "Upper Guide" values are intended to represent the overall envelope arising from both uncertainty in available data and variability in sorption and are appropriate for use in sensitivity calculations carried out with the SwiBAC model.

While many factors influence sorption capacities of soils or sediments, very generally, greater sorption capacities are associated with smaller grain sizes (and hence higher specific surface areas), higher Fe-oxide/oxyhydroxide contents and higher clay contents. However, there is an inverse correlation between mean grain size and contents of clay and organic matter. Taking these characteristics together, for many radionuclides, sorption under a given set of conditions (temperature, pH, Eh, water composition) will increase between the three broad soil/sediment types in the following order:

Coarse low-organic content < fine-grained, low organic content < fine-grained higher organic content.

The cation exchange capacity (CEC) of a soil or sediment is linearly related to its sorption capacity, and hence K_d, when cation exchange is the dominant sorption mechanism (see Tits & van Dorp (1999) for justification). The CEC of a soil or sediment depends on the proportions of the different solid phases of which it is comprised and the CEC of each phase. Common solid phases are quartz, feldspar, phyllosilicates (e.g. smectite, kaolinite, illite, chlorite, which often dominate the clay (< 2 μm fraction), Fe-oxyhydroxides and organic matter. Quartz and feldspar have CEC values close to zero, but the other constituents may have widely varying CEC (Appelo & Postma 1994):

- Kaolinite 3 – 15 cmolc/kg (or meq/100 g)
- Montmorillonite 80 – 120 cmolc/kg
- Illite 20 – 50 cmolc/kg
- Chlorite 10 – 40 cmolc/kg
- Fe-oxyhydroxide up to 100 cmolc/kg, and
- Organic matter 150 – 400 cmolc/kg at pH 8

The soils of Northern Switzerland contain up to about 40vol.-% clay minerals (Chapter 2, Tab. 2-1). The detailed spatial variation in clay mineralogy is unknown, which precludes estimation of bulk soil CEC values from CEC values of separate minerals and their proportions. However, assuming that all clay is montmorillonite (which has the highest CEC among common silicate phases in soil), with a maximum CEC of 120 cmolc/kg, allows estimation of an upper bound on the CEC attributable to clay minerals. This approach implies that, in the absence of organic matter, the most clay rich soil would have a maximum CEC of about 50 cmolc/kg. A

similar approach can be used to estimate an upper bound on the CEC attributable to organic matter. Since the soils have a maximum of about 10 wt.-% organic matter, taking an upper CEC value for organic matter of 400 cmolc/kg gives a corresponding upper CEC value of about 40 cmolc/kg. These values are comparable with the maximum values measured in soils in the considered area (Fig. 4-1).

Considering the above criteria for distinguishing the different soil/sediment types, a "mid-range" fine-grained, lower organic content soil/sediment would contain 35 wt.-% clay and 2.5 wt.-% organic matter, while a "mid-range" fine-grained, higher organic content soil/sediment would contain 35 wt.-% clay and 7.5 wt.-% organic matter. Taking also mid-range CEC values for clay (60 cmolc/kg) and organic matter (275 cmolc/kg) gives CEC values of 28 cmolc/kg and 42 cmolc/kg for fine-grained, lower organic content soil/sediment and fine-grained, higher organic content soil/sediment, respectively. These estimated "mid-range" CEC values for the two groups of fine-grained soils/sediments defined for use in SwiBAC are comparable with the maximum CEC measured in soil from Northern Switzerland at depths at different depths (Fig. 4-1).

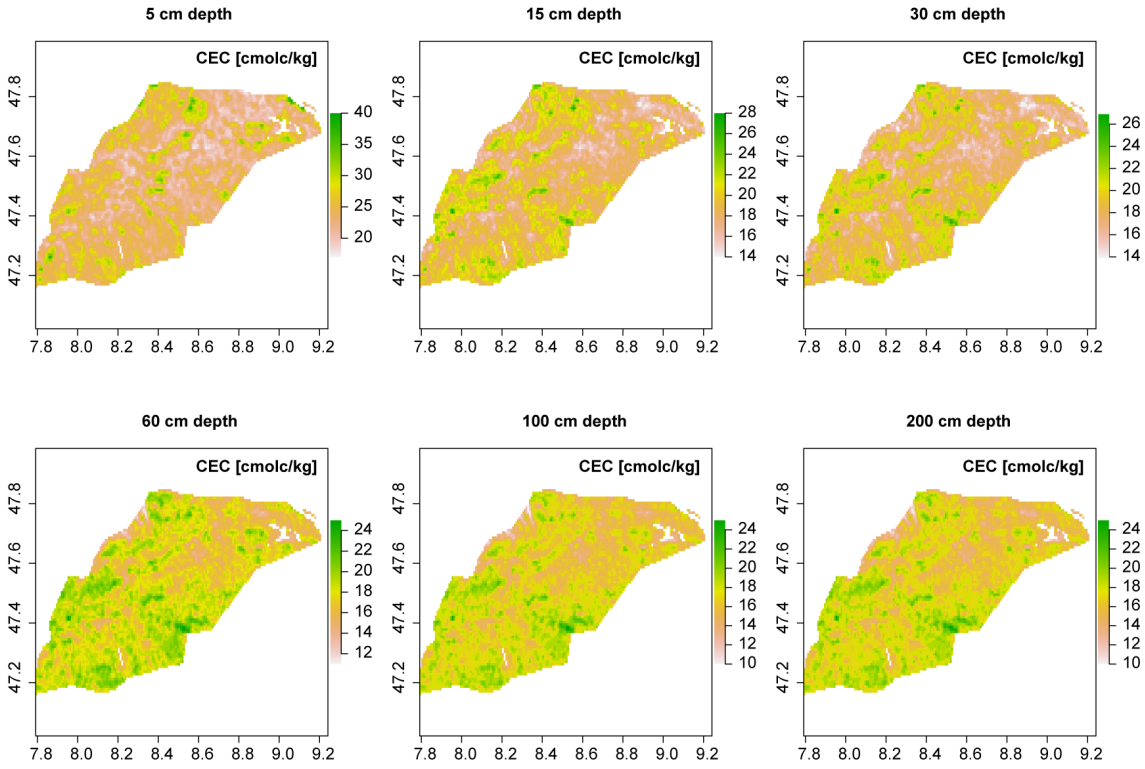

Fig. 4-1: CEC for six different soil depths. Cation exchange capacity (CEC) of soils in cmolc/kg at six different soil depths predicted using a compilation of soil ground observations

For the coarse, low-organic content soils/sediment a mid-range clay content would be 15 wt.-%. Assuming that the silt fraction does not sorb in the same way as clay, and using the same approach as for the fine soils/sediments, this clay content implies a CEC of about 9 cmolc/kg. This value is roughly a third of the value of mid-range fine-grained, lower organic content soil/sediment. The coarse soils/sediments will likely contain a lower content of organic matter than even the fine-grained organic-poor soils/sediments. Assuming that the organic matter content of these coarse

soils/sediments lies at the minimum end of the range reported for soils in the considered areas (1.7 wt.-%) implies an additional contribution to the overall CEC of the coarse soil/sediment from organic matter of about 5 cmolc/kg. Based on these assumptions about clay content and organic matter content a coarse low-organic content soil/sediment would have a CEC of about 14 cmolc/kg. This is about half the value of a mid-range fine-grained lower organic content soil/sediment.

Given the various assumptions about clay and organic matter contents and CEC of these materials, these calculations produce estimated CECs for the three categories of soil/sediment that span almost the same range as observed in northern Swiss soils (Fig. 4-1). The CEC is not simply a function of the identities of the solid phases present, but also reflects the specific surface areas of the phases and the chemistry of the water It should be noted that here, "CEC" refers to measured CEC, which could include other processes besides true cation exchange. While true CEC is independent of pH, because the reported CEC for soils often include other processes, there may be pH-dependence. Solly et al. (2020) report a positive correlation between the effective cation exchange capacity (CEC_{eff}) and contents of clay and organic matter for forest soils in Switzerland. They found that organic matter contributes a much lower proportion of the CEC_{eff} at pH < 5.5 than at pH > 5.5. They concluded that, in the soils they studied, at pH > 5.5 organic matter contributes about 50% of the CEC_{eff} of the topsoil soil (to depth of 30 cm) and between 0% and about 35% of the CEC_{eff} of the sub-soil (30 cm – 120 cm depth). In contrast, at pH < 5.5 a maximum of about 30% CEC_{eff} is contributed by organic matter in the topsoil and about 10% CEC_{eff} in the sub-soil. They report that forest soils with 10 wt.-% organic matter and pH > 5.5 have CEC_{eff} up to 40 cmolc/kg. In contrast, in forest soils with negligible organic matter, they found a maximum clay content of 10 wt.-% and pH > 5.5 had CEC_{eff} mostly < 15 cmolc/kg.

Some elements are also known to sorb preferentially to organic matter compared to clay minerals. As an illustration of this effect, the above calculations can be repeated assuming that, for a given element sorbing on organic matter, the K_d is an order of magnitude greater than the K_d for sorption on clays. In this case the calculations show that the bulk K_d for sorption on higher organic content soil/sediment would be about four times the K_d for sorption on lower organic content soil/sediment. The K_d for the same element sorbing on coarse, low-organic content soil/sediment would, on a similar basis, be about two thirds of the K_d for fine grained, lower organic content soil/sediment.

The estimates of K_d based on CEC are subject to considerable uncertainty. The linear relationship between bulk soil CEC and K_d for a given set of conditions (temperature, pH, Eh, water composition) may not apply if sorption occurs by a mechanism other than cation exchange. It is also clear that there is considerable variability in the nature and proportions of solid-phases and porewater chemistry within each of the soil/sediment types. These differences imply potentially large variations in CEC, and by inference bulk K_d, for any given element within each group of soils/sediment. However, the above discussion shows that differences in CEC between typical examples of the different soil/sediment types (and hence differences in bulk sorption for any given element) are likely to be small-number multiples of one another rather than orders of magnitude differences. In the absence of other data, and taking CEC to be a proxy for sorption capacity, it follows that K_d will also vary by small-number multiples between the different sediment types. It is noteworthy that, on this basis, there is less difference in K_d between the three sediment types considered here, than between the three sediment types considered by Tits & van Dorp (1999). While Tits & van Dorp (1999) generally assigned K_d values to organic soils that are small multiples of the K_d assigned to fine grained soils, typically, they assigned K_d an order of magnitude lower to the coarse-grained soils. It follows that, were it is desired for the biosphere

model to include coarse grained soils/sediments like the coarse-grained soils considered by Tits & van Dorp (1999), it would be appropriate to use K_d values an order of magnitude smaller than the reference values specified in the following sub-chapters.

The possibility that differences in sorption between the different groups of soils/soils may be larger than simple multiples can be accounted for by specifying appropriately high ranges between Upper Guide and Lower Guide bulk K_d values for use in sensitivity calculations. That is, when setting up a biosphere model case, by selecting values from within the ranges it is possible to account for differences in K_d between different substrates that are several orders of magnitude.

The available data suggest that the range of sediment types within lakes and rivers and shallow, unconsolidated aquifers can also be approximated by the same tri-partite division as for soils. Such an approximation is appropriate for the biosphere model, which explores sensitivities of doses to sorption. As noted above, if it is necessary to consider coarse organic-poor and clay- poor material, such as sand or gravel in river bed sediments, then K_d that are an order of magnitude smaller than reference values recommended in the tables below for coarse, organic-poor soil/sediment can be used.

In summary, the approach used to assign K_d values to different soil/sediment types is as follows:

- "Reference" K_d values are given for the pH and Eh conditions of each reference water (Tab. 2-4):
  - Each "Reference" K_d value for the fine grained, *lower organic content* soil/sediment is typically estimated from mid-range or mean values (as judged appropriate taking into account data quality) reported for soil(s)/sediment(s) in the reviewed literature judged most similar to the lower organic content soil/sediment.
  - The "Reference" K_d value for the fine grained, *higher organic content* soil/sediment is 1.5× the "Reference" value for a fine grained, lower organic content soil or lake/river sediment, unless there are data that clearly support an even higher value.
  - The "Reference" K_d value for a *coarse*, lower-organic content soil/sediment is 0.5× the "Reference" value for a *fine grained*, lower organic content soil or lake/river sediment, unless there are data that clearly support an even lower value.
- If there is evidence that an element would sorb preferentially to organic material, then:
  - If the K_d of organic-rich materials is judged to be an order of magnitude greater, than inorganic materials, the fine, higher organic soil/sediment is assigned a K_d value that is 4× higher than the lower organic content soil/sediment.
  - If the K_d of organic-poor materials is judged to be two orders of magnitude greater than inorganic materials, the fine, higher organic soil/sediment is assigned a K_d value that is 5× higher than the lower organic content soil/sediment.
- For each element in each reference water/sediment type combination, guidance is given to indicate ranges of K_d, taking into account:
  - uncertainties in the underlying data in the reviewed literature
  - uncertainties in understanding of sorption mechanisms for the element
  - uncertainties/variability in the actual compositions of the soil/sediment, and
  - ranges in pH and Eh for each kind of water (Soil and Sediment Water, river water, lake water, aquifer water), as illustrated in Fig. 2-10

The starting point for estimating uncertainties is the range of K_d reported in the reviewed literature for soils/sediments as close as possible to those of Northern Switzerland considered in the present work (Appendix A).

By following this approach, a combination of knowledge of the sediment type and chemical conditions in each compartment in the SwiBAC biosphere model can be used to select appropriate K_d values for each radionuclide.

4.2 Actinium (Ac)

Actinium (Ac) is an actinoid (Period 7 of the periodic table), for which thermodynamic data are lacking in most geochemical databases. However, the PSI/Nagra Chemical Thermodynamic Database 2020, Version 1-1, contains data for a small number of species, which show that as pH increases, Ac progressively hydrolyses (Fig. 4-2). The element is not redox-sensitive, with the +III form occurring throughout the range of redox conditions relevant to this study. Over most of the relevant pH range, the trivalent Ac^{3+} is predicted to be the dominant species, with $Ac(OH)^{2+}$ possibly dominating in the highest pH shallow groundwaters and surface waters occurring in Northern Switzerland. At lower pH, where solid surfaces tend to be positively charged, sorption will potentially be less than at higher pH where surfaces are negatively charged.

There are no carbonate species of Ac in the PSI/Nagra thermodynamic database and therefore it is not possible to construct a Pourbaix diagram to investigate their significance. However, Sakamoto et al. (2002) report the results of a study of Ac sorption onto Japanese loam soil, both in the presence and absence of dissolved carbonate. They report that in the absence of carbonate Ac was irreversibly sorbed to silicate phases in the soil and that the K_d increased with increasing carbonate concentration, the dominant Ac species being $AcCO_3^+$. They suggested that the increased K_d of Ac in the presence of dissolved carbonate is due to the irreversible sorption of this carbonate species.

It can be assumed that Ac behaves very broadly in a way similar to other actinoids and lanthanoids (Linklater et al. 2003, Kaplan 2016). Published data suggest little difference in sorption between organic-rich and organic-poor sediments, but increasing sorption with increasing Fe-oxide content of the sediments (Sakamoto et al. 2002). From limited available data, and by analogy with Am (Linklater et al. 2003; Appendix A), it appears that sorption increases with increasing clay content of the sediment.

Previous studies have often considered Ac and Am to be chemical analogues, thereby justifying the specification of similar K_d values (Tits & van Dorp 1999, Bradbury & Baeyens 2003, Kaplan 2016). However, across the range of relevant pH, differences in aqueous speciation are calculated using the PSI/Nagra thermodynamic database 2020v1-1 (cf. Fig. 4-2 and Fig. 4-4). Whereas for all the reference water conditions Ac is calculated to be in the form Ac^{3+}, Am^{3+} is calculated to dominate only under the reference soil water conditions, with cations of progressively lower change and then anions (in carbonate-bearing systems) becoming dominant at progressively higher pH. This difference in speciation suggests that at low pH (and under the reference soil water conditions) Ac and Am would have similar K_d, whereas at higher pH, Ac may have somewhat higher K_d than Am. However, the available data do not justify recommending different K_d values. The approach here is to assign the same K_d values to both Ac and Am. However, in sensitivity calculations it would be appropriate to select a value from within the Upper Guide to Lower Guide range that is larger than the value selected for Am, recognising the different speciation of Ac and Am.

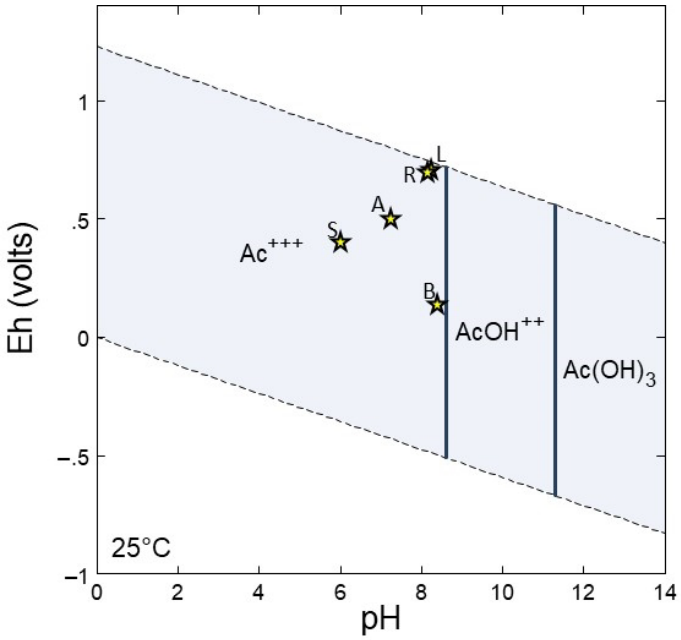

Fig. 4-2: Pourbaix diagram for Ac at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1); log *a* Ac^{3+} = -9

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Ac are given in Tab. 4-3.

Tab. 4-1: Recommended Kd values for Actinium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Geometric mean K_d reported for mineral soils is in the order 1.0E+00 m^3/kg, the same as for Am (Appendix A). Limited data (for Am) suggest higher K_d at higher pH. The K_d in compilations are ambiguous, little difference being reported for many clay-rich and clay-poor materials. It is expected that clay-rich materials would sorb more effectively than clay poor materials (e.g. Linklater et al. 2003). Upper and Lower Guide: Am used as an analogue. Data for Am suggest sorption increases with increasing pH to a maximum between pH 7 and 8 (Bradbury & Baeyens 2003). Considering the range of soil pH (3.9 – 7.4), data for Am sorption on illite reported in Bradbury & Baeyens (2003) that suggest a 2 order of magnitude increase between pH 4 and 7, and uncertainties, Lower Guide is an order of magnitude smaller than the reference while the Upper Guide is an order of magnitude larger.
	Lake/river	1.0E+01	1.0E+02	1.0E+00	Reference: Am used as an analogue. Data for Am in Opalinus Clay suggest approximately an order of magnitude increase between pH 6 and pH 8 (Appendix A; Bradbury & Baeyens 2003). As the reference soil water has pH c. 6 and Lake/river water has pH c. 8, recommend a value an order of magnitude greater than for the reference soil water. Upper and Lower Guide: Data for Am suggest sorption increases with increasing pH to a maximum between pH 7 and 8 (Bradbury & Baeyens 2003). Considering the range of river water pH (6.3 to 8.7) and uncertainties, Lower Guide is one order of magnitude smaller than the reference while the Upper Guide is an order of magnitude larger.
	River bed	1.0E+01	1.0E+02	1.0E+00	Reference: Am used as an analogue. Data for Am in Opalinus Clay suggest approximately an order of magnitude increase between pH 6 and pH 8 (Appendix A; Bradbury & Baeyens 2003). As the reference soil water has pH 6 and the reference river bed water has pH 8.4, recommend a value an order of magnitude greater than for the reference soil water. Upper and Lower Guide: Am used as an analogue. Data for Am suggest sorption increases with increasing pH to a maximum between pH 7 and 8. Considering the range of river bed water pH (7.8 to 9.0) and uncertainties, Lower Guide is one order of magnitude smaller than the reference while the Upper Guide is an order of magnitude larger.
	Aquifer	3.0E+00	3.0E+01	3.0E-01	Reference: Am used as an analogue. Data for Am in Opalinus Clay suggest approximately an order of magnitude increase between pH 6 and pH 8 (Appendix A; Bradbury & Baeyens 2003). As the reference soil water has pH 6 and the reference aquifer water has pH 7.25 recommend a value half an order of magnitude greater than for the reference soil water.

Tab. 4-1: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content					Upper and Lower Guide: Upper and Lower Guide: Am used as an analogue. Data for Am suggest sorption increases with increasing pH to a maximum between pH 7 and 8. Considering the range of aquifer water pH (6.5 to 8.9) and uncertainties, Lower Guide is an order of magnitude smaller than the reference while the Upper Guide is an order of magnitude larger.
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.3 Aluminium (Al)

Aluminium (Al) is a metal (Group 13, Period 3 of the periodic table), and a common constituent of rock and soil-forming minerals, including aluminosilicates and, in highly weathered soils, hydroxide minerals (Fig. 4-3a).

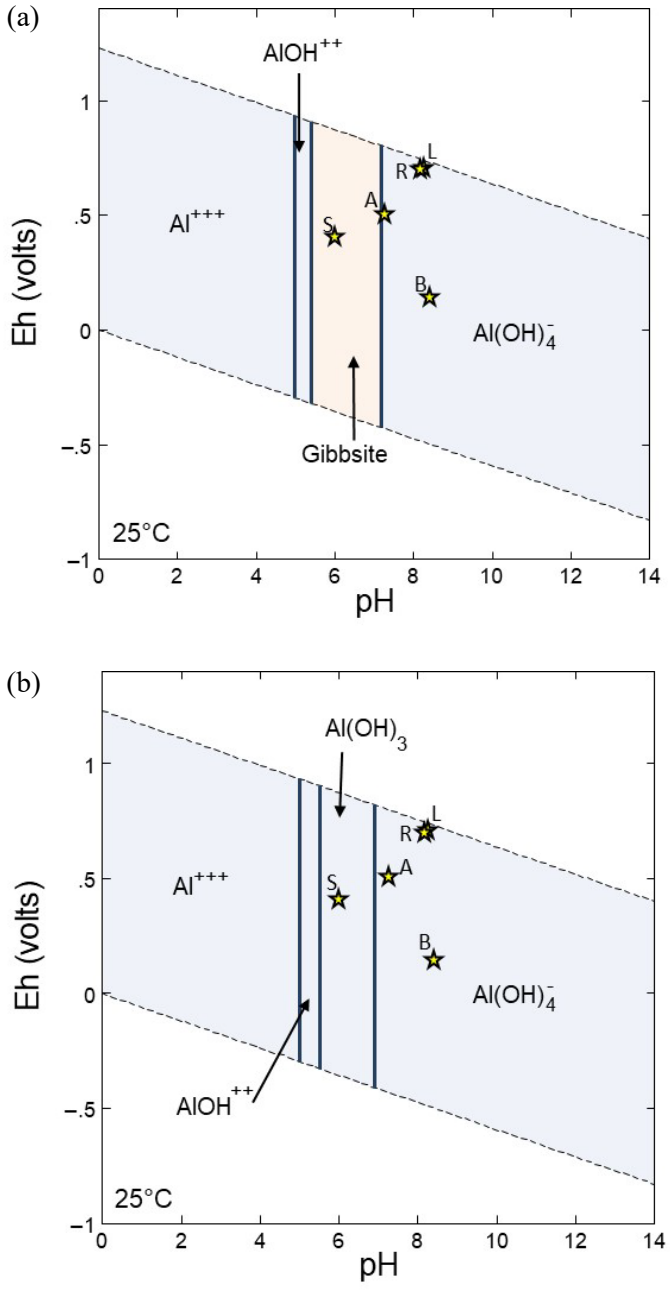

Fig. 4-3: Pourbaix diagrams for Al at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Al^{3+} = -8. Gibbsite is γ-$Al(OH)_3$; (b) log *a* Al^{3+} = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

In aqueous solution Al tends to exist as a charged aquo-ion under acidic conditions, as a neutral aqueous complex at pH ~ 6.0 – 6.5, or a negatively charged hydroxy species at pH > 7 (Fig. 4-3a, Fig. 4-3b).

The variation in charge means that dissolved Al sorption mechanisms will be pH dependent. There is some evidence to suggest (Appendix A) that sorption will be greater at the more alkaline end of the considered range than at the more acid end of the range. It is calculated that a neutral Al-species ($Al(OH)_3$) will dominate the speciation in the reference soil water, but a univalent anionic species ($Al(OH)_4^-$) will dominate the speciation in the other reference waters (Fig. 4-3). Therefore, similar K_d should be applied to all the waters except for the soil water.

It should also be noted that the solubility of Al hydroxides and aluminosilicate minerals is rather limited under near-to-neutral pH conditions, and that dissolved Al concentrations under such conditions could be controlled by aqueous solubility, rather than sorption processes. In general, Al-minerals are considered as key sorption substrates for radionuclides, rather than sources of a contaminant that undergoes sorption. Thus, there is significant uncertainty associated with applicability of the K_d approach concerning Al behaviour, which is likely to be pH dependent, as is the solubility of Al-minerals. It should also be noted that Al tends to form colloids and may sorb to colloids and this has been noted in previous work (Tits & van Dorp 1999).

Recommended K_d values for Al are given in Tab. 4-2.

Tab. 4-2: Recommended K_d values for Aluminium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	4.5E+00	1.0E+02	1.0E+00	Reference: Geometric mean K_d reported for soils and sediments from Sweden (Appendix A). The limited available data suggest that sorption of Al is less at lower pH, hence a lower K_d value is recommended than for other Swiss waters considered. There are no reliable data to justify a different value from those for the other considered soil/sediment types. Upper and Lower Guide: Lower Guide is the lowest recommended in other compilations (from Kaplan 2016; Appendix A – though this is based on a solubility measurement expressed in terms of K_d), Upper Guide is two orders of magnitude higher, based on the maximum values reported in the reviewed literature (Appendix A). Lower values should be used for lower pH conditions across the field of soil waters (Fig. 2-10).
	Lake/river	2.0E+02	3.0E+03	2.0E+00	Reference: Geometric mean K_d reported for glacial clays in Sweden (Appendix A). The pH range for which K_d values are reported for Swedish glacial clays is like that for the considered Swiss waters. The limited available data suggest that sorption of Al is greater at near-neutral pH than at acidic pH, with values decreasing as pH decreases, consistent with the positively charged aqueous species and positively charged surfaces of solid phases at low pH. Hence, considering the higher pH of these reference waters, higher K_d values are recommended than for reference soil water. There are no reliable data to justify different values for these reference waters. Upper and Lower Guide: Based on range of values reported for clays at pH 7 – 8 (Appendix A). The data do not justify specification of different values for the different waters.
	River bed	2.0E+02	3.0E+03	2.0E+00	
	Aquifer	2.0E+02	3.0E+03	2.0E+00	
Fine, higher organic content	Soil	6.75E+00	1.0E+02	1.0E+00	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	3.00E+02	3.0E+03	2.0E+00	
	River bed	3.00E+02	3.0E+03	2.0E+00	
	Aquifer	3.00E+02	3.0E+03	2.0E+00	
Coarse, low-organic content	Soil	2.25E+00	1.0E+02	1.0E+00	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.0E+02	3.0E+03	2.0E+00	
	River bed	1.0E+02	3.0E+03	2.0E+00	
	Aquifer	1.0E+02	3.0E+03	2.0E+00	

4.4 Americium (Am)

Americium (Am) is an actinoid (Period 7 of the periodic table) which tends to exist in aqueous solution as a cation (+III) under acidic pH conditions but forms cationic species at neutral to mildly acidic conditions with hydroxy or carbonate complexation occurring under alkaline conditions, depending on the activity of dissolved carbonate (which is in turn dependent on $pCO_2(g)$) (Fig. 4-4). Different aqueous species of Am could dominate the Am speciation under the considered reference condition (Fig. 4-4), suggesting that sorption could also differ between these conditions.

In general, positively charged ions are likely to dominate under the geochemical conditions of interest (pH 4 – 9.5) and these are likely to sorb to negatively-charged mineral surfaces, especially under neutral and mildly alkaline conditions (also see Choppin 2003 for aqueous speciation). It has been recognised that Group IIIa actinoids such as Am can form colloids, or be sorbed to them (Tits & van Dorp 1999, Swanton et al. 2009) which poses experimental difficulties that should be reflected when uncertainty associated with sorption data is considered. The speciation of Am itself will not be dependent upon redox conditions, but the identity of sorption substrates may vary under different Eh/pe conditions. Factors influencing sorption of Am in soils include pH, surface area, and organic matter content (e.g., Ramírez-Guinart et al. 2016). Greatest sorption appears to occur at pH ~ 7.5 – 9 (Ramírez-Guinart et al. 2016). Am may sorb to clay minerals by ion exchange under lower pH conditions, or by inner-sphere complexation under high pH regimes (Kumar et al. 2013). Humic acid in soils may also affect sorption, with sorption to clays (such as kaolinite) being enhanced at pH 3 – 4, but reduced above pH ~ 6 (Lee et al. 2011).

Previous studies have often considered Am and Ac to be chemical analogues, thereby justifying the specification of similar K_d values (Tits & van Dorp 1999, Bradbury & Baeyens 2003, Kaplan 2016). However, as discussed in Chapter 4.2, across the range of relevant pH, differences in aqueous speciation are calculated using the PSI/Nagra thermodynamic database 2020v1-1 (cf. Fig. 4-4 and Fig. 4-2). The approach here is to assign the same K_d values to both Am and Ac. However, in sensitivity calculations it would be appropriate to select a value from within the Upper Guide to Lower Guide range that is larger than the value selected for Am, recognising the different speciation of Ac and Am.

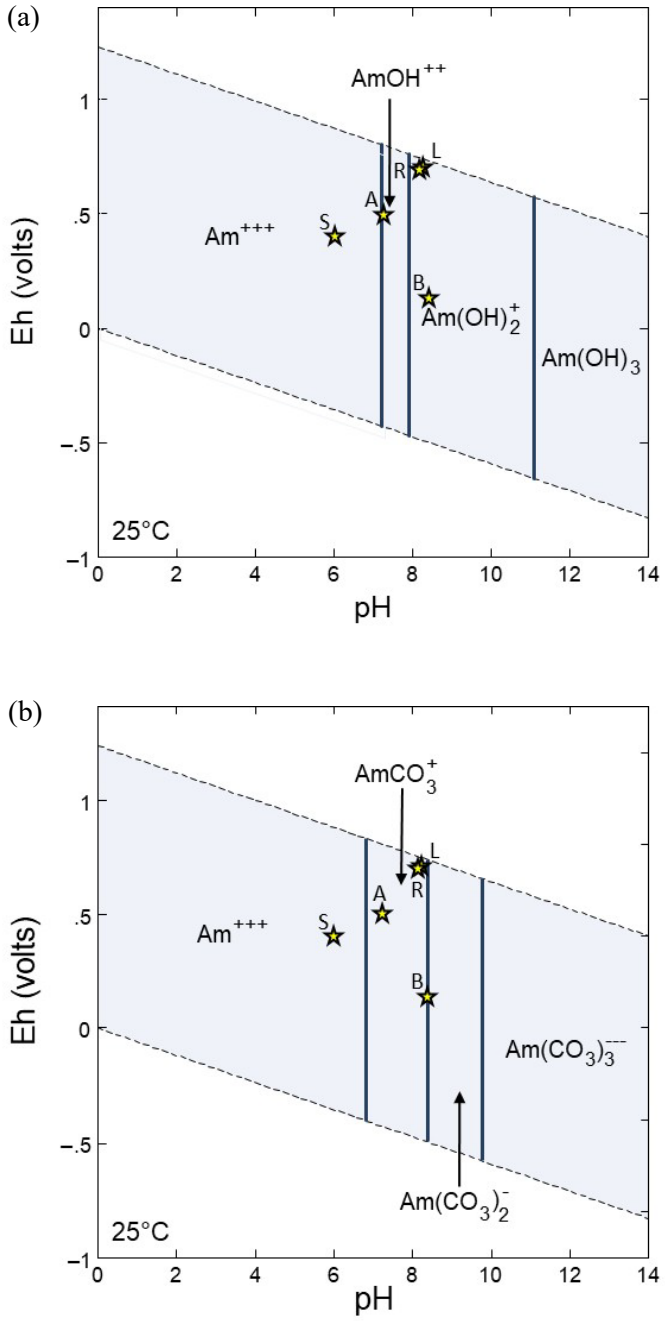

Fig. 4-4: Pourbaix diagrams for Am

(a) without CO_2; (b) log pCO_2 = -3.5 (ambient atmospheric conditions) at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1); log a Am^{3+} = -11 in both diagrams. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Am are given in Tab. 4-3.

Tab. 4-3: Recommended K_d values for Americium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Limited data at the relevant pH (c. 6) suggest sorption in the order 1.0E+00 m^3/kg (based on Ce, Eu analogue measurements reported by Kaplan (2016)) (Appendix A). Data are ambiguous, little difference being reported for many clay-rich and clay-poor materials. However, it is expected that clay-rich materials would sorb more effectively than clay poor materials (e.g. Linklater et al. 2003). Upper and Lower Guide: Data suggest sorption increases with increasing pH to a maximum between pH 7 and 8 (Bradbury & Baeyens 2003). Considering the range of soil pH (3.9 – 7.4), data for Am sorption on illite reported in Bradbury & Baeyens (2003) that suggest a 2 order of magnitude increase between pH 4 and 7, and uncertainties, Lower Guide is an order of magnitude smaller than the reference while Upper Guide is an order of magnitude larger.
	Lake/river	1.0E+01	1.0E+02	1.0E+00	Reference: Data for Opalinus Clay suggest about an order of magnitude increase between pH 6 and pH 8 (Appendix A; Bradbury & Baeyens 2003). The reference soil water has pH c. 6 and Lake/river water has pH c. 8, so K_d an order of magnitude greater than for the reference soil water is recommended. Upper and Lower Guide: Data suggest sorption increases with increasing pH to a maximum between pH 7 and 8 (Bradbury & Baeyens 2003). Considering the range of river water pH (6.3 to 8.7) and uncertainties, Lower Guide is one order of magnitude smaller than the reference while Upper Guide is the largest reported for any soil/sediment in the reviewed literature (Appendix A).
	River bed	1.0E+01	1.0E+02	1.0E+00	Reference: Data for Opalinus Clay suggest about an order of magnitude increase between pH 6 and pH 8 (Appendix A; Bradbury & Baeyens 2003). The reference soil water has pH 6 and the reference river bed water has pH 8.4, so K_d an order of magnitude greater than for the reference soil water is recommended. Upper and Lower Guide: Data suggest sorption increases with increasing pH to a maximum between pH 7 and 8. Considering the range of river bed water pH (7.8 to 9.0) and uncertainties, Lower Guide is one order of magnitude smaller than the reference while Upper Guide is the largest reported for any soil/sediment in the reviewed literature (Appendix A).

Tab. 4-3: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content					Upper and Lower Guide: Upper and Lower Guide: Data suggest sorption increases with increasing pH to a maximum between pH 7 and 8. Considering the range of aquifer water pH (6.5 to 8.9) and uncertainties, Lower Guide is an order of magnitude smaller than the reference while Upper Guide is the largest reported for any soil/sediment in the reviewed literature (Appendix A).
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.5 Cesium (Cs)

Caesium (or "cesium"; Cs) is an alkali metal (Group 1, Period 6 of the periodic table). It tends to exist as a monovalent cation under a wide range of pH conditions (Fig. 4-5). While Cs can complex with Cl, at the maximum Cl concentration in the shallow groundwaters of Northern Switzerland (0.5 mol/kg) Cs^+ will still dominate.

Cs is likely to sorb to negatively charged mineral surfaces, including the edges of layer silicates where there are OH- or O_2^- groups, and interlayers regions for 2:1 clays, such as smectite and vermiculite where negativelycharged layers arise due to isomorphous substitution (e.g., Missana et al. 2014, Cherif et al. 2017). Variations in redox conditions will not affect sorption significantly, either directly or indirectly; Cs does not sorb strongly to Fe-oxides (Linklater et al. 2003). In soils, pH conditions affect Cs sorption, with values tending to be greatest at pH ~ 8 where negative charge density on mineral surfaces is highest (Giannakopoulou et al. 2007). However, across the pH range of the difference reference waters (pH = 6 to 8.4; Fig. 4-5) sorption will vary little (Bradbury & Baeyens 2003).

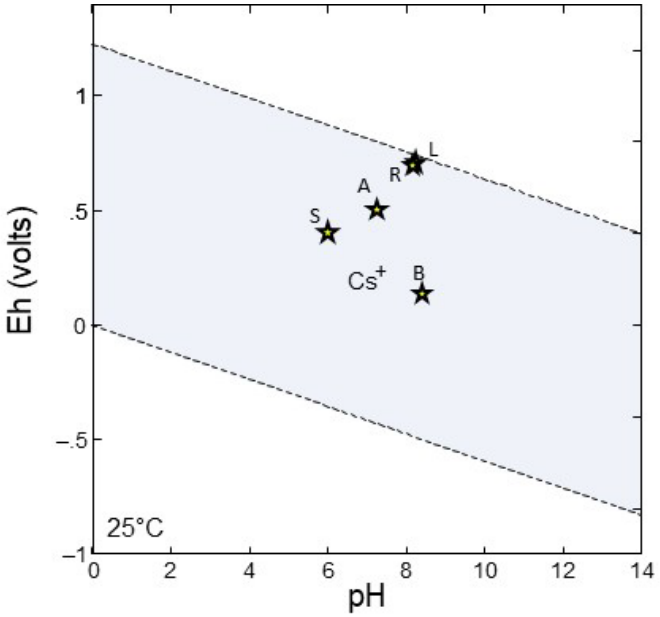

Fig. 4-5: Pourbaix diagram for Cs at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1), plotted for log *a* Cs^+ = -5

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Cs are given in Tab. 4-4.

Tab. 4-4: Recommended K_d values for Cesium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+02	1.0E-01	Reference: Geometric mean reported for all soils in IAEA (2010), which is also a mid-order value considering the reviewed literature (1.0E+00 to 1.0E+05 reported; Appendix A). The very wide range of reported K_d means that there is large uncertainty. Tits & van Dorp (1999) calculated a K_d three times larger using measured Cs-K selectivity coefficients and K_d for K. Upper and Lower Guide: Lower Guide based on reported change in K_d over the pH range of the reference soil water conditions. Kaplan (2016) quotes an approximately 1 order increase in K_d between pH 4.2 and 6.4. for sediments at Savannah River, U.S.A. Lower Guide is therefore relevant to lower pH in the range. Upper Guide takes into account uncertainty and is in the same order as the highest K_d reported for clay soil/sediment in the reviewed literature (Appendix A), but would be appropriate for the upper end of the pH range for the reference soil water conditions.
	Lake/river	1.0E+00	1.0E+02	1.0E-01	Reference: Same as for the reference soil water conditions. Bradbury & Baeyens (2003) present experimental data that show little difference between pH 6.3 and 7.8. Upper and Lower Guide: Little variation in sorption is expected across the range of pH. Upper Guide and Lower Guide are in the same orders as the largest and smallest K_d reported for soils sediments in the reviewed literature as a basis for sensitivity analyses.
	River bed	1.0E+00	1.0E+02	1.0E-01	
	Aquifer	1.0E+00	1.0E+02	1.0E-01	Reference: Same as for the reference soil water conditions. Bradbury & Baeyens (2003) present experimental data that show little difference between pH 6.3 and 7.8. Possibly K_d would be lower than for the other waters, owing to the higher ionic strength of aquifer waters. However, this effect is expected to be small (none of the waters are saline) and the data do not justify specifying difference values. Upper and Lower Guide: Little variation in sorption is expected across the range of pH. Upper Guide and Lower Guide are in the same orders as the largest and smallest K_d reported for soils sediments in the reviewed literature (Appendix A) as a basis for sensitivity analyses.
Fine, higher organic content	Soil	1.5E+00	1.0E+02	1.0E-01	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. No evidence that Cs sorbs significantly to organic material. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/ sediments.
	Lake/river	1.5E+00	1.0E+02	1.0E-01	
	River bed	1.5E+00	1.0E+02	1.0E-01	
	Aquifer	1.5E+00	1.0E+02	1.0E-01	

Tab. 4-4: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Coarse, low-organic content	Soil	5.0E-01	1.0E+02	1.0E-01	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E-01	1.0E+02	1.0E-01	
	River bed	5.0E-01	1.0E+02	1.0E-01	
	Aquifer	5.0E-01	1.0E+02	1.0E-01	

4.6 Calcium (Ca)

Calcium (Ca) is an alkaline-earth metal (Group 2, Period 4 of the periodic table) which is commonly found as a constituent of rock/soil-forming carbonate minerals. Under acidic and near-neutral pH conditions it exists as a divalent cation in aqueous solution (Fig. 4-6), under alkaline conditions it tends to exist as $CaCO_3$(aq). Calcium concentrations in natural waters often reflect the solubility of carbonate minerals and can be influenced by ion exchange processes. K_d values are often specified based on a consideration of soil/sediment CEC, cation distribution and equilibrium solubility (e.g., Tits & van Dorp 1999). However, if carbonate mineral solubility (or the solubility of another Ca-bearing solid phase) controls aqueous Ca concentrations it is inappropriate to model aqueous Ca behaviour using linear sorption isotherms. As can be seen from Fig. 4-6, at least some of the considered waters could be in equilibrium with calcite.

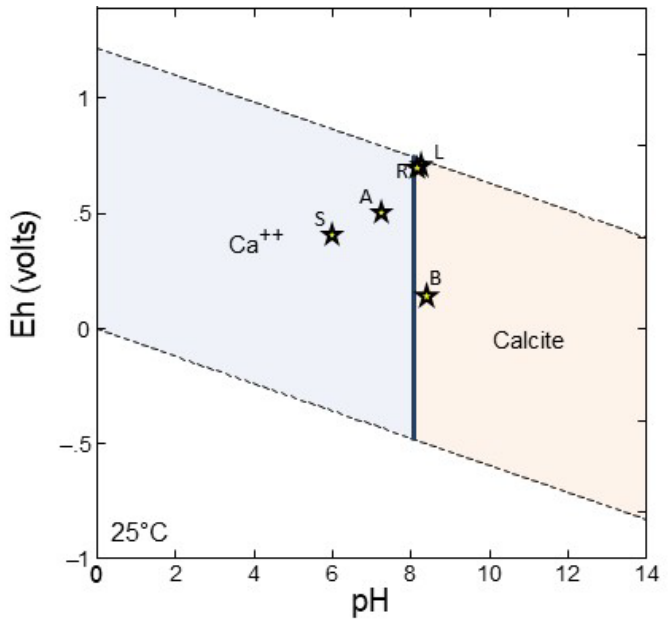

Fig. 4-6: Pourbaix diagram for Ca at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

Log *a* Ca^{2+} = -3 (comparable with concentrations in river and lake waters; Chapter 2). Calcite has the composition $CaCO_3$. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Ca are given in Tab. 4-5.

Tab. 4-5: Recommended K_d values for Calcium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+00	7.0E-04	Reference: 2 orders of magnitude less than reference K_d for Cs, consistent with the understanding that Cs will tend to sorb more strongly than Ca (Linklater et al. 2003, Wissoq et al. 2018). This is also consistent with reviewed data in which K_d are generally 1 to 3 orders of magnitude smaller than for Cs which also sorbs by cation exchange (Appendix A). It is near the lower end of the range of K_d produced by a calculation similar to Tits & van Dorp (1999) based on limited Ca concentrations available for waters and estimates of CEC for soil/sediment, assuming 80% is accounted for by Ca. This calculation gives K_d in range 7.0E-2 m^3/kg to 3.5E-01 m^3/kg. The K_d is the same as that for Sr, consistent with available data that show Sr and Ca to have similar K_d (Tits & van Dorp 1999, Bradbury & Baeyens 2003). Upper and Lower Guide: Lower Guide and Upper Guide are based on reported range of K_d for clay-rich soil and sediment in the reviewed literature (Appendix A).
	Lake/river	1.0E-02	1.0E+00	7.0E-04	Reference: Same K_d as the reference K_d for reference soil water conditions in fine, lower organic content soil/sediment since data do not justify assigning different K_d. Upper and Lower Guide: Same range of K_d as the K_d range for reference soil water conditions in fine, lower organic content soil/sediment since data do not justify assigning different values.
	River bed	1.0E-02	1.0E+00	7.0E-04	
	Aquifer	1.0E-02	1.0E+00	7.0E-04	
Fine, higher organic content	Soil	1.5E-02	1.0E+00	7.0E-04	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.5E-02	1.0E+00	7.0E-04	
	River bed	1.5E-02	1.0E+00	7.0E-04	
	Aquifer	1.5E-02	1.0E+00	7.0E-04	
Coarse, low-organic content	Soil	5.0E-03	1.0E+00	7.0E-04	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E-03	1.0E+00	7.0E-04	
	River bed	5.0E-03	1.0E+00	7.0E-04	
	Aquifer	5.0E-03	1.0E+00	7.0E-04	

4.7 Californium (Cf)

Californium (Cf) is an actinoid (Period 7 of the periodic table), for which geochemical data are very limited. Most thermodynamic databases contain no data for this element, but the PSI/Nagra PSI/Nagra thermodynamic database 2020v1-1 contains data for Cf^{3+}, CfF^{2+}, $CfCN^{2+}$ and $CfSO_4^+$. Predominance fields for Cf^{3+} and $CfSO_4^+$ are shown in Fig. 4-7.

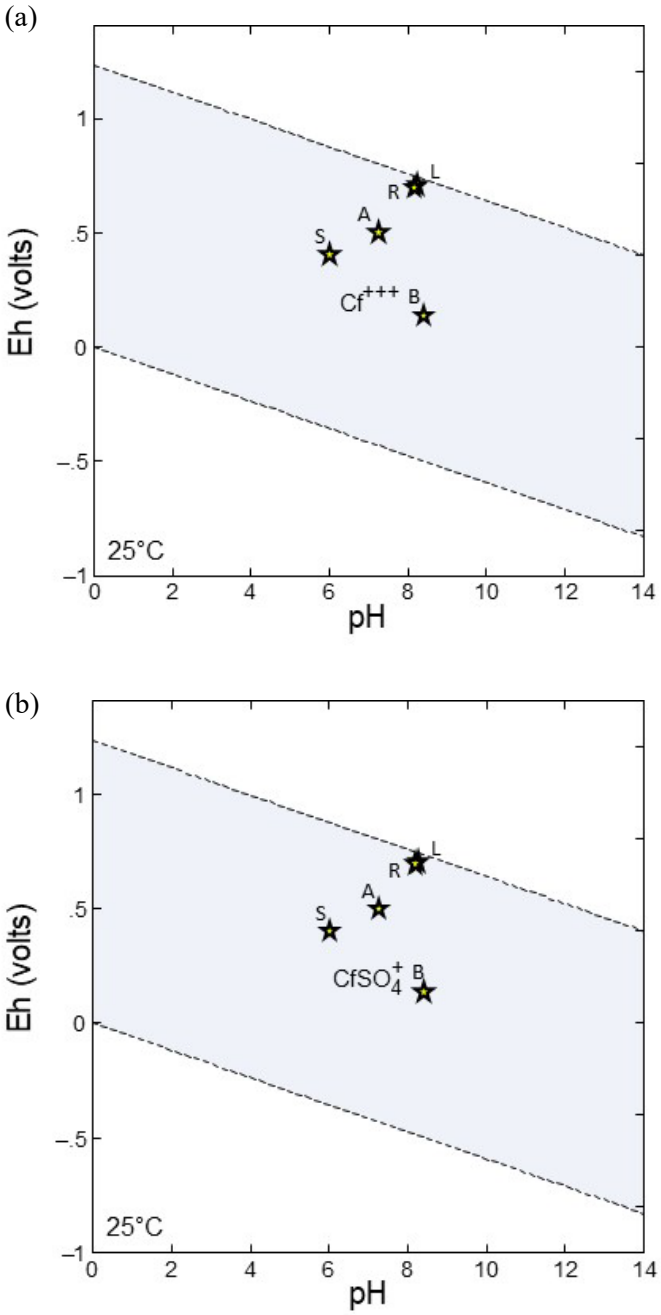

Fig. 4-7: Pourbaix diagrams for Cf at 25 °C, 1 bar

(a) log a Cf3+ = -11; (b) log a SO42- = -1.52 (PSI/Nagra thermodynamic database 2020v1-1). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Based on these data, in northern Swiss surface waters and most near-surface groundwaters, Cf will be present as uncomplexed trivalent cations (Fig. 4-7a); the element is not redox-sensitive. However, the shallow groundwaters may contain up to 2820 mg/kg SO_4 and the thermodynamic data in the PSI/Nagra database suggest that in such waters, Cf will be dominantly $CfSO_4^+$(Fig. 4-7b). In either case, the Pourbaix diagram suggests that there may be little difference in sorption between the different reference water conditions, except in so far as the surface charge of the solid phases present in the soil/sediment are pH dependent. The surface charge of clay minerals and Fe-oxyhydroxides generally is positive at low pH, near zero at slightly acidic to near-neutral pH and then progressively more negative at increasing pH. Therefore, the speciation of Cf calculated using the PSI/Nagra thermodynamic database implies that sorption will be least at low pH, but increase as pH increases. However, in waters with higher SO_4 content Cf may sorb more strongly at low pH than in lower SO_4 waters.

Kaplan (2016) considered Cf and Am to be chemical analogues, thereby justifying the application of measured Am K_d values to Cf. However, across the range of relevant pH, differences in aqueous speciation are calculated using the PSI/Nagra thermodynamic database 2020v1-1 (cf. Fig. 4-7 and Fig. 4-4). Whereas for all the reference water conditions Cf is calculated to be in the form Cf^{3+}, or $Cf(SO_4)^+$, Am^{3+} is calculated to dominate only under the reference soil water conditions, with cations of progressively lower change and then anions (in carbonate-bearing systems) becoming dominant at progressively higher pH. This difference in speciation suggests that at low pH and at lowSO_4 concentrations (and under the reference soil water conditions), Cf and Am may have similar K_d. However, at higher pH, Cf may have somewhat higher K_d than Am unless $Cf(SO_4)^+$ dominates. In this case, it is not possible to deduce whether Am or Cf would sorb similarly or differently.

It is noted that hydrolysed species of Cf are not present in the PSI/Nagra database thermodynamic database. This is likely due to lack of data, rather than these species not being important. Hence, it cannot be ruled out that the speciation of Cf would in reality be more like Am than is apparent from Fig. 4-7 and Fig. 4-4.

As the available data do not justify recommending different K_d values for Cf and Am, the approach here is to recommend the use of Am K_d values for Cf.

Recommended K_d values for Cf are given in Tab. 4-6.

Tab. 4-6: Recommended K_d values for Californium (m^3/kg)

Americium analogue

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A). Upper and Lower Guide: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A).
	Lake/river	1.0E+01	1.0E+02	1.0E+00	
	River bed	1.0E+01	1.0E+02	1.0E+00	
	Aquifer	3.0E+00	3.0E+01	3.0E-01	
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.8 Carbon (C)

Carbon (C) is a non-metal (Group 14, Period 2 of the periodic table) which is commonly found as a constituent of carbonate minerals, as dissolved carbonate species and metal-carbonate complexes. In the presence of carbonate minerals, the most common of which is calcite, aqueous concentrations of inorganic carbon are likely to be solubility controlled. Under such circumstances, it is inappropriate to model aqueous inorganic carbon concentrations using linear isotherms (K_d). However, for a specific set of chemical conditions partitioning of C between aqueous and solid phases can be modelled using a partition coefficient, which like a K_d value is the ratio of the concentration of C in the solid phase to the concentration in the aqueous phase. This was the approach taken by Tits & van Dorp (1999). Their calculation considered the fraction of $CaCO_3$ available for isotopic exchange and the solubility of $CaCO_3$, which is not done here, because there is insufficient data with which to justify such a fraction. However, Tits & Van Dorp (1999) considered that 1% of the C in solid carbonate would exchange isotopically with the aqueous C. If the same assumption is applied here, the K_d recommended in Tab. 4-7 would be reduced by 2 orders of magnitude.

Under more acidic conditions, dissolved $CO_2(g)$ is stable, with hydrogen carbonate ("bicarbonate", HCO_3^-) occurring at pH ~ 6 to 10, with carbonate (CO_3^{2-}) occurring under highly alkaline conditions (Fig. 4-8). Over the ranges of Eh and pH relevant to the present project, C will be in an oxidised form (-IV). However, graphite is possibly stable under the most reducing soil water conditions (cf. Fig. 2-10, Fig. 4-8). Under all the reference water conditions considered here, except for soil water, HCO_3^- is calculated to be the dominant aqueous species (Fig. 4-8). For soil water, $CO_2(aq)$ could be the dominant species (Fig. 4-8).

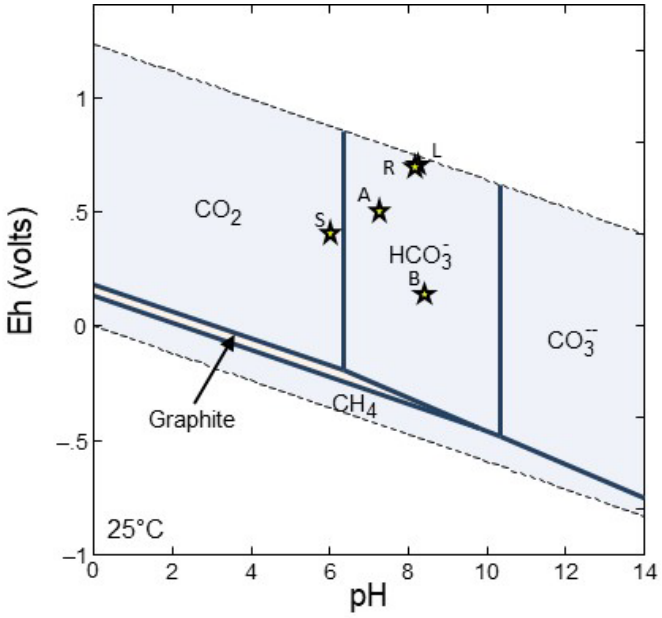

Fig. 4-8: Pourbaix diagram for inorganic C at 25 °C, 1 bar; log *a* HCO_3^- = -3 (PSI/Nagra thermodynamic database 2020v1-1)

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for C are given in Tab. 4-7.

Tab. 4-7: Recommended K_d values for Carbon (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-01	1.0E+00	0.0E+00	Reference: Same order of magnitude as measurements on carbonate mineral-poor clay at pH 5.5 reported by Kaplan (2016). Expect inorganic carbon to be dominant in a neutral species (CO_2(aq) and hence poorly sorbing. The reference K_d is for dissolved inorganic carbon in total. The appropriate K_d for ^{14}C will be less than this value if there are solid carbonate phases present, reflecting isotope exchange/dilution. Upper and Lower Guide: Lower Guide assumes no sorption between negatively charged species and negatively charged surfaces; it would be appropriate for more alkaline pH (> 9). Upper Guide is in the same order as the maximum reported in the reviewed literature (Appendix A) and would be appropriate for pH 8 – 8.5, when dissolved C is dominantly anionic and solid surfaces are positively charged.
	Lake/river	1.0E+00	1.0E+00	0.0E+00	Reference: An order of magnitude greater than for the reference soil water conditions in fine, lower organic content soils/sediments, reflecting roughly the 1 order of magnitude increase between pH 6.3 and pH 7.8 reported by Bradbury & Baeyens (2003) and the expectation that inorganic carbon will be dominant in negatively charged species (HCO_3^-). The reference K_d is for dissolved inorganic carbon in total. The appropriate K_d for ^{14}C will be less than this K_d if there are solid carbonate phases present, reflecting isotope exchange/dilution. Upper and Lower Guide: Lower Guide assumes no sorption between negatively charged species and negatively charged surfaces; it would be appropriate for more alkaline pH (> 9). Upper Guide is in the same order of magnitude as the maximum reported in the reviewed literature (Appendix A) and would be appropriate for pH 8 – 8.5, when dissolved C is dominantly anionic and solid surfaces are positively charged.
	River bed	1.0E+00	1.0E+00	0.0E+00	
	Aquifer	1.0E+00	1.0E+00	0.0E+00	
Fine, higher organic content	Soil	1.0E-01	1.0E+00	0.0E+00	Reference: For each reference water the K_d is the same as for the corresponding reference water in fine, lower organic content soil/sediment. The available data do not justify specifying different values for each reference water in different soils/sediments. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for each water in the different soils/sediments.
	Lake/river	1.0E+00	1.0E+00	0.0E+00	
	River bed	1.0E+00	1.0E+00	0.0E+00	
	Aquifer	1.0E+00	1.0E+00	0.0E+00	
Coarse, low-organic content	Soil	1.0E-01	1.0E+00	0.0E+00	
	Lake/river	1.0E+00	1.0E+00	0.0E+00	
	River bed	1.0E+00	1.0E+00	0.0E+00	
	Aquifer	1.0E+00	1.0E+00	0.0E+00	

4.9 Chlorine (Cl)

Chlorine (Cl) exists as the chloride anion (Cl^-) in aqueous solution (Fig. 4-9), with a relatively low tendency to sorb to mineral surfaces, especially under neutral/mildly alkaline conditions. These conditions tend to favour negatively charged sorption surface sites on hydroxide minerals and clay "edge" sites. Accordingly, several authors who have recommended K_d values for safety assessment purposes have considered Cl to be non-sorbing (e.g., Bradbury & Baeyens 2003, Krupka et al. 2004). However, many authors have found Cl to be weakly sorbing (Appendix A). There is also some evidence that Cl may sorb to organic matter (e.g., Söderlund et al. 2011). Chloride can also form complexes with Group 1 and Group 2 dissolved metals in aqueous solution e.g., $M(II)Cl_2(aq)$, $M(II)Cl^+$, M(I)Cl(aq), where M is a metal ion, which may influence the degree to which Cl can sorb.

A factor that complicates the specification of K_d values is isotope dilution, whereby Cl-36 originating in the waste (and hence of concern to safety assessment) exchanges for natural stable Cl-35 and Cl-37 present in the rock/soil/sediment. It is outside the scope of this work to consider this process.

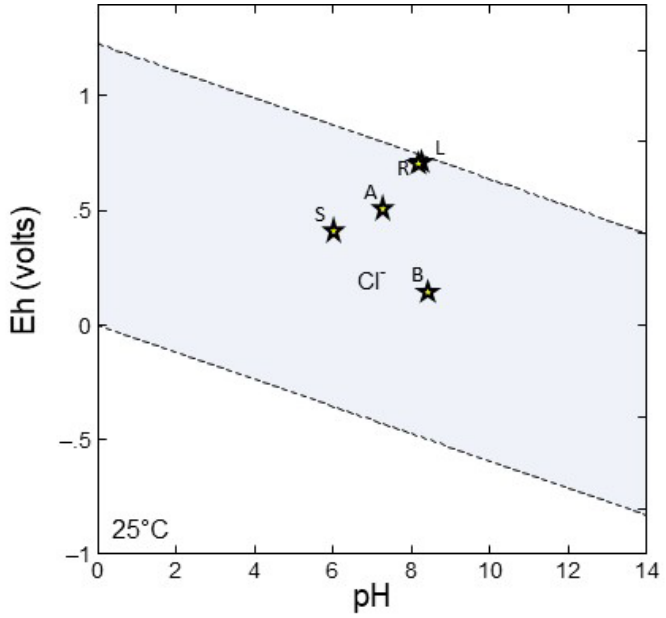

Fig. 4-9: Pourbaix diagram for Cl at 25 °C, 1 bar, log *a* Cl^- = -3, (PSI/Nagra thermodynamic database 2020v1-1)

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Taking the above considerations into account, the approach adopted here is to recommend reference K_d values of 0 m^3/kg in all water/substrate combinations, but to recommend Upper Guideline values that recognise the possibility that some sorption may occur. It is suggested that these Upper Guideline values should be used in sensitivity calculations to help determine whether Cl sorption could be significant for the assessment outcomes.

Recommended K_d values for Cl are given in Tab. 4-8.

Tab. 4-8: Recommended K_d values for Chlorine (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	0.0E+00	1.0E-03	0.0E+00	Reference: Cl^- would be non-sorbing on negatively charged surfaces of solid phases. Reliable data with which to recommend a K_d value, considering the possibility for isotope dilution, are not available. Upper and Lower Guide: Lower Guide reflects the possibly non-sorbing nature of Cl^-, especially under alkaline conditions where the surfaces of many solid phases are negatively charged. Upper Guide is the most commonly reported order of magnitude of the greatest K_d among the different reviewed studies (Appendix A) and would be more likely to be attained at significantly acidic conditions, where the surfaces of many solid phases are positively charged.
	Lake/river	0.0E+00	1.0E-03	0.0E+00	
	River bed	0.0E+00	1.0E-03	0.0E+00	
	Aquifer	0.0E+00	1.0E-03	0.0E+00	
Fine, higher organic content	Soil	0.0E+00	1.0E-03	0.0E+00	Reference: Cl^- would be non-sorbing on negatively charged surfaces of solid phases. Reliable data with which to recommend a K_d value, considering the possibility for isotope dilution, are not available. Upper and Lower Guide: Lower Guide reflects the possibly non-sorbing nature of Cl^-, especially under alkaline conditions where the surfaces of many solid phases are negatively charged. Upper Guide is the most commonly reported order of magnitude of the greatest K_d among the different reviewed studies (Appendix A) and would be more likely to be attained at significantly acidic conditions, where the surfaces of many solid phases are positively charged. There is some evidence that Cl will sorb preferentially to organic matter. Under a given set of chemical conditions (and at a given pH), K_d is likely to be higher than in fine, lower organic content soil/sediment under the same conditions.
	Lake/river	0.0E+00	1.0E-03	0.0E+00	
	River bed	0.0E+00	1.0E-03	0.0E+00	
	Aquifer	0.0E+00	1.0E-03	0.0E+00	
Coarse, low-organic content	Soil	0.0E+00	1.0E-03	0.0E+00	Reference: Cl^- would be non-sorbing on negatively charged surfaces of solid phases. Reliable data with which to recommend a K_d value, considering the possibility for isotope dilution, are not available. Upper and Lower Guide: Lower Guide reflects the possibly non-sorbing nature of Cl^-, especially under alkaline conditions where the surfaces of many solid phases are negatively charged. Upper Guide is the most commonly reported order of magnitude of the greatest K_d among the different reviewed studies (Appendix A) and would be more likely to be attained at significantly acidic conditions, where the surfaces of many solid phases are positively charged. Under a given set of chemical conditions (and at a given pH), K_d is likely to be lower than in fine, lower organic content soil/sediment under the same conditions.
	Lake/river	0.0E+00	1.0E-03	0.0E+00	
	River bed	0.0E+00	1.0E-03	0.0E+00	
	Aquifer	0.0E+00	1.0E-03	0.0E+00	

4.10 Cobalt (Co)

Cobalt (Co) is a first-row transition element (Group 9, Period 4 of the periodic table). The element is not present in the PSI/Nagra thermodynamic database 2020v1-1 and therefore no Pourbaix diagram is presented showing predominance fields of aqueous Co species and solid phases in Eh-pH space. However, calculations using the thermodynamic database Thermochimie v 10a, which does contain thermodynamic data for Co aqueous species and minerals, shows that Co^{2+} is likely to be the dominant aqueous species under all the reference water compositions. However, in the cases of lake water and river water the solid $Co_2O_4(s)$ could plausibly be thermodynamically stable; if so, and the aqueous Co concentrations are solubility-limited, it would be inappropriate to model aqueous Co^{2+} behaviour using sorption isotherms.

There are very few data available for Co sorption on relevant materials under relevant conditions. Grütter et al. (1994) investigated sorption of Co and Ni on clays and unconsolidated glacio-fluvial deposits, in the presence of synthetic fresh groundwater with pH 7.9. They reported that Co sorption is kinetically controlled and did not reach equilibrium even over a period of 60 days, but was apparently irreversible. On illite Co and Ni seem to sorb similarly, whereas on montmorillonite and glacial clays Co sorbed more strongly at low loadings, but similarly at higher loadings.

Crawford (2013) recommended using Ni as a chemical analogue for Co and accordingly assigned the same K_d values for both elements. However, the data reported by Grütter et al. (1994) call into question the validity of Ni as an analogue for at least some materials under certain conditions.

Kaplan (2016) reports measurements of Co sorption on sediments from Savannah River, U.S.A. These results show that Co sorption has a strong dependence on pH, with K_d increasing slightly from pH 2 to 4.8 (sediment with 23% clay had K_d = 2.9E-02 m^3/kg at this pH) then sharply between pH 4.8 and 7 (at which K_d = 2.0E+04 m^3/kg), before decreasing steadily to pH 9.5 (at which K_d = 2.0E-02 m^3/kg).

Krupka & Serne (2002) present data for Co sorption in sediments at the Hanford site, U.S.A. which show that Co is not very mobile, having K_d > 1 m^3/kg. At high loadings surface-mediated precipitation processes may occur, which could explain very large K_d (in the order 1.0E+02 m^3/kg) that are sometimes measured. However, these authors note the ability of Co to complex with many mobile organic compounds (EDTA, light organic acids etc.), which results in decreased sorption. On the other hand, surface-bound humic acid is thought to be able to bind with Co thereby causing increased K_d.

Recommended K_d values for Cm are given in Tab. 4-9.

Tab. 4-9: Recommended K_d values for Cobalt (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+01	1.0E-05	Reference: K_d is three orders of magnitude smaller than the geometric mean of K_d reported for clayey sediment at pH 7 – 8, considering that the reference soil water has pH 6. In the reviewed literature the geometric mean K_d for clayey sediments at pH 7 – 8 is around 2.0E+01 m^3/kg (Appendix A). For sandy sediments, Kaplan (2016) reports an increase in K_d by around 6 orders of magnitude between pH 5 and 7. Upper and Lower Guide: Upper Guide and Lower Guide reflect the sorption edge between pH 4 and 7, with very low sorption below pH 4 (Krupka & Serne 2002).
	Lake/river	1.0E+01	1.0E+02	1.0E-02	Reference: K_d is three orders of magnitude larger than the K_d for reference soil water in fine, lower organic content soil/sediment. This difference reflects the higher pH (c. 2 units higher) of the reference lake/river water compared to the reference soil water, and the reported pH-dependence of Co sorption (Kaplan 2016). The data do not justify specifying different K_d for reference lake/river water and reference river bed water. Upper and Lower Guide: Lower Guide is three orders of magnitude smaller than the reference K_d, reflecting the pH difference between the lowest end of the river water field (pH 6.25) and the reference river water (pH 8.11) and noting that the former is almost the same pH as the reference soil water. Upper Guide is in the same order as the largest K_d reported in the reviewed literature, appropriate for a pH of c. 8; the data suggest little difference in K_d between this pH and the maximum pH of the lake/river water field (pH 8.73).
	River bed	1.0E+01	1.0E+02	1.0E+00	Reference: K_d is three orders of magnitude larger than the K_d for reference soil water in fine, lower organic content soil/sediment. This difference reflects the higher pH (c. 2 units higher) of the reference river bed water compared to the reference soil water, and the reported pH-dependence of Co sorption (Kaplan 2016). The data do not justify specifying different K_d for reference lake/river water and reference river bed water. Upper and Lower Guide: Lower Guide is one order of magnitude smaller than the reference K_d, reflecting the pH difference between the lowest end of the river water field (pH 7.8) and the reference river water (pH 8.4). Upper Guide is in the same order as the largest K_d reported in the reviewed literature, appropriate for a pH of c. 8; the data suggest little difference in K_d between this pH and the maximum pH of the river bed water field (pH 9).

Tab. 4-9: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Aquifer	5.0E-01	1.0E+02	1.0E-02	Reference: K_d is 1.5 orders of magnitude bigger than the K_d value for the reference soil water in fine lower organic content soil/sediment. This difference reflects the higher pH (1.25 units higher) of the reference aquifer water compared to the reference soil water, and the reported pH-dependence of Co sorption (Kaplan 2016). Upper and Lower Guide: Lower Guide is the same as the Lower Guide for reference soil water in lower organic content soil/sediment, reflecting the similar pH of the reference soil water (pH 6) and the lowest pH of aquifer waters (pH 6.5). Upper Guide is in the same order as the largest K_d reported in the reviewed literature, appropriate for a pH of c. 8; the data suggest little difference in K_d between this pH and the maximum pH of the aquifer water field (pH 8.9).
Fine, higher organic content	Soil	1.5E-02	1.0E+01	1.0E-05	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.5E+01	1.0E+02	1.0E-02	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	7.5E-01	1.0E+02	1.0E-02	
Coarse, low-organic content	Soil	5.0E-03	1.0E+01	1.0E-05	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E+00	1.0E+02	1.0E-02	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	2.5E-01	1.0E+02	1.0E-02	

4.11 Curium (Cm)

Curium (Cm) is a lanthanoid (Period 7 of the periodic table), which tends to exist as trivalent Cm^{3+} form under acidic conditions, with hydroxide or carbonate species occurring under neutral and alkaline conditions (Fig. 4-10). Its chemistry is like that of Am.

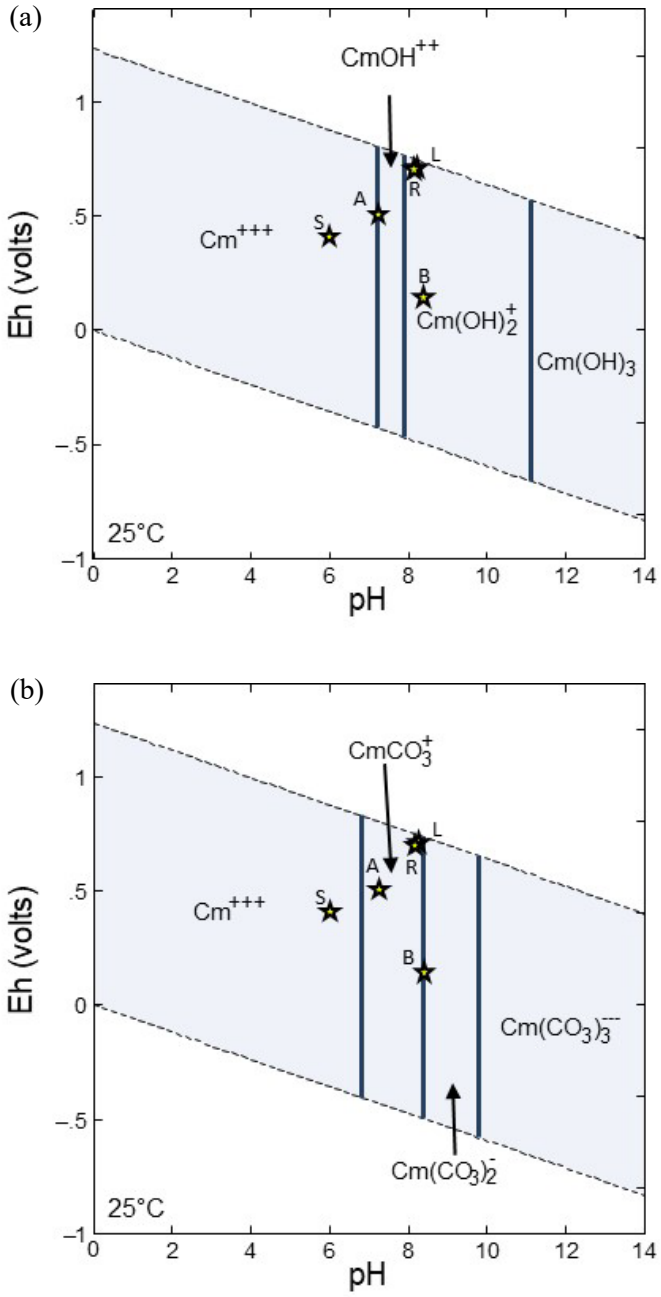

Fig. 4-10: Pourbaix diagram for Cm at 25 °C, 1 bar

(a) excluding CO_2; (b) including CO_2(g) (ambient atmospheric conditions, log pCO_2 = -3.5); log a Cm^{3+} = -11 in both, (a) and (b) (PSI/Nagra thermodynamic database 2020v1-1). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

If pCO_2 is at least as high as it would be corresponding to ambient atmospheric conditions, positively charged species occur under mildly alkaline conditions, but the negatively charged carbonate complex occurs under more strongly alkaline conditions (pH exceeding ~ 8.5). Therefore, there is the potential for sorption to be influenced by aqueous speciation which varies as a function of pH.

No reliable sorption data for Cm under relevant conditions have been identified. Nagra's thermodynamic database "PSI/Nagra thermodynamic database 2020v1-1" contains the same log K constants for Cm species and Am species, such that the same speciation is calculated (cf. Fig. 20 with Fig. 4-4). Reported K_d values in the reviewed literature are similar for Cm and Am (Appendix A) and many previous compilations have assigned the same K_d values to both elements (e.g., Tits & van Dorp 1999, Bradbury & Baeyens 2003, Crawford 2013, Kaplan 2016). For these reasons the same K_d values as for Am are recommended for Cm.

Recommended K_d values for Cm are given in Tab. 4-10.

Tab. 4-10: Recommended K_d values for Curium (m^3/kg)
(Americium analogue)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A). Upper and Lower Guide: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A).
	Lake/river	1.0E+01	1.0E+02	1.0E+00	
	River bed	1.0E+01	1.0E+02	1.0E+00	
	Aquifer	3.0E+00	3.0E+01	3.0E-01	
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.12 Holmium (Ho)

Holmium (Ho) is a lanthanoid (Period 7 of the periodic table) which is predicted to have the +III oxidation state under all conditions. The trivalent cation dominates under acidic and neutral pH conditions (Fig. 4-11a, Fig. 4-11b), between pH ~ 8.5 to 12.5 the neutral hydroxy complex dominates (Fig. 4-11a) and under highly alkaline conditions (> 12.5) the anionic hydroxide complex occurs (Fig. 4-11a).

However, in waters containing aqueous carbonate at levels consistent with atmospheric equilibration, the $HoCO_3^+$ species dominates over the range pH ~ 6.5 to 8.5 and at higher pH the $Ho(CO_3)_2^-$ species is predicted to dominate (Fig. 4-11b). These results imply that in surface waters in contact with the atmosphere, sorption may decrease as pH increases above pH ~ 8.5.

Few sorption data for Ho under relevant conditions have been identified. Very similar variations in aqueous speciation of Ho and Am are calculated in Eh-pH space using Nagra's thermodynamic database "PSI/Nagra thermodynamic database 2020v1-1" (cf. Fig. 4-11 with Fig. 4-4). The chief differences in speciation are that the $Ho(OH)_3$ field extends to lower pH than the $Am(OH)_3$ field, while this latter extends to pH 14, whereas $Ho(OH)_4^-$ is predominant above pH c. 12.5. However, none of the reference water conditions plot in the Ho(OH)3 field.

Reported K_d values in the reviewed literature are similar for Ho and Am (Appendix A) and several previous compilations have assigned the same K_d values to both elements (e.g. Tits & van Dorp 1999, Crawford 2013). For these reasons the same K_d values as for Am are recommended for Cm.

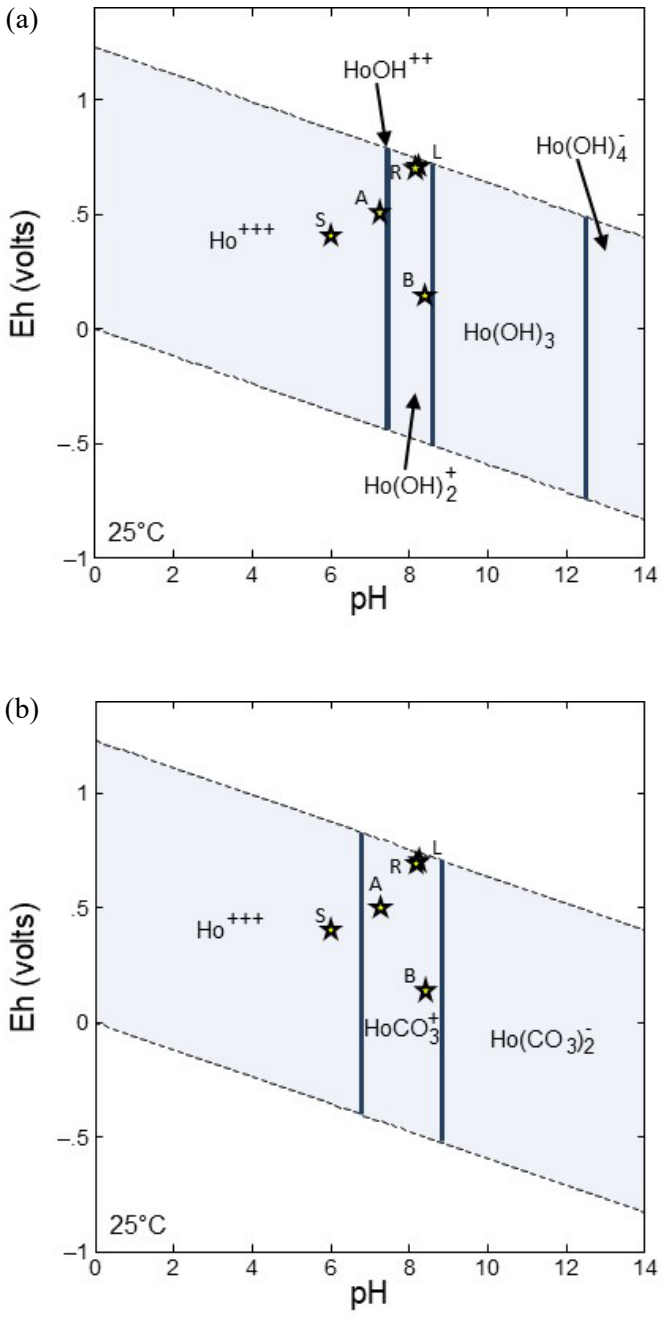

Fig. 4-11: Pourbaix diagram for Ho at 25 °C, 1 bar

(a) excluding CO_2; (b) including CO_2(g) (ambient atmospheric conditions, log pCO_2 = -3.5); log a Ho^{3+} = -11 in both, (a) and (b) (PSI/Nagra thermodynamic database 2020v1-1). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Ho are given in Tab. 4-11.

Tab. 4-11: Recommended K_d values for Holmium (m^3/kg)

(Americium analogue)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A). Upper and Lower Guide: Same K_d values assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A).
	Lake/river	1.0E+01	1.0E+02	1.0E+00	
	River bed	1.0E+01	1.0E+02	1.0E+00	
	Aquifer	3.0E+00	3.0E+01	3.0E-01	
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.13 Iodine (I)

Iodine (I) is a halogen (Group 17, Period 5 of the periodic table) which exists in aqueous solution as iodide (I^-) or iodate (IO_3^-), depending on the redox conditions (Fig. 4-12). At pH > 5.5, negatively charged species are likely to dominate. The sorption behaviour of I is not well known, though some authors consider sorption to be dominated by weak surface complexation (e.g. Linklater et al. 2003). Liu & von Gunten (1988) concluded that sorption of I at low pH could be possible in view of the positively charged mineral surfaces, and by analogy with other anions (SO_4^{2-}, PO_4^{3-}, NO_3^-, Cl^-). However, since solid phase surfaces will tend to become progressively more negatively charged at higher pH, under alkaline conditions sorption is likely to be relatively weak compared to many cations. Liu & von Gunten (1988) note that I is likely to sorb more effectively than Cl under acidic pH conditions. The available data suggest that IO_3^- would sorb more effectively than I^- under a given set of pH-Eh conditions (Appendix A). Kaplan (2016) report experimental results that suggest K_d values for IO_3^- sorption would be 2× to 6× greater than for I^- sorption.

Sorption of iodine species is dependent on soil type and properties; in mineral soils with low organic carbon content, iodide sorption is dominant, whereas organic rich soils are more favourable for iodate sorption (Shetaya et al. 2012, Duborská et al. 2019, Köhler et al. 2019). Organic carbon, clay content, pH and the abundance of iron, aluminium and manganese oxides and hydroxides are the most important soil properties controlling iodine sorption (Duborská et al. 2019). I may undergo anion exchange with Cl in soil (Sheppard et al. 1995) and it has been suggested that retention in soil may arise due to oxidation of I^- to I_2 with complexation to organic functional groups or oxides (Sheppard et al. 1996).

A factor that complicates the specification of K_d values is isotope dilution, whereby I-129 originating in the waste (and hence of concern to safety assessment) exchanges for natural stable I-127 present in the rock/soil/sediment. It is outside the scope of this work to consider this process.

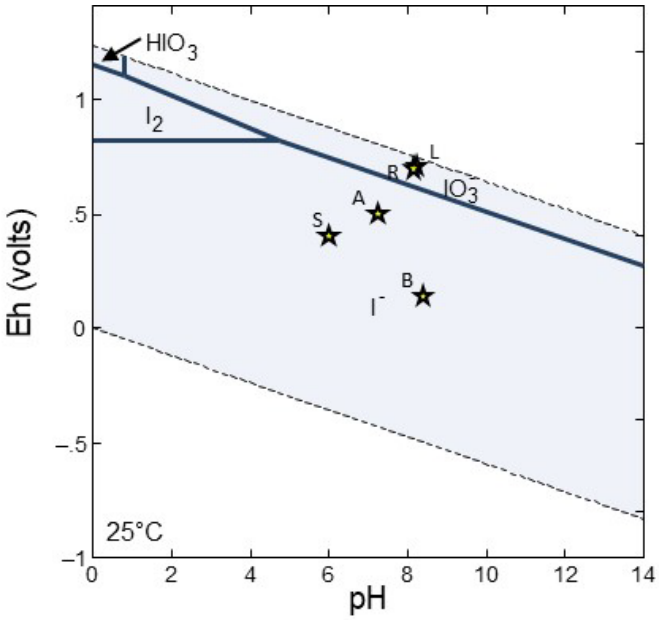

Fig. 4-12: Pourbaix diagram for I at 25 °C, 1 bar; log *a* I^- = -8 (PSI/Nagra thermodynamic database 2020v1-1)

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for I are given in Tab. 4-12.

Tab. 4-12: Recommended K_d values for Iodine (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	5.0E-03	5.0E-02	5.0E-03	Reference: Many quoted mean K_d values for different materials are in the order of 1.0E-03 (Appendix A). A mid-range value is proposed. Upper and Lower Guide: Lower Guide is an order of magnitude lower than the reference K_d, Upper Guide is an order of magnitude higher than the reference K_d. This difference is consistent with the ranges of K_d reported for sandy soil/sediment in the reviewed literature (Appendix A).
	Lake/river	1.0E-02	1.0E-01	1.0E-03	Reference: 2× the K_d for the reference soil water conditions in fine, lower organic content soil/sediment. Kaplan (2016) reports K_d for IO_3^- that are 2× to 6× higher than for I^- at similar pH. However, the pH for the reference lake/river water conditions is c. 2 units greater than for reference soil water conditions, and sorption of IO_3^- is therefore expected to be lower than would be the case at the same pH as reference soil water conditions. Upper and Lower Guide: Lower Guide is an order of magnitude lower than the reference K_d, Upper Guide is an order of magnitude higher than the reference K_d. This difference is consistent with the ranges of K_d reported for sandy soil/sediment in the reviewed literature (Appendix A).
	River bed	5.0E-03	5.0E-02	5.0E-03	Reference: The reference river bed water and aquifer water conditions have higher pH than the reference soil water conditions and therefore I is likely to sorb less than under reference soil water conditions in fine, lower organic content soil/sediment. However, data are insufficient to recommend a different K_d value from that in the presence of reference soil water conditions. Upper and Lower Guide: Lower Guide is an order of magnitude lower than the reference K_d, Upper Guide is an order of magnitude higher than the reference K_d. This difference is consistent with the ranges of K_d reported for sandy soil/sediment in the reviewed literature (Appendix A).
	Aquifer	5.0E-03	5.0E-02	5.0E-03	
Fine, higher organic content	Soil	2.00E-02	5.0E-02	5.0E-03	Reference: For each reference water 4× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Organic-rich materials tend to sorb I more effectively than organic-poor materials (Li et al. 2017). The available data suggest that differences between organic-poor and organic-rich clay-rich soil/sediment are likely to be less than an order of magnitude (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	4.00E-02	1.0E-01	1.0E-03	
	River bed	2.00E-02	5.0E-02	5.0E-03	
	Aquifer	2.00E-02	5.0E-02	5.0E-03	

Tab. 4-12: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Coarse, low-organic content	Soil	2.5E-03	5.0E-02	5.0E-03	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Based on experimental data, Kaplan (2016) estimated that K_d for sorption of I on sandy sediments at Savannah River is 30% of the K_d appropriate for sorption of I on clay sediments at the same site. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E-03	1.0E-01	1.0E-03	
	River bed	2.5E-03	5.0E-02	5.0E-03	
	Aquifer	2.5E-03	5.0E-02	5.0E-03	

4.14 Iron (Fe)

Iron (Fe) is a first-row transition metal (Group 8, Period 4 of the periodic table), which is commonly found in soil (as oxyhydroxide/hydroxide/carbonate minerals) and rock-forming minerals (as hydroxides, oxides, carbonates, sulphates, sulphides and silicates). Potentially dissolved Fe concentrations could be controlled by the solubility of an Fe-bearing mineral (as it was noted by Tits and van Dorp (1999)). Under such circumstances, it is inappropriate to model aqueous inorganic carbon concentrations using linear isotherms (K_d).

Iron exists as Fe(II) and Fe(III), with Fe^{2+} dominating as an aqueous species under lower Eh conditions up to a pH of ~ 8 (Fig. 4-13).

Depending on the pH, at higher Eh, magnetite or goethite could be stable phases (Fig. 4-13a), while at lower Eh and for pH between ~ 8 and ~ 10 $FeCO_3(aq)$ could be the dominant species (Fig. 4-13a). However, at aqueous Fe concentrations only slightly higher than those for which the Pourbaix plots in Fig. 4-13a are constructed, siderite ($FeCO_3(s)$) would occupy the field of aqueous $FeCO_3$.

Under relatively higher Eh conditions, iron hydroxide complexes exist with positively charged species occurring under acidic conditions and neutral/negatively-charged species existing under alkaline conditions (Fig. 4-13). Under low Eh conditions where high pH > 8 and < 10 the neutral, the $FeCO_3(aq)$ dominates when pCO_2 corresponds to ambient atmospheric conditions (Fig. 4 13b). The sensitivity of Fe to pH and redox could impact the nature and extent of sorption.

There are few reliable data for Fe sorption onto geological materials. In water in contact with the atmosphere, Fe(II) is readily oxidised to Fe(III), which has a very low solubility. Van Groeningen et al. (2020) found that Fe(II) initially sorbed on montmorillonite, was rapidly oxidised to form Fe(III) solid phases such as ferrihydrite and lepidocrocite when the montmorillonite was exposed to the atmosphere. Thus, experiments in contact with the atmosphere may not correctly investigate sorption of Fe and instead the measured aqueous Fe concentrations may have been solubility-controlled. Especially considering the difficulty of maintaining reducing conditions in sorption experiments, potentially this could mean that many reported K_d values are overestimated.

In view of the lack of data it is assumed that at near-neutral pH under anoxic conditions Fe(II) would sorb in a similar way to Ni(II), such that the reference values assigned to Fe(II) for the different materials are the same as those assigned to Ni(II). Lower and upper guide values are then assumed to be respectively an order of magnitude smaller and larger than each reference values. For conditions that are sufficiently oxidising for Fe(III) to be dominant, K_d values are not specified.

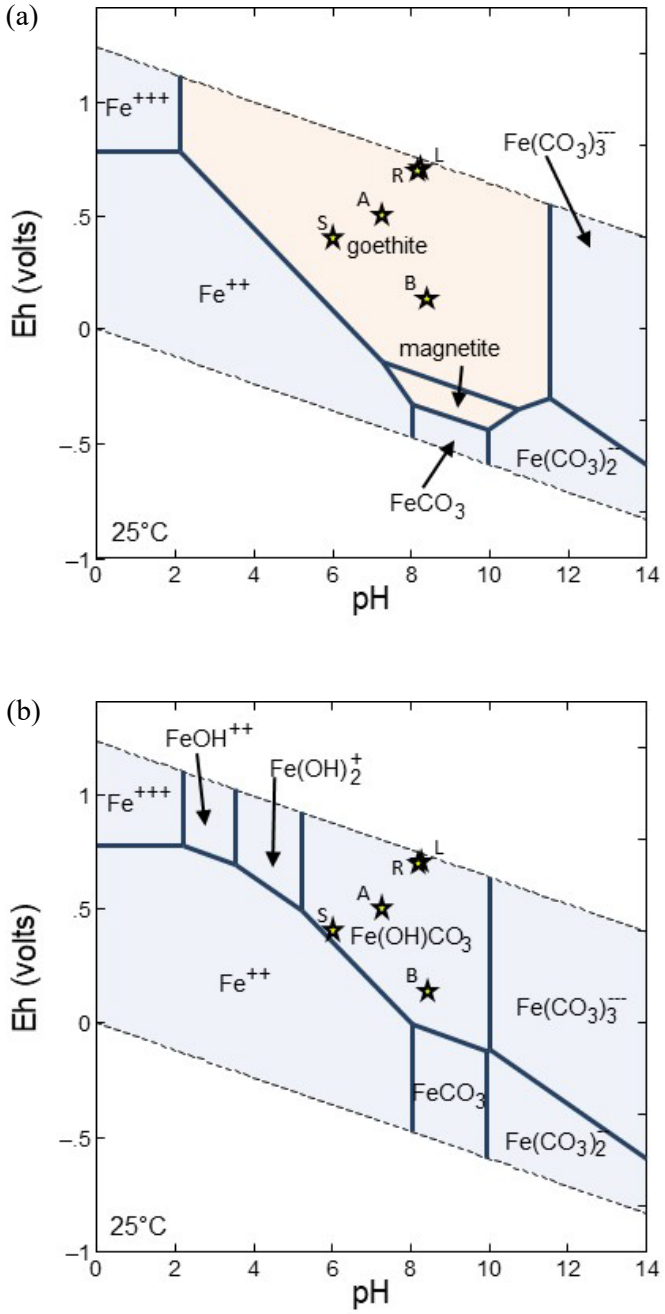

Fig. 4-13: Pourbaix diagrams for Fe at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1); log.*a* Fe^{2+} = -6; log pCO_2(g) = -3.5

(a) showing most stable minerals; (b) minerals excluded, only aqueous species shown. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Fe are given in Tab. 4-13.

Tab. 4-13: Recommended K_d values for Iron (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	None	5.0E-01	5.0E-03	Reference: Fe(III) dominates the speciation, such that probably the aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxyhydroxide or Fe-oxide phase. No K_d is recommended. Upper and Lower Guide: Upper Guide and Lower Guide are based on the range of values reported in the reviewed literature for which pH is < 7, such that Fe(II) is likely to be the dominant Fe form. The most reducing/lowest pH part of the soil water Eh-pH field lies in the Fe(II) predominance field.
	Lake/river	None	None	None	Reference: Fe(III) dominates the speciation, such that probably the aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxyhydroxide or Fe-oxide phase. No K_d is recommended. Upper and Lower Guide: Fe(III) is calculated to predominate Fe-speciation across the Eh-pH fields of lake/river water and river bed water. Hence aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxyhydroxide or Fe-oxide phase. No range of K_d is recommended.
	River bed	None	None	None	
	Aquifer	None	5.0E-01	5.0E-03	Reference: Fe(III) dominates the speciation, such that probably the aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxyhydroxide or Fe-oxide phase. No K_d is recommended. Upper and Lower Guide: Upper Guide and Lower Guide are based on the range of values reported in the reviewed literature for which pH is < 7 (Appendix A), such that Fe(II) is likely to be the dominant Fe form. The most reducing/ lowest pH part of the aquifer water Eh-pH field lies in the Fe(II) predominance field.
Fine, higher organic content	Soil	None	5.0E-01	5.0E-03	Reference: For each reference water Fe(III) dominates the speciation, such that probably the aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxy-hydroxide or Fe-oxide phase. No K_d is recommended. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	None	None	None	
	River bed	None	None	None	
	Aquifer	None	5.0E-01	5.0E-03	

Tab. 4-13: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Coarse, low-organic content	Soil	None	5.0E-01	5.0E-03	Reference: For each reference water Fe(III) dominates the speciation, such that probably the aqueous Fe concentration will be very small and controlled by the solubility of an Fe-oxy-hydroxide or Fe-oxide phase. No K_d is recommended. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	None	None	None	
	River bed	None	None	None	
	Aquifer	None	5.0E-01	5.0E-03	

4.15 Lead (Pb)

Lead (Pb) is a metal (Group 14, Period 6 of the periodic table) and most commonly occurs in the oxidation state of +II, though less commonly +IV may occur (e.g. in the oxide minimum, Pb_3O_4, which contains both Pb(II) and Pb(IV), or plattnerite, PbO_2), but the 0 state may exist under very reducing conditions. The metal is commonly found in soil (especially as lead carbonate, cerussite) and rock-forming minerals (especially carbonates and sulphide). The solubility of cerussite could influence measured solute concentrations at pH between ~ 7.5 and ~ 9.5 (Fig. 4-14a). If the concentration of aqueous Pb is controlled by solubility of this phase or another Pb-bearing solid, then it is inappropriate to model aqueous Pb behaviour using linear sorption isotherms.

Under acidic and neutral pH conditions, Pb^{2+} dominates in aqueous solution, with $PbCO_3(aq)$ occurring under mildly alkaline conditions (pH ~ 7 – 9), and $Pb(CO_3)^{2-}$ dominating under strongly alkaline conditions (pH > 9.3 under ambient atmospheric pCO_2 conditions) (Fig. 4-14).

Sorption of Pb is known to be pH dependent, consistent with it sorbing predominantly by surface complexation (Linklater et al. 2003). The variation of charge of the dominant form of dissolved Pb with pH (Fig. 4-14a) could also lead to variation in the nature and extent of interaction with mineral surfaces under the potential range of pH conditions (pH 4.0 – 9.5). Overall, sorption is lowest at acidic pH and increases to a maximum under near-neutral pH.

In general, Pb can sorb quite strongly to clays, solid organic matter and (oxy)hydroxide and oxide minerals, with some irreversibility being noted in some studies, suggesting update into crystals (e.g., Bryan 2016). For the reference conditions of soil water and aquifer water, Pb^{2+} is likely to be the dominant aqueous species, whereas under the reference conditions of river water, lake water and river bed water, neutral $PbCO_3(aq)$ is likely to be the dominant aqueous species (Fig. 24). Accounting for the increasingly positive charge on solid surfaces at increasingly acidic pH, it seems plausible that sorption will be less in the soil water and aquifer water than in the other waters.

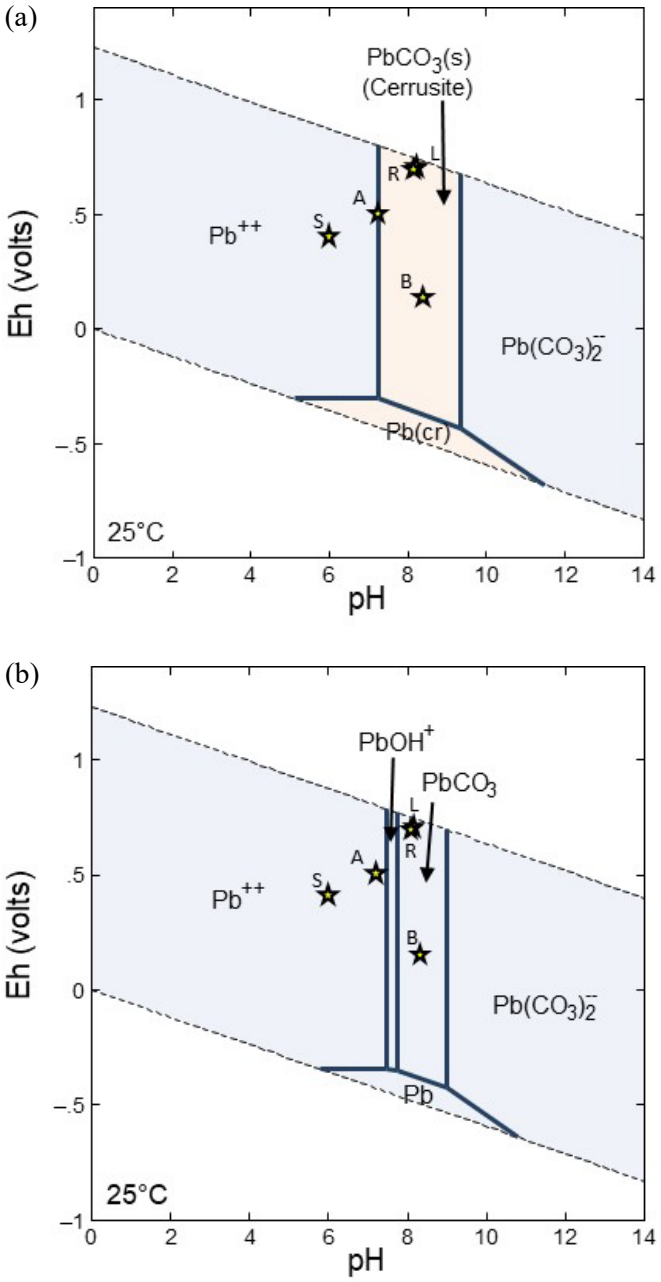

Fig. 4-14: Pourbaix diagrams for Pb at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1), log.aPb^{2+} = -6; log pCO$_2$(g) = -3.5 (ambient atmospheric conditions

(a) including Pb minerals; (b) excluding lead minerals (aqueous species only). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Pb are given in Tab. 4-14.

Tab. 4-14: Recommended K_d values for Lead (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	5.0E+00	1.0E+02	1.0E-03	Reference: Similar to K_d reported by Kaplan (2016) for slightly acidic clayey sediments, in the same order of magnitude as the geometric mean for all soils in IAEA (2010). Upper and Lower Guide: Lower Guide is in the same order as the lowest K_d reported in the reviewed literature (Appendix A), Upper Guide is in the same order as the largest K_d reported in the reviewed literature. Lower values of K_d are expected at lower pH, with the Lower Guide being applicable to the lowest pH of the soil field.
	Lake/river	1.0E+01	1.0E+02	1.0E+00	Reference: 2× the K_d for the reference soil water conditions in the fine, lower organic content soil/sediment. This value recognises the likely higher sorption under near-neutral conditions. Upper and Lower Guide: Lower Guide an order of magnitude smaller than the reference K_d, Upper Guide an order of magnitude larger than the reference K_d, reflecting the range of values for clay-rich soil/sediment in the reviewed literature with pH > 6 (Appendix A). Smaller K_d would be appropriate for lower pH conditions.
	River bed	1.0E+01	1.0E+02	1.0E+00	
	Aquifer	5.0E+00	1.0E+02	1.0E+00	Reference: Same K_d value as for the reference soil water conditions in the fine, lower organic content soil/sediment. This value recognises the lower pH, and hence likely lower sorption, than in the reference lake/river water and reference river bed water conditions in fine, lower organic content soils/sediments. While the pH of the reference aquifer water conditions is higher than that of the reference soil water conditions, such that higher sorption would be expected under the former, the available data do not justify specification of different K_d values under these two conditions. Upper and Lower Guide: Lower Guide an order of magnitude smaller than the reference K_d, Upper Guide an order of magnitude larger than the reference K_d reflecting the range of values for clay-rich soil/sediment in the reviewed literature with pH > 6 (Appendix A). The Lower Guide is larger than the Lower Guide for reference soil water conditions in fine, lower organic content soil/sediment because the aquifer water conditions do not extend to such low pH as the soil water conditions. Smaller K_d would be appropriate for lower pH conditions.
Fine, higher organic content	Soil	7.5E+00	1.0E+02	1.0E-03	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	7.5E+00	1.0E+02	1.0E+00	

Tab. 4-14: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Coarse, low-organic content	Soil	2.5E+00	1.0E+02	1.0E-03	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	2.5E+00	1.0E+02	1.0E+00	

4.16 Mercury (Hg)

Mercury (Hg) is a metal (Group 12, Period 6 of the periodic table), usually a liquid under room temperature conditions. Over the ranges of redox and pH conditions relevant to soils, surface waters and shallow groundwaters in Northern Switzerland, aqueous Hg is predicted to be predominant in neutral species (Fig. 4-15).

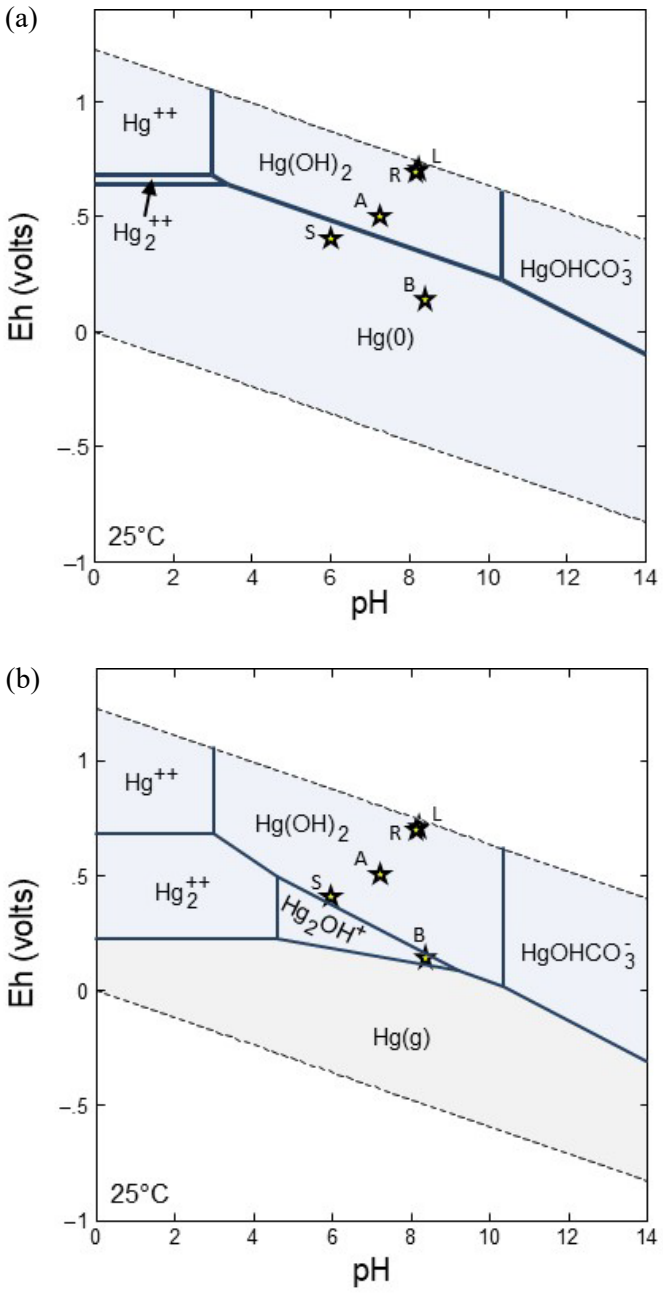

Fig. 4-15: Pourbaix diagram for Hg at 25 °C, 1 bar; log *a* Hg^{2+} = -8 (PSI/Nagra thermodynamic database 2020v1-1)

(a) showing all species calculated to be stable; (b) excluding Hg(0). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

However, speciation calculated using the PSI/Nagra database thermodynamic database suggests that possibly univalent $Hg_2(OH)^+$ could exist in a metastable manner/state (Fig. 4-15b).

Hg mobility in ecosystems is enhanced when complexed with organic ligands (e.g., as methylmercury). Hg(II) undergoes sorption to Fe(III) oxyhydroxides, organic matter and clay minerals (Debure et al. 2020), while Fe(II)-bearing minerals (magnetite and siderite) induce Hg(II) reduction (Debure et al. 2020), along with Fe(II)-bearing clays (O'Loughlin et al. 2020). The reduction of Hg(II) to Hg(0) could result in release of Hg from soil to the atmosphere with available literature suggesting volatilization depending on soil temperature and water content (O'Loughlin et al. 2020).

There are few sorption data for Hg under relevant conditions. However, based on the similarity of its chemical speciation to that of Pd, plausible K_d for Hg are specified using a combination of published sorption data for Pd and Hg.

Recommended K_d values for Hg are given in Tab. 4-15.

Tab. 4-15: Recommended K_d values for Mercury (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+02	1.0E-01	Reference: K_d a typical value for clay-rich materials (Appendix A; c.f. Kaplan (2016) who recommended this value for clayey sediment). This value is specified for all reference waters because the available data do not support the specification of different values. Upper and Lower Guide: Lower Guide and Upper Guide are based on reported range of K_d for clay-rich soil and sediment in the reviewed literature.
	Lake/river	1.0E+00	1.0E+02	1.0E-01	
	River bed	1.0E+00	1.0E+02	1.0E-01	
	Aquifer	1.0E+00	1.0E+02	1.0E-01	
Fine, higher organic content	Soil	4.0E+00	1.0E+02	1.0E-01	Reference: For each reference water 4× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Organic-rich materials appear to sorb Hg more effectively than organic-poor materials (e.g. c.f values for glacial clay and cultivated peat in Appendix A). The available data do not justify specification of different values for the different reference waters. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	4.0E+00	1.0E+02	1.0E-01	
	River bed	4.0E+00	1.0E+02	1.0E-01	
	Aquifer	4.0E+00	1.0E+02	1.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+02	1.0E-01	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Clay-poor samples will sorb less (e.g. c.f values for glacial clay and cultivated peat in Appendix A). The available data do not justify specification of different values for the different reference waters. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E-01	1.0E+02	1.0E-01	
	River bed	5.0E-01	1.0E+02	1.0E-01	
	Aquifer	5.0E-01	1.0E+02	1.0E-01	

4.17 Molybdenum (Mo)

Molybdenum (Mo) is a transition metal (Group 6, Period 5 of the periodic table) and it can exist in numerous oxidation states (+II, +IV, +V, +VI). However, in natural groundwater the only relevant redox state is +VI and under the conditions of interest (pH 4.0 – 9.5), the dominant species is molybdate (MoO_4^{2-}) (Fig. 4-16).

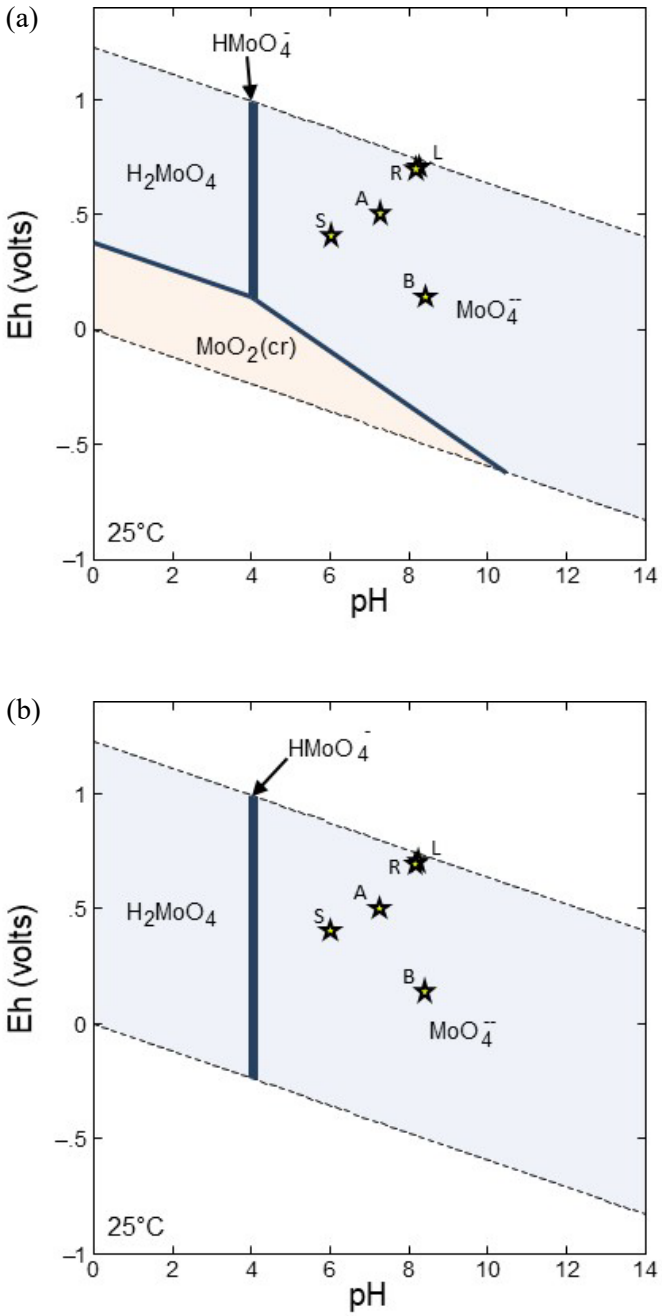

Fig. 4-16: Pourbaix diagrams for Mo at 25 °C, 1 bar; log *a* MoO_4^{2-} = -9

(a) including solids; (b) excluding solids (PSI/Nagra thermodynamic database 2020v1-1). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Under reducing conditions within the relevant pH range, potentially a solid oxide phase such as MoO_2(cr) could control aqueous concentrations of Mo. If such a solubility control were to occur, then it would be inappropriate to model Mo migration using sorption isotherms.

Molybdenum has been considered an analogue of TcO_4^- which sorbs poorly (Tits & van Dorp 1999). It has been suggested that Mo sorption is greater under acid conditions (e.g., Xu et al. 2013, Sun & Selim 2020). Soil minerals and organic matter may act as sorption substrates and the presence of competing anions can have implications for sorption (Xu et al. 2013). It has been noted that Ca-molybdate may precipitate under alkaline conditions (e.g., Yang & Wang 2021).

Recommended K_d values for Mo are given in Tab. 4-16.

Tab. 4-16: Recommended K_d values for Molybdenum (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E-01	1.0E-03	Reference: The geometric means of many different soils and sediments in the reviewed literature are in the order of 1.0E-02 m^3/kg (Appendix A). Upper and Lower Guide: Lower Guide is an order of magnitude smaller than the reference K_d, Upper Guide is an order of magnitude larger than the reference K_d, taking into account the reported range of K_d in the reviewed literature (Appendix A) and considering that sorption will be greater at higher pH than at lower pH, reflecting the anionic character of Mo and the increasingly negative charge on the surfaces of solid phases at higher pH.
	Lake/river	2.5E-03	2.5E-02	2.5E-04	Reference: 0.25× the K_d in the reference soil water in fine, lower organic content soil/ sediment based on the pH difference between the reference conditions and a reported increase of a factor of 2 for each unit pH decrease (Bradbury & Baeyens 2003). Upper and Lower Guide: Lower Guide is an order of magnitude smaller than the reference K_d, Upper Guide is an order of magnitude larger than the reference K_d, taking into account the reported range of K_d in the reviewed literature (Appendix A) and considering that sorption will be greater at higher pH than at lower pH, reflecting the anionic character of Mo and the increasingly negative charge on the surfaces of solid phases at higher pH. The pH of reference lake river water and river bed water extend to higher values than the pH of reference soil water, justifying a smaller Lower Guide than for reference soil water in fine, lower organic content soil/sediment.
	River bed	2.5E-03	2.5E-02	2.5E-04	
	Aquifer	5.0E-03	5.0E-02	5.0E-04	Reference: 0.5× the K_d under the reference soil water in fine, lower organic content soil/ sediment based on the pH difference between the reference and a reported increase of a factor of 2 for each unit pH decrease (Bradbury & Baeyens 2003). Upper and Lower Guide: Lower Guide is an order of magnitude smaller than the reference K_d, Upper Guide is an order of magnitude larger than the reference K_d. The rationale is the same as for reference lake/river water and river bed water in fine, lower organic content soil/sediment.

Tab. 4-16: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, higher organic content	Soil	4.0E-02	1.0E-01	1.0E-03	Reference: For each reference water 4× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. This is based on the limited data for organic rich and organic poor materials in the reviewed literature (Appendix A) and considering that sorption will be greater at higher pH than at lower pH, reflecting the anionic character of Mo and the increasingly negative charge on the surfaces of solid phases at higher pH. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.0E-02	2.5E-02	2.5E-04	
	River bed	1.0E-02	2.5E-02	2.5E-04	
	Aquifer	2.0E-02	5.0E-02	5.0E-04	
Coarse, low-organic content	Soil	5.0E-03	1.0E-01	1.0E-03	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.3E-03	2.5E-02	2.5E-04	
	River bed	1.3E-03	2.5E-02	2.5E-04	
	Aquifer	2.5E-03	5.0E-02	5.0E-04	

4.18 Neptunium (Np)

Neptunium (Np) is an actinoid (Period 7 of the periodic table) which can have different oxidation states, typically Np(+V) in solution, and Np(+IV) in solid compounds (Fig. 4-17).

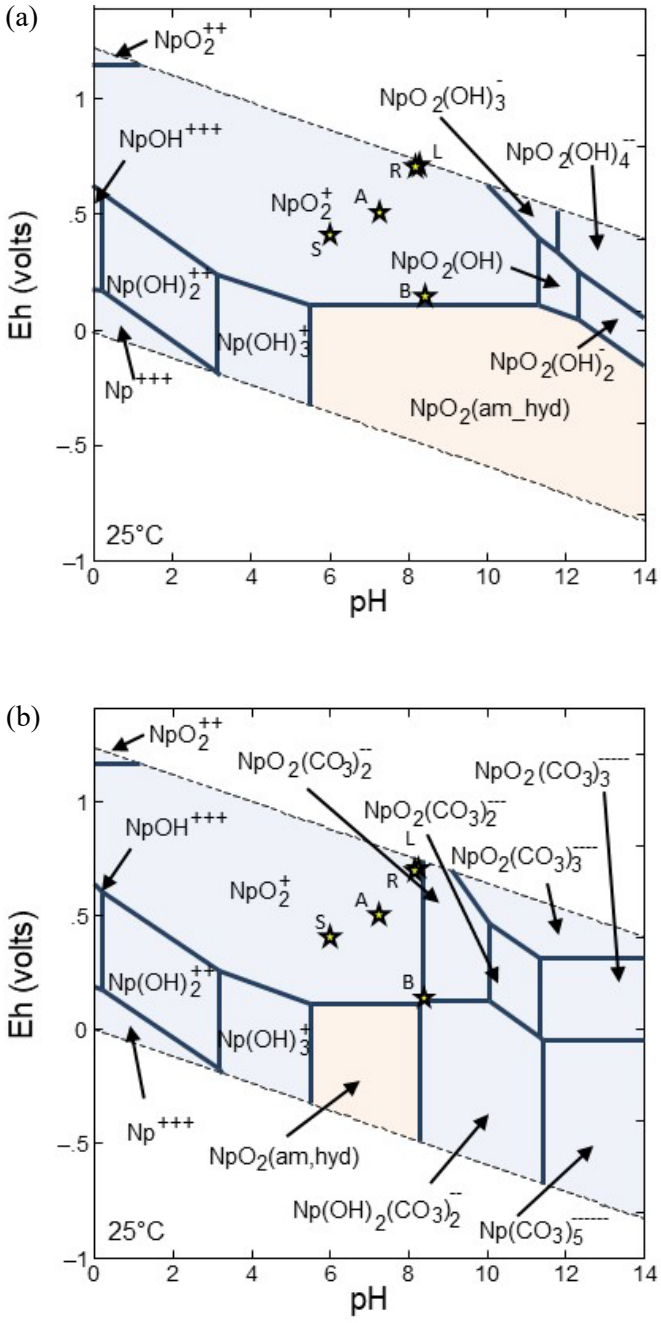

Fig. 4-17: Pourbaix diagrams for Np at 25 °C, 1 bar

(a) log *a* NpO_2^{2+} = -9; (b) log *a* NpO_2^{2+} = -9, log pCO_2(g) = -3.5 (ambient atmospheric conditions). (PSI/Nagra thermodynamic database 2020v1-1). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Depending on Eh, Np exists as NpO_2^+ or positively charged hydroxy complexes under acidic conditions. $Np(OH)_4(aq)$ dominates under lower Eh conditions when pH is > 6 (occupying the same field as solid NpO_2(amhyd) in Fig. 4-17a), while under higher Eh conditions (~ 0.25 V) NpO_2^{2+} dominates. In water that has pCO_2 consistent with atmospheric equilibration, negatively charged carbonate complexes occur at pH 8 – 10 (Fig. 4-17b). Under the reference water conditions, NpO_2^+ is predicted to be the dominant aqueous species (Fig. 4-17b).

Np is believed to sorb by surface complexation (Linklater et al. 2003). The sorption of Np to soil minerals can exhibit complex behaviour with hysteresis effects (e.g., Tinnacher et al. 2011) and carbonate complexation may reduce the sorption of Np(+V) to clay minerals such as montmorillonite (Turner et al. 1998). The ability of Np to undergo changes in oxidation state means that it may also participate in redox reactions which can influence sorption behaviour (e.g., Nakata et al. 2002). However, Kaplan (2016) considered it unlikely that in clayey and sandy sediments at the Savannah River site, U.S.A, Np(V) would in practice be reduced to Np(IV). Similarly, Crawford (2013) considered that Np(IV) would dominate in the geosphere around the SFR repository in Sweden. Sorption mechanisms may include inner sphere and ion exchange reactions (e.g., Wu et al. 2009, Amayri et al. 2011, Li et al. 2015).

Recommended K_d values for Np are given in Tab. 4-17.

Tab. 4-17: Recommended K_d values for Neptunium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+01	1.0E-03	Reference: Geometric mean K_d values for a range of soils in the reviewed literature are in the order of 1.0E-02 m^3/kg (Appendix A). Based on experimental studies, Kaplan (2016) proposed a value of 9.0E-03 m^3/kg for clayey sediment at the Savannah River site, U.S.A. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported in the reviewed literature (Appendix A), reflecting that lowest sorption is expected under the most oxidising, lowest pH conditions (these are within the field of soil water). Upper Guide is in the same order as the largest K_d, reported in the reviewed literature (Appendix A) reflecting the fact that in the most reducing soil waters Np(IV) dominates Np speciation and will sorb to a greater extent than Np(V).
	Lake/river	4.0E-02	4.0E-01	4.0E-03	Reference: 4× the K_d in the reference soil water in fine, lower organic content soil/sediment based on the pH difference between the reference conditions and a reported increase of a factor of c. 2 for each unit pH increase, assuming the pH – K_d relationship is similar for Np(IV) as it is for Np(V) (Bradbury & Baeyens 2003). Data are insufficient to justify different K_d for reference lake/river water and river bed water. Upper and Lower Guide: Lower Guide is an order of magnitude lower than the reference K_d consistent with being greater than the Lower Guide for reference soil water in fine, lower organic content soil/sediment, reflecting the higher pH of reference lake/river water and river bed water. Upper Guide is an order of magnitude greater than the Reference K_d, consistent with being smaller than the Upper Guide for reference soil water in fine, lower organic content soil/sediment, reflecting Np being dominantly Np(V) which sorbs less strongly than Np(IV). Data are insufficient to justify specification of different Upper Guide and Lower Guide values for reference lake/river water and river bed water.
	River bed	4.0E-02	4.0E-01	4.0E-03	
	Aquifer	2.0E-02	1.0E+01	1.0E-03	Reference: 2× the K_d under the reference soil water in fine, lower organic content soil/ sediment based on the pH difference between the reference conditions and a reported increase of a factor of c. 2 for each unit pH increase, assuming the pH – K_d relationship is similar for Np(IV) as it is for Np(V) (Bradbury & Baeyens 2003). Upper and Lower Guide: Lower Guide and Upper Guide values are the same as for reference soil water in fine, lower organic content soil/ sediment. Data are insufficient to justify specification of different Upper Guide and Lower Guide values for reference aquifer water and reference soil water.

Tab. 4-17: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, higher organic content	Soil	1.50E-02	1.0E+01	1.0E-03	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	6.00E-02	4.0E-01	4.0E-03	
	River bed	6.00E-02	4.0E-01	4.0E-03	
	Aquifer	3.00E-02	1.0E+01	1.0E-03	
Coarse, low-organic content	Soil	5.0E-03	1.0E+01	1.0E-03	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	2.0E-02	4.0E-01	4.0E-03	
	River bed	2.0E-02	4.0E-01	4.0E-03	
	Aquifer	1.0E-02	1.0E+01	1.0E-03	

4.19 Nickel (Ni)

Nickel (Ni) is a first-row transition metal (Period 4 and Group 10 of the periodic table). Under natural conditions relevant to this report it is not redox-sensitive and present only in the divalent state. However, redox conditions may indirectly affect the behaviour of Ni as it is often sorbed or incorporated into Mn and Fe oxides (Ticknor 1994 and Larsen & Postma 1997). Reduction of these oxides may release Ni to solution, while oxidation of reduced Mn- and Fe- minerals may produce Mn- and Fe- oxides that scavenge aqueous Ni. Under reducing conditions Fe^{2+} may reduce Mn-oxides, thereby liberating Ni to solution. Ni may also strongly sorb to clay minerals (Dähn et al. 2003, Merrot et al. 2020) and to calcite (Hoffmann & Stipp 2001).

Speciation calculations using the PSI/Nagra thermodynamic database 2020v1-1 show that dissolved Ni will be in the form of Ni^{2+} at pH < 8 and present as neutral $Ni(OH)_2$ between 9 < pH < 11.5 (Fig. 4-18). These calculations also suggest that at pH greater than ~ 10.5 dissolved Ni will be in anionic form, as $Ni(OH)_3^-$. González-Siso et al. (2018) have questioned whether this species would form under alkaline conditions. However, the pH range over which $Ni(OH)_3^-$ is predicted to dominate Ni speciation is higher than the maximum pH of waters relevant to this study and therefore this uncertainty is not relevant to the assignment of K_d values here. Potentially, at the highest pH of the considered groundwaters solid $Ni(OH)_2$(cr) or $NiCO_3$(cr) could be stable. It has also been suggested that possibly sulphides could be solubility-limiting phases under sufficiently reducing conditions (Linklater et al. 2003). If aqueous Ni concentrations are indeed solubility limited it would be inappropriate to model Ni using a sorption isotherm.

Nickel is believed to sorb dominantly by surface complexation, but cation exchange may also play a role, with competition for alkaline earth elements apparently occurring (Linklater et al. 2003, Crawford 2013). Nickel sorbs strongly to Fe/Mn-oxides and oxyhydroxides and to clay minerals. Sorption to quartz and feldspar is weak (Linklater et al. 2003).

Reflecting the pH-dependent change in aqueous speciation of Ni, and the change in charge on solid surfaces from positive to negative, from acid to alkaline conditions, the sorption of Ni is also pH-dependent (Poinssot et al. 1999, Linklater et al. 2003). Sorption is weakest at acidic pH, when aqueous Ni is dominantly in the form of a divalent cation (Ni^{2+}) and solid surfaces are positively charged. At near-neutral pH when the dominant aqueous form is still Ni^{2+}. but solid surfaces are negatively charged, sorption is a maximum. At higher pH, above pH 9, where neutral $Ni(OH)_2$ dominates the aqueous speciation and solid phase surfaces are negatively charged, sorption possibly weakens. Poinssot et al. (1999) report that K_d for Ni sorption on illite in 0.01 M $NaClO_4$ solution increases by about 2 orders of magnitude between pH 4 and pH 8.

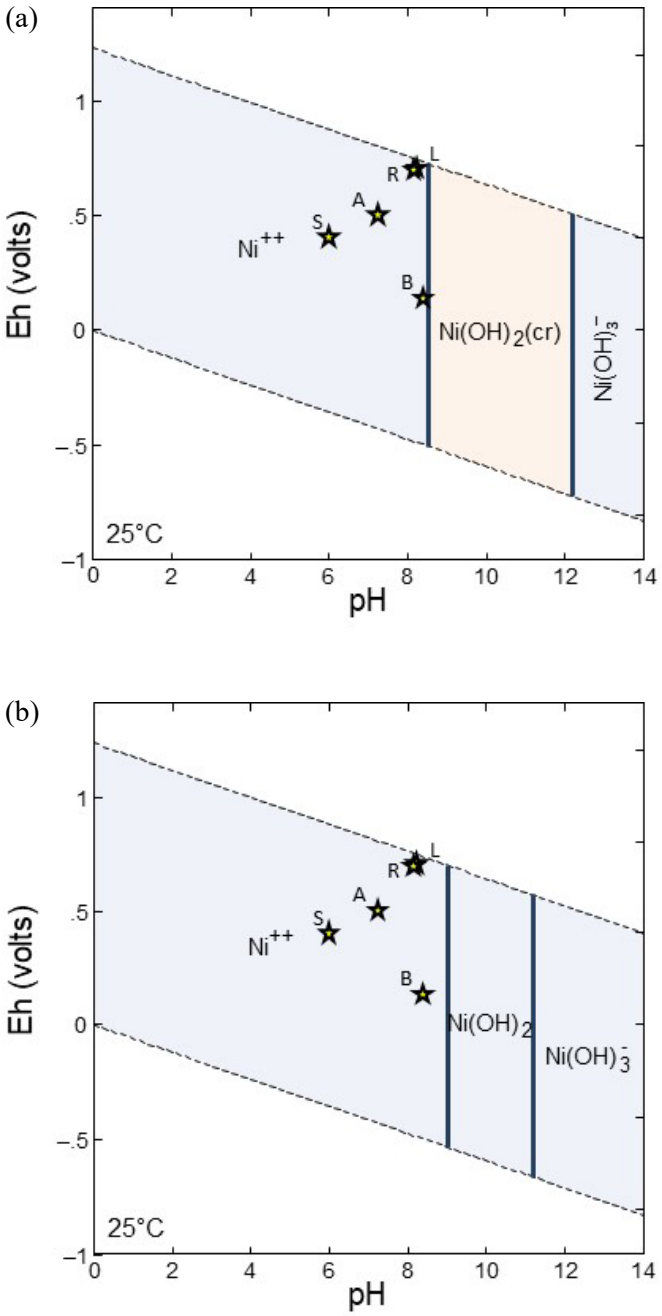

Fig. 4-18: Pourbaix diagrams for Ni at 25 °C, 1 bar, (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Ni^{2+} = -6; (b) log *a* Ni^{2+} = -8 (c) log *a* Ni^{2+} = -6, log $pCO_{2(g)}$ = - 3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

(c)

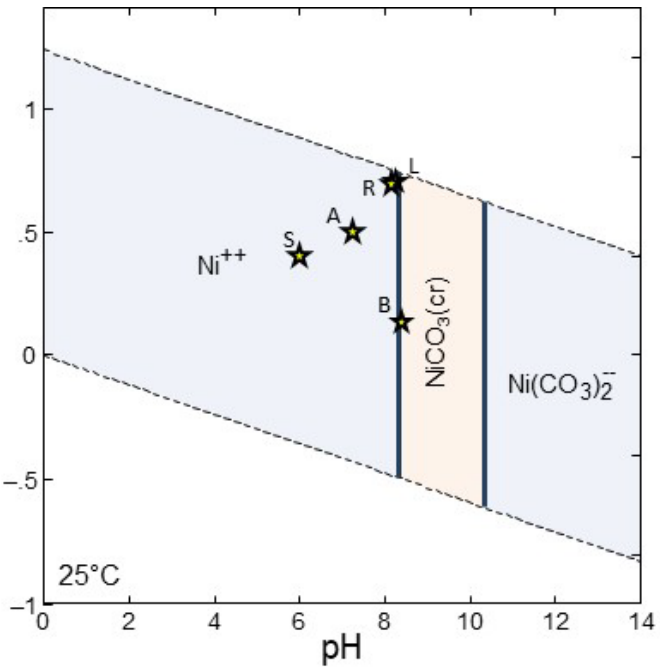

Fig. 4-18: Cont.

Recommended K_d values for Ni are given in Tab. 4-18.

Tab. 4-18: Recommended K_d values for Nickel (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	5.0E-02	1.0E+01	1.0E-03	Reference: Based on experimental data. Kaplan (2016) recommended a K_d value of 3.0E-02 m^3/kg for clayey sediment at Savannah River, U.S.A., while IAEA (2010) gives a geometric mean K_d value of 5.8E-02 m^3/kg for soil with pH between 5.0 and 6.5. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the smallest K_d reported in the reviewed literature, for soil with pH < 5 (Appendix A). Upper Guide is in the same order of magnitude as the largest value reported in the reviewed literature for clay till pH 8.1 (Appendix A). This pH range is comparable to that of the field of soil waters (pH 3.9 to 7.4).
	Lake/river	5.0E-01	1.0E+01	5.0E-02	Reference: K_d value is an order of magnitude greater than the K_d value for the reference soil water in fine lower organic content soil/ sediment. This difference is similar to the difference in K_d reported by Poinssot et al. (1999) for Ni sorption onto illite between pH 6 and 8. Upper and Lower Guide: Lower Guide is the same as for the reference K_d for reference soil water, recognising that the lowest pH of the lake/river water field (pH 6.5) is similar to the pH of the reference soil water (pH 6). Upper Guide is in the same order of magnitude as the largest value reported in the reviewed literature for clay till pH 8.1 (Appendix A), in recognition of the maximum pH of lake/river water being 8.73 and K_d possibly reaching a maximum around pH 8 (Poinssot et al. 1999).
	River bed	5.0E-01	1.0E+01	1.0E-01	Reference: K_d value is an order of magnitude bigger than the K_d value for the reference soil water in fine lower organic content soil/ sediment. This difference is similar to the difference in K_d reported by Poinssot et al. (1999) for Ni sorption onto illite between pH 6 and 8. Upper and Lower Guide: Lower Guide is selected to lie between the reference K_d and the Lower Guide for lake/river water in fine, lower organic content soil/sediment, recognising that the lowest pH of river bed water (7.8) is c. 1.5 units higher than the lowest pH of lake/river water (6.25). Upper Guide is the same as for lake/river water in fine, lower organic content soil/sediment, consistent with pH 9 being the maximum for river bed water, and K_d possibly reaching a maximum around pH 8 (Poinssot et al. 1999).

Tab. 4-18: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Aquifer	5.0E-01	1.0E+01	5.0E-02	Reference: K_d value is an order of magnitude bigger than the K_d value for the reference soil water in fine lower organic content soil/ sediment. This difference is similar to the difference in K_d reported by Poinssot et al. (1999) for Ni sorption onto illite between pH 6 and 7 (there is little difference between pH 7 and 8). Upper and Lower Guide: Lower Guide is the same as for lake/river water, recognising that the lowest pH of lake/river water and aquifer water are similar (6.25 and 6.5 respectively).
Fine, higher organic content	Soil	7.5E-02	1.0E+01	1.0E-03	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	7.5E-01	1.0E+01	5.0E-02	
	River bed	7.5E-01	1.0E+01	1.0E-01	
	Aquifer	7.5E-01	1.0E+01	5.0E-02	
Coarse, low-organic content	Soil	2.5E-02	1.0E+01	1.0E-03	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	2.5E-01	1.0E+01	5.0E-02	
	River bed	2.5E-01	1.0E+01	1.0E-01	
	Aquifer	2.5E-01	1.0E+01	5.0E-02	

4.20 Niobium (Nb)

Niobium (Nb) is a second-row transition metal (Group 5, Period 5 of the periodic table) with common oxidation states of +III and +V. However, under the range of pH and Eh of relevance to soil, surface waters and shallow groundwater in Switzerland Nb will be in the +V state (Åström et al. 2008). In European surface waters, it has a mean concentration of 4E-11 mol/L, although Swiss rivers may contain up to c.2E-10 mol/L (Salminen 2005). For comparison, porewater extracted from the Opalinus Clay has been reported to contain c. 3E-8 mol/L (Pearson et al. 2003).

Åström et al. (2008) report that in European stream waters filtered to < 0.45 μm Nb concentrations correlate with dissolved organic carbon (DOC) and dissolved iron concentrations. The former correlation was interpreted to mean that Nb bonds directly to humic substances, whereas the latter correlation was considered due to an association between Nb and colloidal Fe-oxyhydroxides.

When Nb(V) species are dominant Nb can sorb strongly onto clay minerals and Fe/Mn oxides, probably by surface complexation (Linklater et al. 2003). Ervanne et al. (2014) studied Nb sorption onto kaolinite and illite minerals in Na- and Ca- perchlorate solutions. Distribution coefficients for both minerals were found to be high, around 100 m^3/kg, for pH between 6 and 8, with lower sorption at pH < 5. In Na-perchlorate solution, Nb sorbs less strongly at pH > 8. Similar weakening of sorption at higher pH was not observed for Ca-perchlorate solutions, owing to the effects of Ca on Nb speciation and surface complexation.

The chemical speciation of Nb as a function of pH and Eh is shown in Fig. 4-19. These diagrams show that probably Nb will be present as negatively charged $Nb(OH)_6^-$ over most of the pH range of interest and possibly as the neutral species $Nb(OH)_5$ in the more acidic soil waters. The change between domination of the neutral species and a univalent negatively charged species occurs at pH ~ 6.5. The divalent negative species becomes dominant at pH ~ 9. The possibility that a Nb concentrations may be solubility limited by a phase such as columbite ($(Fe,Mn)Nb_2O_6$) cannot be ruled out. If this is the case, then it would be inappropriate to model aqueous Nb concentrations using sorption isotherms.

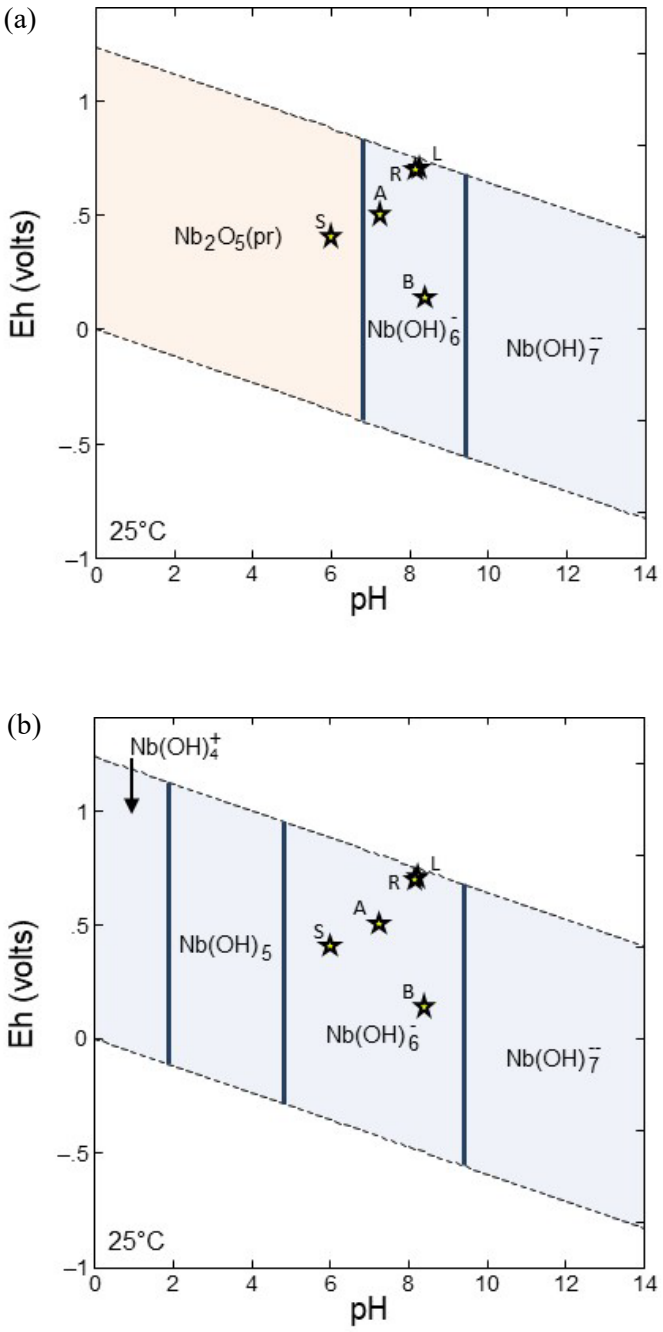

Fig. 4-19: Pourbaix diagrams for Nb at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* $Nb(OH)_4^+$ = -6; (b) log *a* $Nb(OH)_4^{+-}$ = -8. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Nb are given in Tab. 4-19.

Tab. 4-19: Recommended K_d values for Niobium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	2.0E+00	1.0E+02	1.0E-01	Reference: The K_d value is the mid-range of geometric mean and recommended K_d values for clay-rich materials from among the reviewed literature (Appendix A). The data do not justify specification of different values for the different reference water conditions. Upper and Lower Guide: Lower Guide and Upper Guide are in the same orders as the minimum K_d and maximum K_d, respectively, in the reviewed literature (Appendix A). The data do not justify specification of different values for soil waters, lake/river waters, river bed waters, or aquifer waters.
	Lake/river	2.0E+00	1.0E+02	1.0E-01	
	River bed	2.0E+00	1.0E+02	1.0E-01	
	Aquifer	2.0E+00	1.0E+02	1.0E-01	
Fine, higher organic content	Soil	3.0E+00	1.0E+02	1.0E-01	Reference: 1.5× the K_d for reference conditions in fine, lower organic content soil/sediment. The data do not justify specification of different values for the different reference water conditions. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same in each water, and the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	3.0E+00	1.0E+02	1.0E-01	
	River bed	3.0E+00	1.0E+02	1.0E-01	
	Aquifer	3.0E+00	1.0E+02	1.0E-01	
Coarse, low-organic content	Soil	1.0E+00	1.0E+02	1.0E-01	Reference: 0.5× the K_d value for reference soil water conditions in fine, lower organic content soil/sediment. The data do not justify specification of different values for the different reference water conditions. Upper and Lower Guide: Lower Guide and Upper Guide are the same in each water, and the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.0E+00	1.0E+02	1.0E-01	
	River bed	1.0E+00	1.0E+02	1.0E-01	
	Aquifer	1.0E+00	1.0E+02	1.0E-01	

4.21 Palladium (Pd)

Palladium (Pd) is a second-row transition metal (Group 10, Period 5 of the periodic table). The common oxidation states of the element are +IV, +II and 0. However, under Eh, pH and water chemical conditions relevant to this work +II and 0 are the dominant redox states (Fig. 4-20). The element hydrolyses strongly in solution and can form complexes with soft ligands such as Cl^-, HS^- and NH_3.

There are few data for Pd in natural waters. In porewater extracted from the Opalinus Clay Pd concentrations have been reported to lie between 8.5E-10 mol/L and 6.0E-8 mol/L (Pearson et al. 2003). In UK groundwater, Pd concentrations range between < 1.9E-9 mol/L and 2.44E - 8 mol/L (Shand et al. 2007).

The chemical speciation of Pd as a function of pH and Eh is shown in Fig. 4-20. If Pd concentrations were to be towards the higher end of the reported concentration range for natural waters, and towards the more reducing end of the plausible Eh range, elemental Pd could be stable (Fig. 4-20a). Over the range of pH and Eh relevant to Northern Swiss shallow groundwaters and surface waters, probably aqueous Pd will be dominant in the form of the neutral species $Pd(OH)_2$ (Fig. 4-20b). If Cl concentrations are similar to those reported for Swiss surface waters, then the $PdCl_3^-$ species could dominate at pH < 6 and Eh > 0.4 V (Fig. 4-20b), which is relevant to some soil waters in Northern Switzerland. Potentially under very reducing conditions metallic Pd could be stable. If this is the case and aqueous Pd concentrations are solubility-limited it would be inappropriate to model aqueous Pd concentrations using sorption isotherms.

There are few sorption data available for Pd in relevant materials. However, limited data for more sorption of Pd to bentonite, shale and illite in more saline waters suggest that sorption will decrease with increasing pH, consistent with the formation of anionic species under higher pH conditions (Tachi et al. 1999, Vilks & Yang 2018). Some authors have advocated using K_d for one or more of Co, Ni, Cd and Pb, considered as chemical analogues for Pd (Bradbury & Baeyens 2003, Ochs et al. 2016). However, all these elements show different chemical speciation to that calculated for Pd over the relevant range of Eh and pH conditions (cf. Fig. 4-20 with Fig. 4-18, and Fig. 4-14). On the other hand, although the aqueous speciation of Pd and Hg are similar (cf. Fig. 4-20 with Fig. 4-15), which suggests that Pd and Hg should sorb similarly, reported K_d values for these elements (usually estimated using analogue elements) are generally different by around an order of magnitude, with Hg being considered to sorb more strongly (Appendix A).

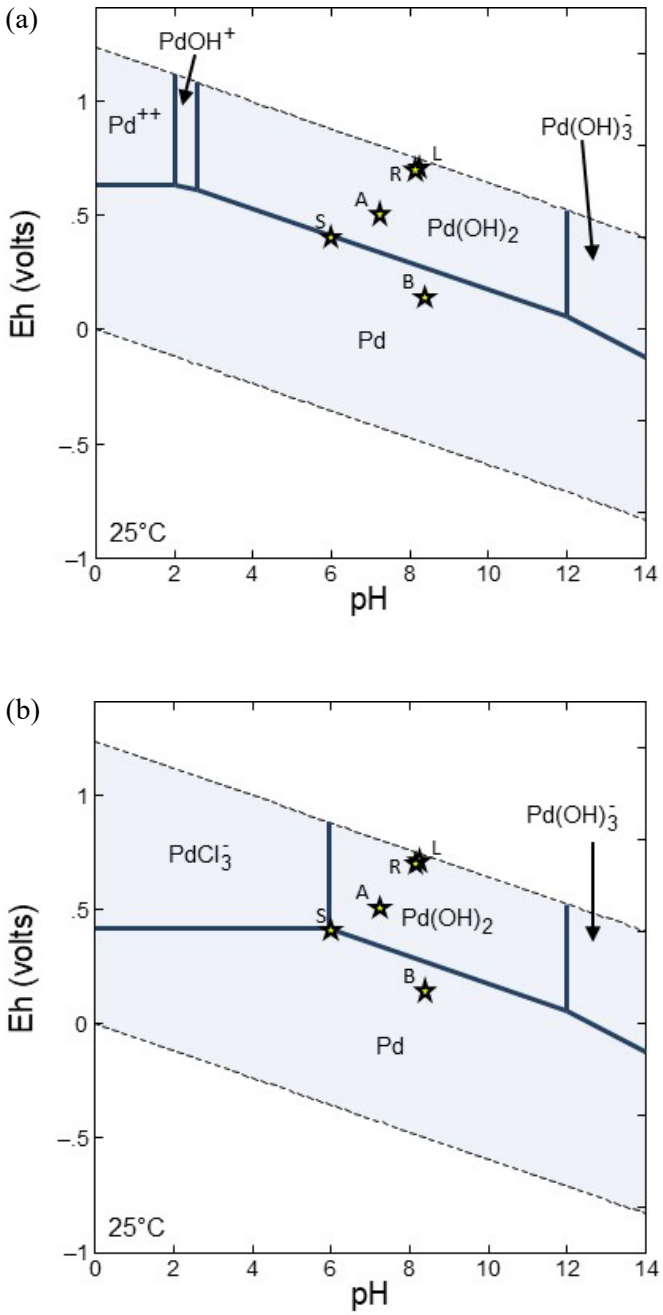

Fig. 4-20: Pourbaix diagrams for Pd at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Pd^{2+} = -8; (b) log *a* Pd^{2+-} = -10 and log *a* Cl^- = -1. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Pd are given in Tab. 4-20.

Tab. 4-20: Recommended K_d values for Palladium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-01	1.0E+00	1.0E-03	Reference: K_d the geometric mean of values for mineral soil (IAEA 2010; Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are in the same orders of magnitude as the lowest and highest K_d in the reviewed literature respectively (Appendix A). Possibly expect higher values in soil waters that have pH < 6 than at higher pH, owing to the possibility of anionic aqueous Cl-species at lower pH, at which solid surfaces are positively charged, but neutral species at higher pH.
	Lake/river	1.0E-02	1.0E+00	1.0E-03	Reference: K_d is an order of magnitude smaller than the K_d for reference soil water on fine, lower organic content soil/sediment. This is based on the decrease of c. 1 order of magnitude in K_d between pH 6 and pH 8 reported by Tachi et al. (1999) for sorption of Pd on bentonite. Upper and Lower Guide: Same values as for soil water in fine, lower organic content soil/ sediment since available data do not justify different values.
	River bed	1.0E-02	1.0E+00	1.0E-03	Reference: K_d is an order of magnitude smaller than the K_d for reference soil water on fine, lower organic content soil/sediment. This is based on the decrease of c. 1 order of magnitude in K_d between pH 6 and pH 8 reported by Tachi et al. (1999) for sorption of Pd on bentonite. Upper and Lower Guide: Same values as for soil water in fine, lower organic content soil/sediment since available data do not justify different values.
	Aquifer	5.0E-02	1.0E+00	1.0E-03	Reference: K_d is midway between the K_d for reference soil water on fine lower organic content soil/sediment and the K_d values for reference lake/river water and reference River bed water in fine, lower organic content soil/sediment. This is based on the decrease of c. 0.5 order of magnitude in K_d between pH 6 and pH 7 reported by Tachi et al. (1999) for sorption of Pd on bentonite. Upper and Lower Guide: Same values as for soil water in fine, lower organic content soil/sediment since available data do not justify different values.
Fine, higher organic content	Soil	1.5E-01	1.0E+00	1.0E-03	Reference: For all reference conditions 1.5× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.5E-02	1.0E+00	1.0E-03	
	River bed	1.5E-02	1.0E+00	1.0E-03	
	Aquifer	7.5E-02	1.0E+00	1.0E-03	

Tab. 4-20: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Coarse, low-organic content	Soil	5.0E-02	1.0E+00	1.0E-03	Reference: For all reference conditions 0.5× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment.
	Lake/river	5.0E-03	1.0E+00	1.0E-03	
	River bed	5.0E-03	1.0E+00	1.0E-03	
	Aquifer	2.5E-02	1.0E+00	1.0E-03	Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment. The data do not justify specification of different values for the different waters.

4.22 Plutonium (Pu)

Plutonium (Pu) is an actinoid (Period 7 of the periodic table) with common oxidation states of +III, +IV, +V and +VI more than one of which may exist in solution at the same time owing to slow kinetics of oxidation and reduction, resulting in a complex aqueous chemistry (Higgo 1988, Linklater et al. 2003). Under oxidising conditions Pu has a low solubility under near neutral to slightly alkaline conditions. Calculations with the PSI/Nagra thermodynamic database 2020v1-1 indicate a minimum solubility of ~ 1E-10 mol/kg at pH ~ 8.1 and Eh of -0.3 V, controlled by the amorphous hydrated solid PuO_2(am,hyd). Under more oxidising conditions the solubility of this phase is even lower.

With increasing pH, Pu has a strong tendency to hydrolyse in carbonate-poor waters (Fig. 4-21a), but to form carbonate complexes in waters that contain dissolved carbonate (Fig. 4-21b). Most of the range of Eh and pH spanned by soil waters in Northern Switzerland lies within the predominance fields of positively charged species (Pu^{3+}, $Pu(OH)_3^+$, PuO_2^+, $PuCO_3^+$). At higher pH, soil waters, surface waters and shallow groundwaters have Eh and pH lying predominantly within the fields of neutral or negative species ($Pu(OH)_4$, $PuCO_3(OH)_3^-$, PuO_2CO_3, $PuO_2CO_3^-$, $PuO_2(CO_3)_2^{2-}$, $PuO2(CO_3)_3^{4-}$). The reference water conditions plot within the fields of $Pu(OH)_3^+$, $Pu(OH)_4$ and PuO_2^+ in carbonate-free waters and in $Pu(OH)_3^+$, PuO_2^+ and $PuCO_3(OH)_3^-$ in water with carbonate concentration buffered by equilibrium with the atmosphere (Fig. 4-21).

Pu sorbs predominantly by surface complexation (Higgo 1988, Linklater et al. 2003), and its more reduced forms, Pu(III) or Pu(IV), sorb significantly more strongly than its more oxidised forms, Pu(V) or Pu(VI) (Linklater et al. 2003). It is reported that the strongest sorption is onto iron oxides/hydroxides, clays, micas and zeolites, and the lowest sorption being on feldspars, gibbsite and quartz (Linklater et al. 2003). Comparison between data for sorption on organic-rich and organic poor substrates provides little evidence for preferential sorption onto organic materials (IAEA 2010).

Sorption varies with pH, which influences both the aqueous speciation at a given redox state and the surface charge of the sorbent. Based on a review of Pu sorption data Linklater et al. (2003) concluded that Pu sorbs least at low pH, but sorption increases rapidly as pH approaches near-neutral values. Under alkaline pH conditions, Pu sorption generally remains high, but in the presence of carbonate, may decrease again at higher pH, reflecting complexation between Pu and carbonate. The pH-dependence of sorption does, however, depend on the oxidation state. It has been reported that in the case sorption on FeOOH, Pu(IV) shows a stable sorption edge between pH 3 and pH 5, whereas Pu(V) initially shows a sorption edge at pH 7, which shifts to lower values over a few hours Higgo (1988). Recently Hormann (2021) modelled Pu(IV) sorption to soils and estimated an increase in K_d of between 1 and 1.5 orders of magnitude between pH 5.6 and 8.

Tits & van Dorp (1999) considered that Pu would sorb similarly to other tri- and tetra-valent radionuclides (Ac, Am, Cm, Eu, Np, Sm, Th and Zr) and accordingly assigned Pu the same K_d values as all these other elements. Bradbury & Baeyens (2003) used Am as a chemical analogue for Pu and assigned Pu the same K_d values as those of Am. However, the speciation calculations undertaken for the present work using the thermodynamic database "PSI/Nagra thermodynamic database 2020v1-1" indicate significant differences in speciation of these elements across the relevant ranges of Eh and pH (for example cf. Fig. 4-21 and Fig. 4-17). These differences suggest that there could be significant differences in sorption.

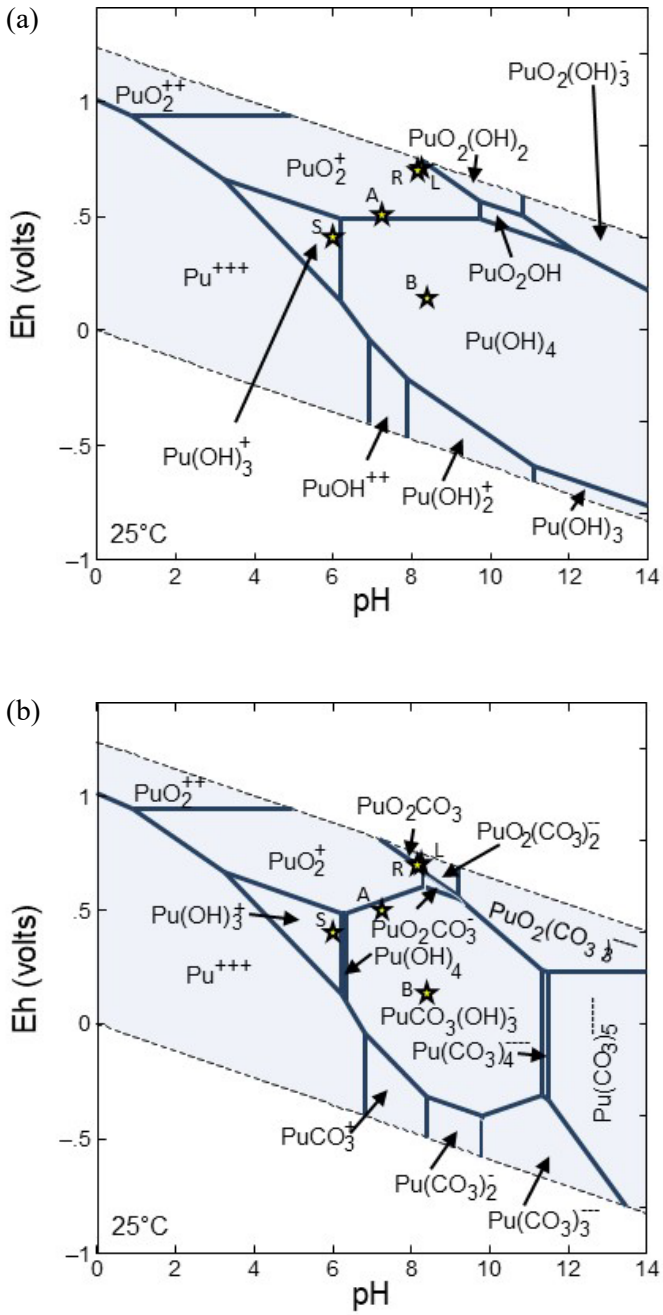

Fig. 4-21: Pourbaix diagrams for Pu at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* PuO_2^{2+-} = -12; (b) log *a* PuO_2^{2+-} = -12, log pCO_2(g) = -3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Pu are given in Tab. 4-21.

Tab. 4-21: Recommended K_d values for Plutonium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	5.0E+00	5.0E+02	1.0E-03	Reference: K_d for clay soils in the reviewed literature are in the order of 1.0E+00 m^3/kg to 1.0E+01 m^3/kg (Appendix A). Based on experimental studies, Kaplan (2016) proposed a K_d value of 6.0E+00 m^3/kg for Pu(IV) in water with pH 4.6 – 7, on clayey sediment at the Savannah River site, U.S.A. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported in the reviewed literature (Appendix A). This is appropriate for the most oxidising, lowest pH soil waters. Upper Guide is two orders of magnitude larger than the reference K_d in recognition of: (i) Pu(III) being dominant in the most reducing soil water, whereas Pu(IV) is dominant in the reference soil water, (Pu(III) likely sorbs more strongly than Pu(IV)); and (ii) the highest soil water pH (7.4) being 1.4 pH units higher than the reference soil water pH (6) (for given speciation, an increase of K_d of between 1 and 2 orders of magnitude between pH 6 and pH 7.4 is reasonable, e.g. based on modelling by Hormann (2021).
	Lake/river	5.0E+01	1.0E+02	5.0E+00	Reference: K_d is an order of magnitude larger than the K_d value for the reference soil water in fine, lower organic content soil/sediment based on the pH difference between the reference conditions and modelled Pu K_d for soils suggesting approximately an order of magnitude larger K_d for Pu(IV) at pH 8 than at pH 6 (Hormann 2021). Upper and Lower Guide: Lower Guide is an order of magnitude smaller than the reference K_d, recognising that for lake/river water the lowest pH (6.25) is similar to the reference soil water pH (6) and in both these waters, univalent cations dominate speciation. Upper Guide is 2× the reference Kd, recognising that for lake/river water the maximum pH (8.73) is c. 0.5 pH units larger than the reference pH (8.1 and 8.2 for river water and lake water respectively).
	River bed	5.0E+01	1.0E+02	5.0E+00	Reference: K_d is an order of magnitude larger than the K_d value for the reference soil water in fine, lower organic content soil/sediment based on the pH difference between the reference conditions and modelled K_d for Pu in soils suggesting approximately an order of magnitude larger K_d for Pu(IV) at pH 8 than at pH 6 (Hormann, 2021). Upper and Lower Guide: Lower Guide and Upper Guide are the same as for lake/river waters. In river bed water, Pu(IV) will dominate, in the form of neutral $Pu(OH)_4$ and possibly would sorb less well than Pu(IV) in the form of cationic PuO_2^+, which will dominate in the lake/river water. However, available data do not justify specification of different guide K_d for these two waters.

Tab. 4-21: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Aquifer	1.5E+02	1.5E+03	1.5E+00	Reference: K_d is 30× larger than the K_d value for the reference soil water in fine, lower organic content soil/sediment based on the pH difference between the reference conditions and modelled Pu K_d for soils suggesting approximately 30× increase in K_d for Pu(IV) between pH 6 and pH 8 (Hormann 2021). Upper and Lower Guide: Lower Guide is two orders of magnitude smaller than the reference K_d, in the same order of magnitude as for the reference soil water in lower organic carbon content soil/sediment. This is reasonable because the lowestpH, most oxidising aquifer water has similar pH and redox to those of the reference soil water. Upper Guide is an order of magnitude greater than the reference K_d recognising that under the reference aquifer water Pu(IV) or Pu(V) will dominate, whereas under the most reducing aquifer conditions Pu(III) will dominate and is likely to sorb more strongly (also noting that the highest K_d found in the reviewed literature is in the order 1.0E+03 m^3/kg (Appendix A).
Fine, higher organic content	Soil	7.5E+00	5.0E+02	1.0E-03	Reference: For all reference conditions 1.5× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	7.5E+01	1.0E+02	5.0E+00	
	River bed	7.5E+01	1.0E+02	5.0E+00	
	Aquifer	2.3E+02	1.5E+03	1.5E+00	
Coarse, low-organic content	Soil	2.5E+00	5.0E+02	1.0E-03	Reference: For all reference conditions 0.5× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	2.5E+01	1.0E+02	5.0E+00	
	River bed	2.5E+01	1.0E+02	5.0E+00	
	Aquifer	7.5E+01	1.5E+03	1.5E+00	

4.23 Polonium (Po)

Polonium (Po) is a metalloid (Group 16, Period 6 of the periodic table), with physical and chemical characteristics intermediate between those typical of metals and non-metals. Po lies in the same group of the periodic table as oxygen, sulphur, selenium and tellurium and has seven naturally occurring isotopes, all of which are radioactive. The longest-lived of these isotopes is Po-210, one of the daughters of uranium-238, with a half-life of c. 138.4 days, the other natural isotopes all having half-lives of < 3 minutes (Carvalho et al. 2017, Ram et al. 2019). Groundwater concentrations of Po-210 are typically < 1E-18 mol/L the maximum concentration identified in the literature consulted in the present study being only 4.5E - 16 mol/L (Carvalho et al. 2017). Often Po-210 approaches secular equilibrium with Pb-210, the distribution of which therefore controls the distribution of Po-210.

Owing to the very small concentrations of Po in natural waters and the difficulty of isolating this element, there are few thermodynamic data available. Based on a literature review Carvalho et al. (2017) state that Po may have stable oxidation states of -II, +II, +IV and +VI, with the +IV oxidation state being the stable state in oxidising fresh waters. In contrast, Brookins (1988) predicted that Po^{2+} would be the most stable aqueous species throughout the range of Eh relevant to the present project. Ulrich & Delgueldre (1993) report that Po hydrolyses readily, forming $PoO(OH)^{+}$, $PoO(OH)_2$ and PoO_2 in slightly acidic to neutral pH regions and PoO_2^{3-} in alkaline solutions.

The latest PSI/Nagra thermodynamic database, 2020v1-1 contains thermodynamic data for Po, in oxidation states of 0, +II and +IV. A Pourbaix diagram constructed using these data indicates that under the Eh-pH conditions of surface waters and shallow groundwaters in Northern Switzerland, and over most of the Eh-pH range spanned by Northern Swiss soil waters, Po will be dominantly in the form of neutral species $Po(OH)_4$ (Fig. 4-22). However, in more oxidising acidic soil waters, with pH 4.5 and Eh > 0.4 V, Po could exist in cationic form, either Po^{2+}, or $PoOH^{3+}$ (Fig. 4-22). Use of this database suggests that a solid phase, Po(cr) could potentially form. If so, then it would be inappropriate to model aqueous concentrations using sorption isotherms. However, as noted above, the thermodynamic data must be viewed with caution and it seems unlikely that a discrete solid phase would form.

There are no reliable sorption data available for Po. Crawford (2013) used Se(IV) as an analogue for Po(IV) but considered other oxidation states to be non-sorbing. However, the Se(IV) analogue was justified on the grounds that Po(IV) would dominantly be in the form of the oxyanion PoO_3^{2-}, whereas this species is not included in the PSI/Nagra database. Based on the similar first hydrolysis constant of Po with those of Pu and U, and the similar ratio charge/metal – oxygen bond length in hydrated complexes of Po, Pu and U, Tits & van Dorp (1999) assigned Po the same K_d values as those for Pu and U (in this latter case only for the fine clay materials and organic materials considered). However, over relevant pH-Eh ranges, as calculated using the PSI/Nagra thermodynamic database, 2020v1-1, the aqueous speciation of Po is considerably different to that of Se, Pu and U (cf. Fig. 4-22 with Fig. 4-21, Fig 36, and Fig. 4-34). Kaplan (2016) assigned Po K_d values for sorption on clayey and sandy sediments based on sorption data for Pb and Sn, arguing that all three elements are divalent soft metals. However, again, the calculated aqueous speciation for Po differs considerably from that of Pb and Sn (cf. Fig. 4-22 with Fig. 4-14 and Fig. 4-32). These differences in speciation call into question the validity of all these proposed chemical analogues for Po.

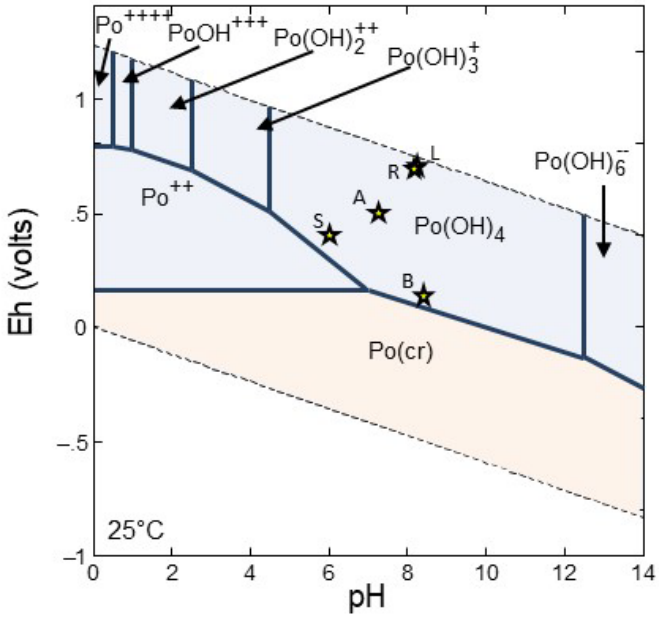

Fig. 4-22: Pourbaix diagram for Po at 25 °C, 1 bar: log *a* Po^{2+-} = -16 (PSI/Nagra thermodynamic database 2020v1-1)

Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Po are given in Tab. 4-22.

Tab. 4-22: Recommended K_d values for Polonium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	2.0E-01	7.0E+00	1.0E-02	Reference: K_d recommended by Vandenhove et al. (2009) based on geometric means of reported measurements on soils (Appendix A). Following these authors, the same value is recommended for all soils since data are insufficient to determine differences. Upper and Lower Guide: Maximum and minimum K_d reported by Vandenhove et al. (2009) for soils, which also bracketed all reported values (Appendix A). When choosing K_d from the ranges for use in sensitivity calculations, it is recommended to choose K_d ordered according to the pH of the reference water conditions (larger K_d values for higher pH reference water conditions). Vandenhove et al. (2009) report some data that suggest larger K_d at higher pH.
	Lake/river	2.0E-01	7.0E+00	1.0E-02	
	River bed	2.0E-01	7.0E+00	1.0E-02	
	Aquifer	2.0E-01	7.0E+00	1.0E-02	
Fine, higher organic content	Soil	2.0E-01	7.0E+00	1.0E-02	
	Lake/river	2.0E-01	7.0E+00	1.0E-02	
	River bed	2.0E-01	7.0E+00	1.0E-02	
	Aquifer	2.0E-01	7.0E+00	1.0E-02	
Coarse, low-organic content	Soil	2.0E-01	7.0E+00	1.0E-02	
	Lake/river	2.0E-01	7.0E+00	1.0E-02	
	River bed	2.0E-01	7.0E+00	1.0E-02	
	Aquifer	2.0E-01	7.0E+00	1.0E-02	

4.24 Protactinium (Pa)

Protactinium (Pa) is the third actinoid in the periodic table (Period 7 of the periodic table). It occurs naturally only in uranium ores and there are few thermodynamic data available. It is reported to exist in +IV and +V forms, the latter being dominant under the range of pH and Eh that are relevant to the present work. Both these forms have a strong tendency to hydrolyse (Gillberg-Wickman 1983).

Although limited, the available thermodynamic data for Pa suggest the variation in speciation of Pa as a function of pH and Eh shown in Fig. 4-23. At the lower end of the range of pH relevant to this work Pa is predicted to be in a univalent cationic form ($PaO(OH)_2^+$). However, across most of the relevant pH range, aqueous Pa is predicted to be in a neutral form ($PaO(OH)_3$). At the more alkaline end of the relevant pH range, Pa is predicted to be in an anionic form ($PaO(OH)_4^-$). Potentially, aqueous Pa concentrations could be controlled by the solubility of P_2O_5, in which case it would be inappropriate to model aqueous concentrations using sorption isotherms.

Sorption data for Pa are scarce but based on the available data Linklater et al. (2003) concluded that this element will sorb dominantly by surface complexation, with progressively lower degrees of sorption at progressively more acidic pH. By analogy with data for other elements in the form of neutral hydroxy-species, and based on limited available data, it has been concluded that Pa would be strongly sorbing at near-neutral to slightly alkaline pH (Linklater et al. 2003, Bradbury & Baeyens 2003). Pa-233 has been reported to sorb irreversibly on Mn- and Fe- oxides, with the result that different soils may show markedly different sorption of Pa-233 depending on the contents of these minerals (Sakamoto et al. 2002). Tits & van Dorp (1999) considered Th(IV) and Am(III) to be chemical analogues of Pa and accordingly assigned the same K_d values to all three elements. For the reference water conditions, as calculated using the PSI/Nagra thermodynamic database 2020v1-1, the aqueous speciation of Th(IV) is predicted to be dominated by the neutral species $Th(OH)_4$ and therefore this analogue may be valid (cf. Fig. 4-23 with Fig. 4-31). However, the calculated aqueous speciation of Pa is considerably different from that of Am (cf. Fig. 4-23 with Fig. 4-4) and therefore Am is not a good chemical analogue for Pa. Kaplan (2016) used Np as an analogue for Pa and recommended the same K_d values for both elements. However, again the speciation of each of these elements over relevant Eh-pH ranges are quite different (cf. Fig. 4-23 with Fig. 4-17), meaning that Np cannot be considered a good analogue for Pa.

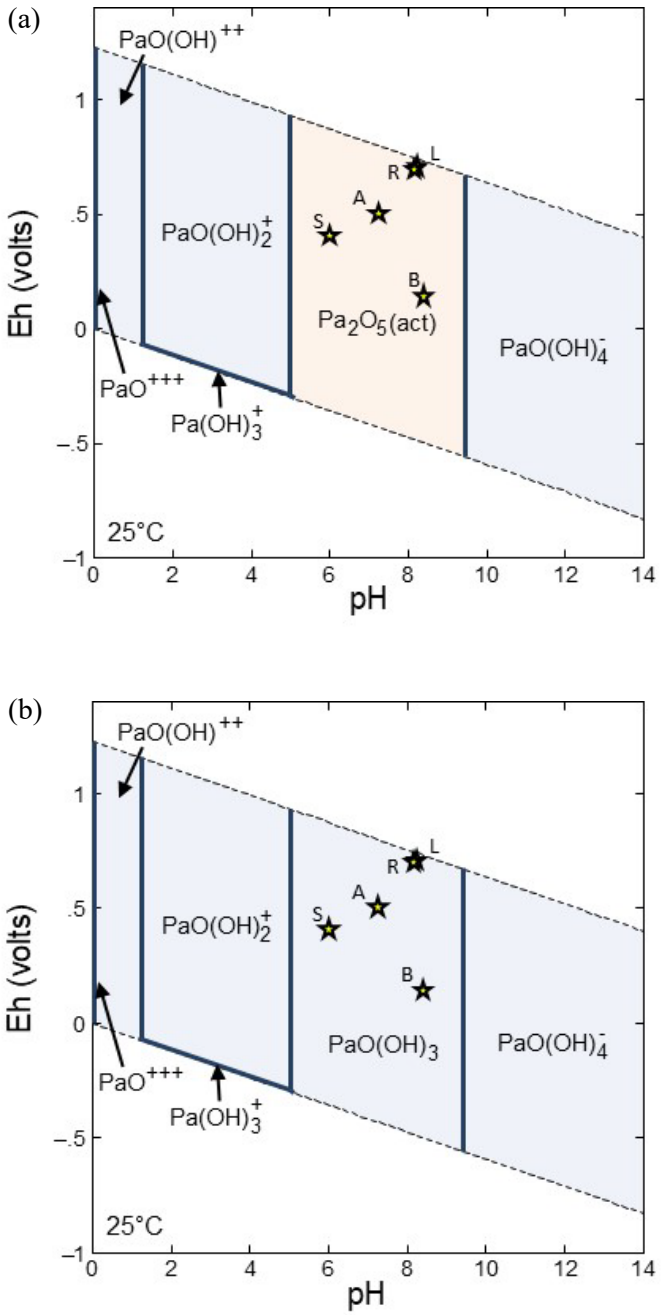

Fig. 4-23: Pourbaix diagrams for Pa at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Pa^{4+-} = -7; (b) log *a* Pa^{4+} = -8. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Pa are given in Tab. 4-23.

Tab. 4-23: Recommended K_d values for Protactinium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Most reported K_d are in the order 1.0E+00 m^3/kg (Appendix A), with the geometric mean of all soils reported by Gil-García et al. (2009) being 2.0E+00 m^3/kg. Bradbury & Baeyens (2003) recommended a value of 5.0E+00 m^3/kg for Opalinus Clay. Upper and Lower Guide: Lower Guide is lowest K_d reported by Higgo (1988) (quoting Allard et al. 1981) for sorption of Pa on SiO_2 and Al_2O_3 in the pH range 2-4, which overlaps the lowest pH of soil waters considered (pH 3.9). Upper Guide is in the same order as the largest K_d reported for soils by Sakamoto et al. (2002), 5.2E+01 m^3/kg at pH 8.9. Higgo (1988), referencing Allard et al. (1981), give an upper K_d of 1.0E+01 m^3/kg for sorption at pH 8 – 10 onto SiO_2 and Al_2O_3.
	Lake/river	3.0E+00	1.0E+01	1.0E+00	Reference: 3× the K_d for reference soil water in fine, lower organic content soil/sediment, considering the difference in pH between reference lake/river water and soil water, and assuming that the pH dependency is similar to that of Th(IV). Bradbury & Baeyens (2003) estimated c. 2.5× increase in sorption between pH 6.3 and pH 7.8 for Th(IV) in Opalinus Clay. Upper and Lower Guide: Lower Guide is the same as the reference K_d for soil water recognising that the lowest pH of lake/river water (6.25) is comparable to the reference soil water pH (6). Upper Guide is the same as for soil waters in fine, lower organic content soil/ sediment given that there are insufficient data to justify a different value and noting that Higgo (1988), referencing Allard et al. (1981), give an upper K_d of 1.0E+01 m^3/kg for sorption at pH 8 – 10 onto SiO_2 and Al_2O_3.
	River bed	3.0E+00	1.0E+01	1.0E+00	
	Aquifer	2.5E+00	1.0E+01	1.0E+00	Reference: 2.5× the K_d value for reference soil water in fine, lower organic content soil/ sediment, considering the difference in pH between reference aquifer water and soil water, and assuming that the pH dependency is similar to that of Th(IV). Bradbury & Baeyens (2003) estimated c. 2.5× increase in sorption between pH 6.3 and pH 7.8 for Th(IV) in Opalinus Clay. Upper and Lower Guide: Lower Guide is the same as for the reference soil water conditions in lower organic carbon content soil/sediment. This is reasonable because the lowestpH aquifer water (pH 6.5) has similar pH to the reference soil water (pH 6) and the data do not justify specifying different values. Upper Guide is the same as for soil waters in fine, lower organic content soil/sediment given that the maximum pH of aquifer water is 8.9 and noting that Higgo (1988), referencing Allard et al. (1981), give an upper K_d of 1.0E+01 m^3/kg for sorption at pH 8 – 10 onto SiO_2 and Al_2O_3. There are insufficient data to justify different Upper Guideline values for the different waters.

Tab. 4-23: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	Reference: For all reference conditions 1.5× the K_d for reference conditions in fine, lower organic content soil/sediment. Sakamoto et al. (2002) report little association between Pa and organic matter. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment. The data do not justify specification of different values for the different waters.
	Lake/river	4.5E+00	1.0E+01	1.0E+00	
	River bed	4.5E+00	1.0E+01	1.0E+00	
	Aquifer	3.8E+00	1.0E+01	1.0E+00	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	Reference: For all reference conditions 0.5× the K_d for reference conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.5E+00	1.0E+01	1.0E+00	
	River bed	1.5E+00	1.0E+01	1.0E+00	
	Aquifer	1.3E+00	1.0E+01	1.0E+00	

4.25 Radium (Ra)

Radium (Ra) is an alkaline earth metal (Group 2, Period 7 of the periodic table), with chemical characteristics like those of Ba. The element exists only in the +II oxidation state and as the uncomplexed divalent cation (Ra^{2+}) throughout the pH range of interest to the present project (Fig. 4-24).

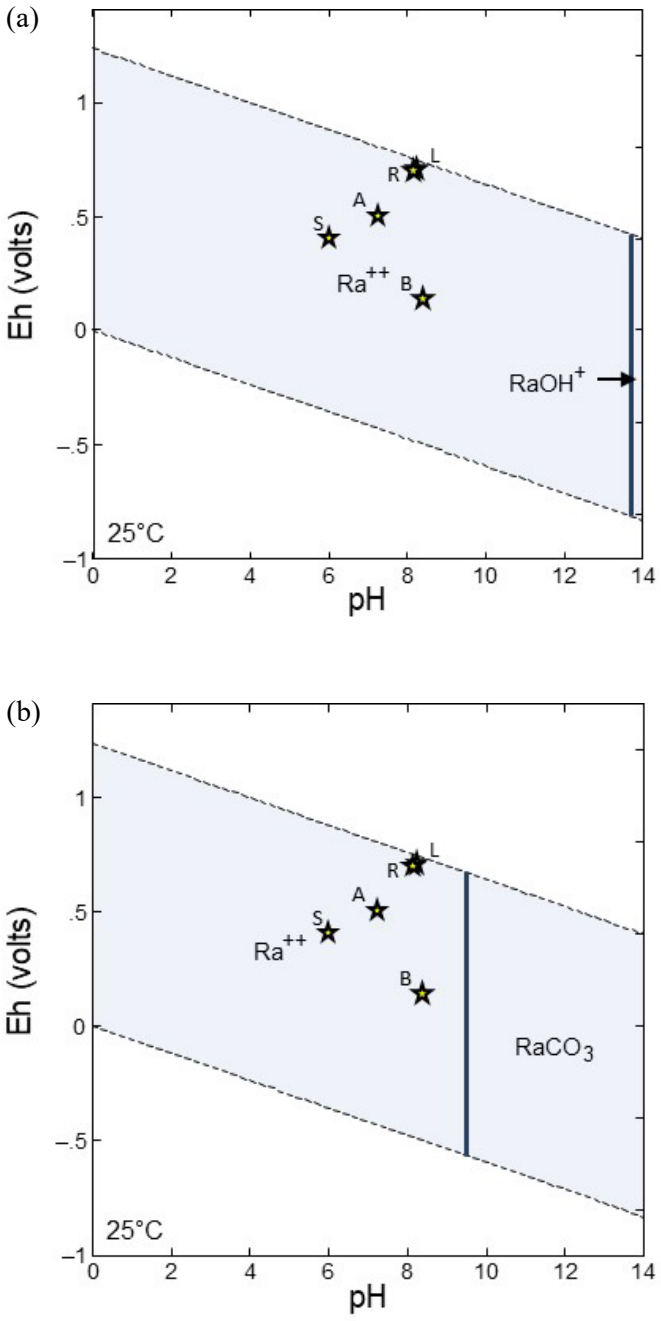

Fig. 4-24: Pourbaix diagrams for Ra at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Ra^{2+} = -9; (b) log *a* Ra^{2+} = -9, log pCO_2(g) = -3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

A neutral carbonate species ($RaCO_3$) could dominate the aqueous speciation of Ra under atmosphere-equilibrated conditions at slightly higher pH than the highest pH of Northern Swiss surface waters or groundwaters. In SO_4-rich waters, or carbonate-rich waters, Ra could precipitate in solid sulphate (most likely with Ba) or carbonate phases (most likely with another alkaline earth metal, particularly Ca or Mg). Should such precipitation occur, it would be inappropriate to model Ra retardation using sorption isotherms.

Compared to other alkaline earth elements, Ra sorbs more strongly on clay minerals (USEPA 2004, IAEA 2014, Chen & Kocar 2018). The sorption mechanism is cation exchange and hence Ra sorption is influenced by competition with other divalent cations and decreases with increasing ionic strength of the water. Fe- oxides and oxyhydroxides sorb Ra strongly, particularly when pH is near-neutral (Sajih et al. 2014). There are also some experimental data that show Ra may be strongly sorbed to organic matter in soils (IAEA 2014). However, among the data compilations reviewed in the present study there is ambiguity regarding the significance of sorption on organic materials (Appendix A).

Recommended K_d values for Ra are given in Tab. 4-24.

Tab. 4-24: Recommended K_d values for Radium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+03	1.0E-04	Reference: Most geometric means of different datasets in the reviewed literature are in the order of 1.0E+00 m^3/kg (Appendix A). Some data suggest Ra sorbs less strongly to a given substrate than does Cs, whereas other data suggests the reverse. However, there is clear evidence that Ra sorbs more strongly than Sr and Ca. Since Ra is likely to sorb by cation exchange, little pH-dependence is expected in clay-rich soil/sediment. Given this, the fact that aqueous speciation is calculated to be the same in all the reference waters, and limited data, the same reference K_d is recommended for all waters. Upper and Lower Guide: Lower Guide and Upper Guide are the lowest and highest K_d values respectively, among the reviewed literature (Appendix A). Generally higher values are expected in more clay-rich soil/sediment. Available data do not justify specification of different Lower Guide and Upper Guide K_d for the different reference waters.
	Lake/river	1.0E+00	1.0E+03	1.0E-04	
	River bed	1.0E+00	1.0E+03	1.0E-04	
	Aquifer	1.0E+00	1.0E+03	1.0E-04	
Fine, higher organic content	Soil	1.5E+00	1.0E+03	1.0E-04	Reference: 1.5× the K_d for reference conditions in fine, lower organic content soil/sediment. The data do not justify specification of different values for the different reference water conditions. There is no evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same in each water, and the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.5E+00	1.0E+03	1.0E-04	
	River bed	1.5E+00	1.0E+03	1.0E-04	
	Aquifer	1.5E+00	1.0E+03	1.0E-04	
Coarse, low-organic content	Soil	5.0E-01	1.0E+03	1.0E-04	Reference: 0.5× the K_d for reference conditions in fine, lower organic content soil/sediment. The data do not justify specification of different values for the different reference water conditions. Upper and Lower Guide: Lower Guide and Upper Guide are the same in each water, and the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	5.0E-01	1.0E+03	1.0E-04	
	River bed	5.0E-01	1.0E+03	1.0E-04	
	Aquifer	5.0E-01	1.0E+03	1.0E-04	

4.26 Samarium (Sm)

Samarium (Sm) is a lanthanoid element (Period 6 of the periodic table), which may exist in oxidation states of +III and +II, although only the former is relevant to the waters considered in this study; the speciation of Sm is not redox sensitive in these waters. At low pH (< 8) this element may be uncomplexed Sm^{3+}, but it has a tendency to hydrolyse as pH increases, forming successively less highly charged species (Fig. 4-25). In all the soil waters in Northern Switzerland, Sm speciation is calculated to be dominated by Sm^{3+}. If carbonate is present, as pH increases, Sm may complex with carbonate. In most shallow groundwaters and surface waters in Northern Switzerland, Sm could potentially exist in the form of a positively charged carbonate complex ($Sm(CO_3)^+$). Millero (1992) reports that carbonate complexes dominate for natural waters in which the carbonate alkalinity is > 0.001 eq/ L at pH c. 8.

Sm has been found to sorb strongly on clays, Fe-oxides and carbonate phases (Ramírez-Guinart et al. 2018) and to biochars (Serra-Ventura et al. 2021). There is some evidence that in dilute, near-neutral waters, Sm will sorb less strongly than lighter lanthanoids, but more strongly than heavier lanthanoids (Tertre et al. 2008).

There are very few sorption data for Sm sorption under the combinations of chemical conditions and substrates considered in this work. Many authors use data for one of the other lanthanides (most commonly Eu (e.g. Bradbury & Baeyens 2003, Kaplan 2016) or Ce (Kaplan 2016). Am is also sometimes used as a chemical analogue (Crawford 2013).

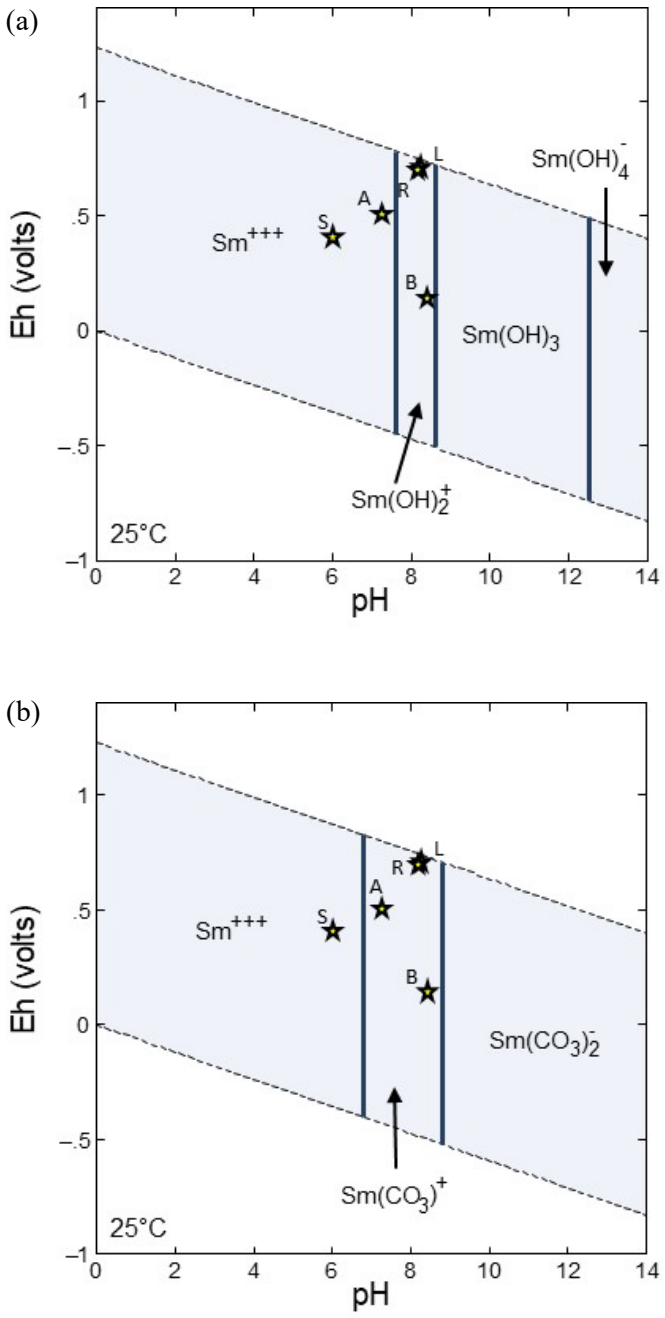

Fig. 4-25: Pourbaix diagrams for Sm at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Sm^{3+} = -8, aqueous species only; (b) log *a* Sm^{3+} = -8, log pCO_2(g) = -3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Sm are given in Tab. 30.

Tab. 30: Recommended K_d values for Samarium (m^3/kg)
(Americium analogue)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+01	1.0E-01	Reference: Same K_d assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A). Upper and Lower Guide: Same K_d assigned as for Am, in view of the similar chemistry of these elements, consistent with approaches taken in other compilations of K_d data (Appendix A).
	Lake/river	1.0E+01	1.0E+02	1.0E+00	
	River bed	1.0E+01	1.0E+02	1.0E+00	
	Aquifer	3.0E+00	3.0E+01	3.0E-01	
Fine, higher organic content	Soil	1.5E+00	1.0E+01	1.0E-01	
	Lake/river	1.5E+01	1.0E+02	1.0E+00	
	River bed	1.5E+01	1.0E+02	1.0E+00	
	Aquifer	4.5E+00	3.0E+01	3.0E-01	
Coarse, low-organic content	Soil	5.0E-01	1.0E+01	1.0E-01	
	Lake/river	5.0E+00	1.0E+02	1.0E+00	
	River bed	5.0E+00	1.0E+02	1.0E+00	
	Aquifer	1.5E+00	3.0E+01	3.0E-01	

4.27 Selenium (Se)

Selenium (Se) is a non-metal, though with some metal properties resulting in it sometimes being considered a metalloid (Group 16, Period 4 of the periodic table). The element is chemically like sulphur and may have oxidation states of -II, 0, +IV and +VI. All these oxidation states are possible within the overall ranges of pH and Eh relevant to soils, surface waters and shallow groundwaters in Northern Switzerland (Fig. 4-26). However, irrespective of the redox state, in these waters, Se is likely to be dominant in the form of neutral or anionic species (Fig. 4-26). All the reference water conditions plot either in the field of SeO_4^{2-} (selenate) or $HSeO_3^-$ (selenite).

Selenite (+IV) is adsorbed onto Fe-oxides, Fe-oxyhydroxides, Al-hydroxides and clay minerals in soil more strongly than selenate (+VI), with sorption increasing as pH decreases (Johnson et al. 2010, Zafeiriou et al. 2020). A study of Japanese soils showed that sorption characteristics of Se was similar to those of Sb, although Se sorbs slightly more strongly (Nakamura & Sekine 2008). Sorption in these soils was interpreted to occur via a ligand exchange mechanism, which allows for competition between Se and dissolved PO_4^3; higher PO_4^{3-} concentrations in porewaters were found to result in decreased Se sorption. An experimental study of selenite and selenate sorption onto Fe-oxide showed that SO_4^- may compete for sorption sites with selenate, but not with selenite (González et al. 2012). Possibly, under reducing conditions if selenide (Se^{2-}) or hydrogen selenide (HSe^-) is dominant, Se might co-precipitate with sulphide, since the chemistries of reduced Se and reduced S are similar (Linklater et al. 2003). If such co-precipitation were to occur, then aqueous Se concentrations may be solubility controlled and it would be inappropriate to model them using a sorption isotherm.

Some authors have proposed that Po as a chemical analogue for Se (Crawford 2013). However, the chemical speciation of Po and Se, as calculated using the PSI/Nagra thermodynamic database 2020v1-1, are substantially different over relevant Eh and pH ranges (cf. Fig. 4-26 and Fig. 4-22). The differences show that these elements cannot be considered analogues for the purposes of assigning K_d values.

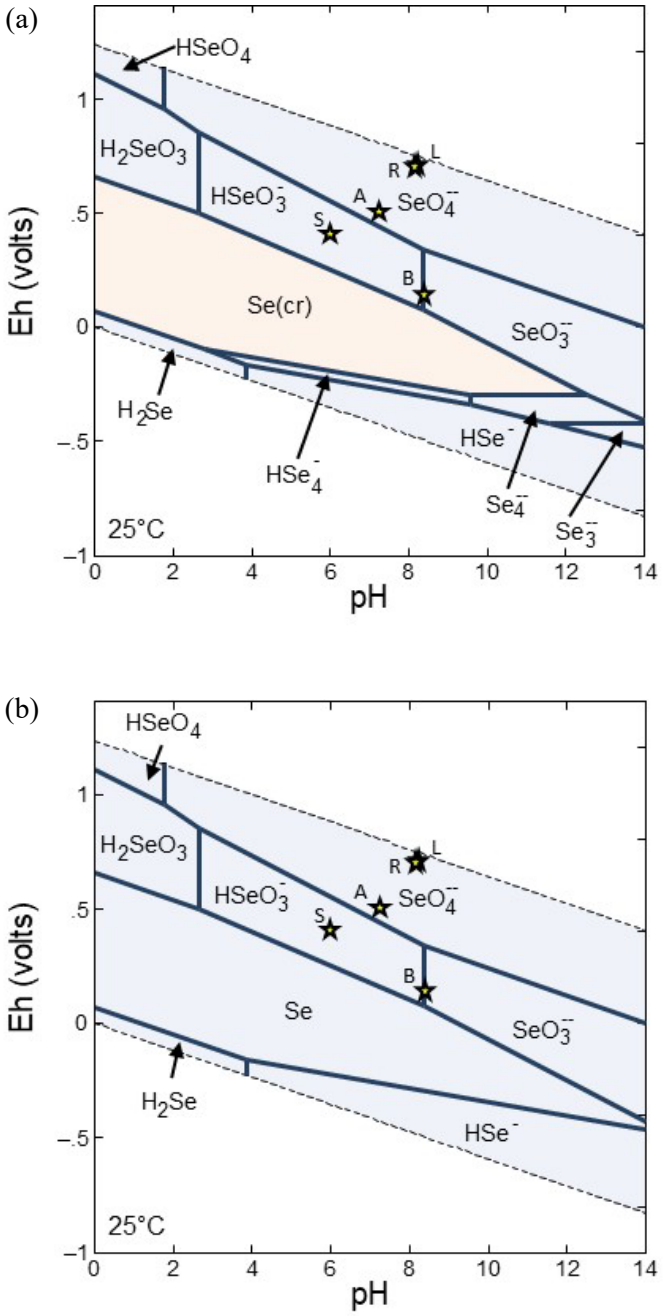

Fig. 4-26: Pourbaix diagrams for Se at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* SeO_3^{3-} = -6; (b) log *a* SeO_3^{3-} = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Se are given in Tab. 4-26.

Tab. 4-26: Recommended K_d values for Selenium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+00	1.0E-03	Reference: K_d assumes that a Se(IV) species is dominant and has the same order of magnitude as the mean of K_d reported for Se(IV) sorption on soil in USEPA (2005). Upper and Lower Guide: Lower Guide is an order of magnitude smaller than the Reference K_d, in the same order of magnitude as the smallest measured K_d in the reviewed literature (Appendix A). This is appropriate for the most oxidising, highest pH soil water. Upper Guide is in the same order as the highest K_d reported for soils in the reviewed literature (Appendix A). This is appropriate for the most reducing, lowest pH soil water. It should be noted that the redox condition under which the highest K_d for soil water in the reviewed literature was obtained is unknown. It cannot be verified that Se(II) was the dominant form of Se (which is expected to sorb most strongly) in the experiment that yielded this high K_d.
	Lake/river	1.0E-03	1.0E-01	1.0E-04	Reference: K_d assumes that a Se(VI) species is dominant and is an order of magnitude smaller than for Se(IV) sorption, consistent with data reviewed in USEPA (2005). Upper and Lower Guide: Lower Guide and Upper Guide are each an order of magnitude smaller than the Lower Guide and Upper Guide respectively for soil water. This is an assumption based on Se being in the form of Se(VI), which tends to sorb less strongly than more reduced forms of Se, and accounting for the highest pH of lake river water (8.73) being higher than the highest pH of soil water (7.4), such that sorption is likely to be weaker.
	River bed	1.0E-02	1.0E-01	1.0E-03	Reference: K_d based assuming that Se(IV) is the dominant species and has the same order of magnitude as the mean of K_d values reported for Se(IV) sorption on soil in USEPA (2005). Upper and Lower Guide: Lower Guide is the same as the Lower Guide for soil water and greater than the Lower Guide for river/lake water, taking into account the competing effects of weaker sorption at higher pH, but stronger sorption under more reducing conditions. The highest pH of river bed water (9.0) is greater than the highest pH of soil water (7.4) (implying weaker sorption), but the river bed water is more reducing than the most oxidising soil water, such that Se(IV) occurs rather than Se(VI) (implying stronger sorption). The highest pH of river bed water is higher than that of lake/river water (8.73) (implying similar sorption), but the river bed water is more reducing than the lake/river water, such that Se(IV) occurs rather than Se(VI) (implying stronger sorption). Upper Guide is an order of magnitude larger than the reference K_d, taking into account that in the reference River bed water Se(VI) dominates, but over most of the field of river bed water Se(IV) dominates, which will sorb more strongly than Se(VI).

Tab. 4-26: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Aquifer	1.0E-03	1.0E-02	1.0E-04	Reference: K_d assumes that a Se(VI) species is dominant and is an order of magnitude smaller K_d than for Se(IV) sorption, consistent with data reviewed in USEPA (2005). Upper and Lower Guide: Lower Guide is the same as the Lower Guide for lake/river water since the highest pH/most oxidising aquifer water has similar pH (8.9) to that of the highest pH river water (8.73) and Se(VI) dominates. Upper Guide is the same as the reference K_d for soil water, taking into account that the lowest pH of aquifer water (6.5) is similar to the pH of the reference soil water (6) and in both cases the same Se(IV) species dominate.
Fine, higher organic content	Soil	1.5E-02	1.0E+00	1.0E-03	Reference: For all reference conditions 1.5× the K_d for the corresponding reference conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.5E-03	1.0E-01	1.0E-04	
	River bed	1.5E-02	1.0E-01	1.0E-03	
	Aquifer	1.5E-03	1.0E-02	1.0E-04	
Coarse, low-organic content	Soil	5.0E-03	1.0E+00	1.0E-03	Reference: For all reference conditions 0.5× the K_d for reference soil water conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	5.0E-04	1.0E-01	1.0E-04	
	River bed	5.0E-03	1.0E-01	1.0E-03	
	Aquifer	5.0E-04	1.0E-02	1.0E-04	

4.28 Silicon (Si)

Silicon (Si) is a metalloid (Group 14, Period 3 of the periodic table) and can exist in oxidation states of +IV and -IV, although only the former occurs under the water conditions that are relevant to this work. Throughout the pH and redox range considered aqueous Si will be hydrolysed, with a solid silica phase such as micro-crystalline or amorphous silica being stable at lower pH and aqueous silica concentrations greater than about 1E-3.5 mol/L (Fig. 4-27).

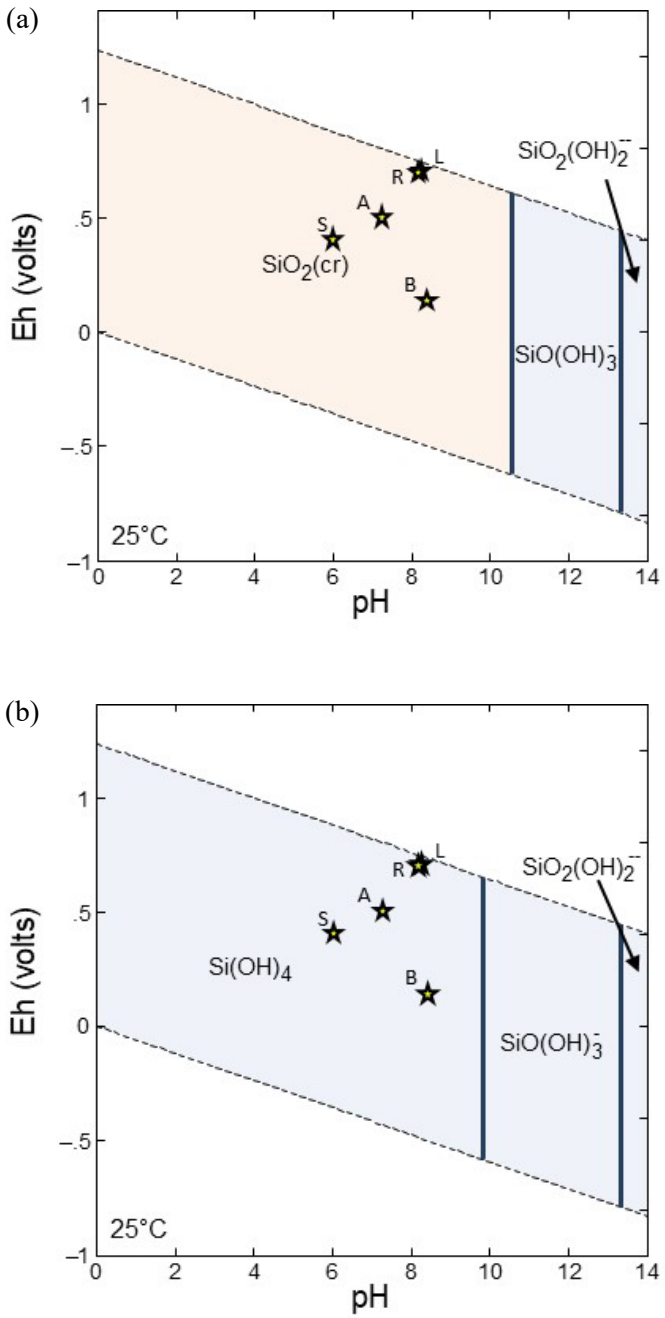

Fig. 4-27: Pourbaix diagrams for Si at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* $Si(OH)_4$ = -3; (b) log *a* $Si(OH)_4$ = -4. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

In many natural groundwaters and surface waters aqueous silica concentrations are at or close to equilibrium with a solid silica phase, in which cases it is inappropriate to model aqueous Si concentrations using the K_d approach. Tits & van Dorp (1999) calculated a notional K_d value based on the assumption that 1% of the silica in a soil is amorphous and therefore readily exchangeable, and data suggesting that an average soil contains 25% quartz. The notional K_d value was then obtained by dividing this quantity of exchangeable solid-phase Si by the aqueous concentration of Si in a typical soil porewater. This approach gave a "K_d" of 2.0E-01 m^3/kg.

Si can sorb strongly to Fe-oxides and oxyhydroxides, with a maximum at pH around 9 (Taylor 1995). Silica adsorption has been reported to affect the sorption of other anion, with the pH limit for anion sorption being shifted to lower values, but to have little impact on cation sorption (Taylor 1995). A factor complicating the sorption of Si to Fe-oxides and oxyhydroxides is that the presence of Si influences the nature of these Fe minerals and transformations among them (Kinsela et al. 2016 and references therein).

Si has been found to sorb to Fe-oxyhydroxides in acid forest soils, but to be desorbed owing to sorption competition when dissolved PO_4^{2-} and dissolved organic matter concentrations are high (Klotzbücher et al. 2020).

Recommended K_d values for Si are given in Tab. 4-27.

Tab. 4-27: Recommended K_d values for Silicon (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	2.0E-01	1.0E+00	1.0E-02	Reference: The aqueous concentration of Si is likely to be controlled by the solubility of quartz (or a metastable silica polymorph) and therefore use of sorption isotherms to model Si is inappropriate. A notional "K_d" was calculated by Tits & van Dorp (1999) based on an assumed proportion of Si in the solid phase that is exchangeable and typical aqueous Si concentrations in soil porewater (see text). The value calculated is similar to measured K_d reported in published literature (Appendix A) and hence is retained as a reference value here. The data do not justify different values being specified for the three considered soils/sediments. Upper and Lower Guide: Upper Guide and Lower Guide are in the same orders of magnitude as the largest and smallest values reported in the reviewed literature (Appendix A). By analogy with other tetravalent elements that hydrolyse to form neutral hydroxy species it is expected that K_d will decrease at increasing pH. While the magnitude of this change (if any) cannot be estimated, it would be appropriate to bear this in mind when selecting K_d values for sensitivity studies; lower-pH waters should have higher K_d than higher pH waters.
	Lake/river	2.0E-01	1.0E+00	1.0E-02	
	River bed	2.0E-01	1.0E+00	1.0E-02	
	Aquifer	2.0E-01	1.0E+00	1.0E-02	
Fine, higher organic content	Soil	2.0E-01	1.0E+00	1.0E-02	
	Lake/river	2.0E-01	1.0E+00	1.0E-02	
	River bed	2.0E-01	1.0E+00	1.0E-02	
	Aquifer	2.0E-01	1.0E+00	1.0E-02	
Coarse, low-organic content	Soil	2.0E-01	1.0E+00	1.0E-02	
	Lake/river	2.0E-01	1.0E+00	1.0E-02	
	River bed	2.0E-01	1.0E+00	1.0E-02	
	Aquifer	2.0E-01	1.0E+00	1.0E-02	

4.29 Silver (Ag)

Silver (Ag) is a second-row transition metal (Group 11, Period 5 of the periodic table). Ag can have oxidation states of 0, +I and +II, although only the former is relevant in solution across the range of natural pH and Eh (Fig. 4-28). Except at pH greater than the highest pH of shallow groundwaters and surface waters in Northern Switzerland, Ag shows little tendency to hydrolyse (Fig. 4-28a). It can, however, form complexes with dissolved chloride. At the highest dissolved Cl concentration reported for shallow Swiss groundwaters (799 mg/L) the field of Ag^+ in Fig. 4-28a is replaced by a field of $AgCl_2^-$ (Fig. 4-28b).

Over most of the relevant field of pH and Eh, in the absence of chloride, aqueous Ag is dominantly in univalent cationic form at Eh > 0.45 V. Under conditions more reducing than this, in the shallow groundwaters of Northern Switzerland, Ag could be dominant in the neutral solid Ag form. Similarly, Ag is predicted to be in the neutral Ag form over most of the Eh-pH field of Northern Swiss soils . However, in more reducing soil pore waters with Eh <0 V, in the presence of dissolved sulphur the univalent negative aqueous species $Ag(HS)_2^-$ could dominate the aqueous speciation of Ag (Fig. 4-28c). Potentially, under these reducing conditions, a solid Ag-sulphide phase such as Ag_2S(cr) could be stable. If such a phase did exert a solubility control on aqueous Ag concentrations, it would be inappropriate to use sorption isotherms to model Ag partitioning between aqueous and solid phases.

Tits & van Dorp (1999) note that very large values of K_d reported in some literature (20 m^3/kg originally reported by Legoux et al. (1992)) probably reflect precipitation of Ag. They argued that owing to its univalent character and the fact that it does not significantly hydrolyse, Ag should sorb similarly to Na. Consequently, K_d values for Ag should have similar magnitudes to those for Na.

At equilibrium with the atmosphere a negatively charged carbonate species ($AgCO_3^-$) could dominate the speciation at pH more than c. 9.5 (Fig. 4-28b). Solid AgCl is unlikely to be stable in the considered Swiss groundwaters and surface waters (Fig. 4-28c).

Ag^+ can sorb on clay minerals, Fe-oxyhydroxides and organic matter. In a study of aquatic sediments Kyziol-Kominska et al. (2020) found that sorption capacities decreased in the order kaolinite > montmorillonite > ferrihydrite. They also observed little pH-dependence in the range pH 4 – 8. An investigation of soils by Jacobson et al. (2005) determined that Ag^+ would sorb more strongly on organic-rich soils than on relatively organic poor, illite-rich soils. Furthermore, they found that Ag^+ sorption increased over time and suggested that this is due to its incorporation into the structure of Fe-oxyhydroxides.

In soils and aquatic sediments Ag-nanoparticles have received considerable attention in recent years (e.g. Sekine et al. 2015, Huang et al. 2019, Kyziol-Komosinska et al. 2020). While the primary motivation has been to understand the fate of anthropogenic Ag, Huang et al. (2019) report evidence that Ag-nano-particles can form in soils due to the reduction of aqueous Ag^+ to solid silver by organic matter. Martin et al. (2020) report that the mobility of Ag in solution is strongly influenced by its ability to bind strongly to humic acid. They also conclude that Ag^+ can compete effectively with divalent cations for binding sites on natural organic matter at neutral and acid pH.

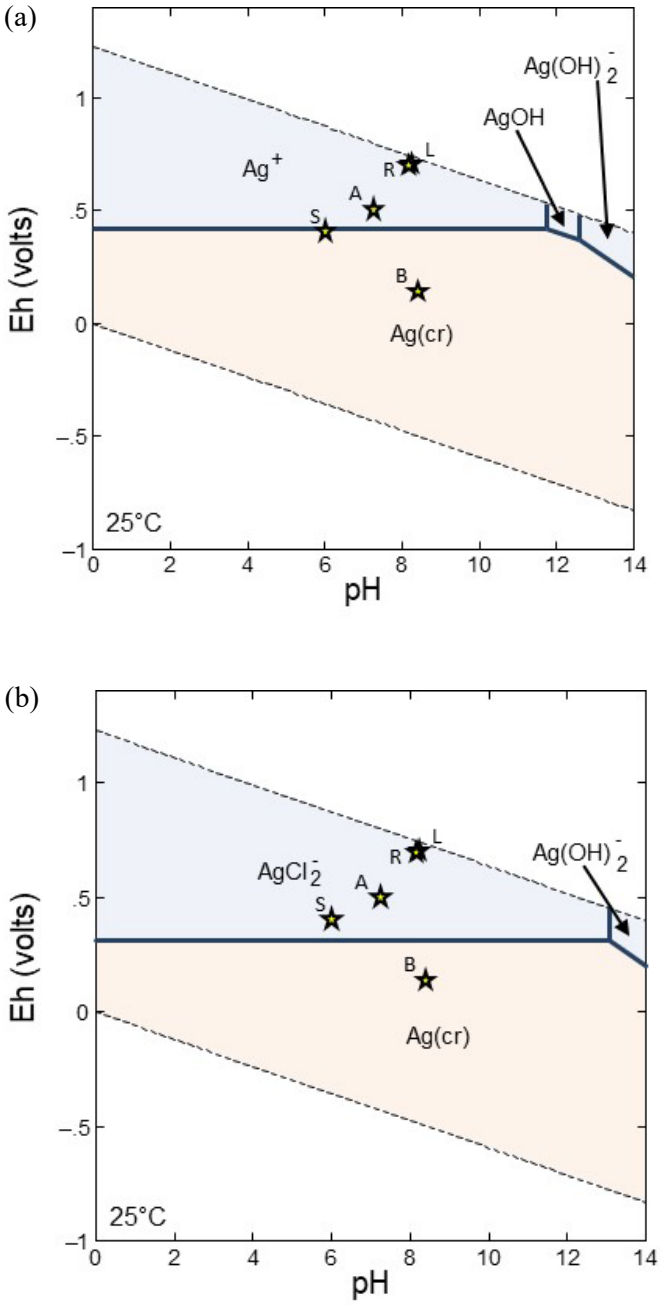

Fig. 4-28: Pourbaix diagrams for Ag at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Ag^{+-} = -8; (b) log *a* Ag^{+-} = -8, log *a* Cl^- = -1.65; (c) log *a* Ag^{+-} = -8, log *a* SO_4^{--} = -5, log *a* Cl- = -2, log.*p*CO_2(g) = -3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

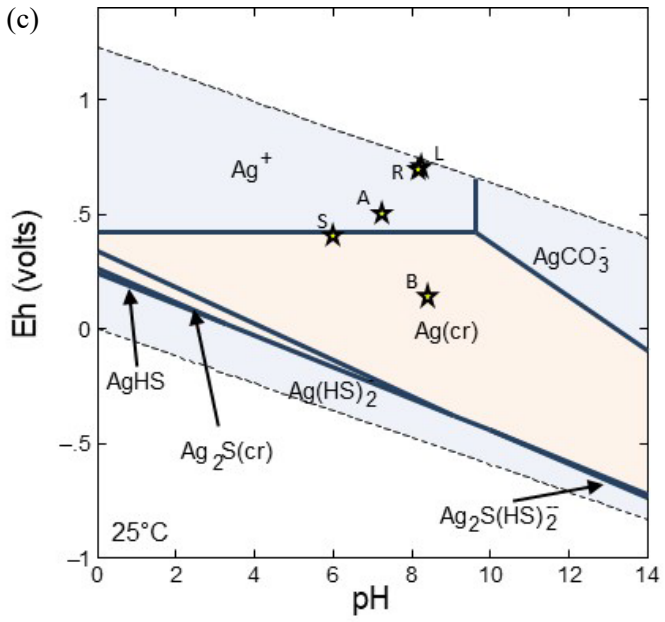

Fig. 4-28: Cont.

Recommended K_d values for Ag are given in Tab. 4-28.

Tab. 4-28: Recommended K_d values for Silver (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+00	0.0E+00	Reference: In the same order as measured K_d value for clayey sediments at Savannah River U.S.A., reported by Kaplan (2016), which is approximately an order of magnitude smaller than reported measured for montmorillonite by Kyziol-Komosinska et al. (2020). As pure clay would be expected to have a higher K_d than clay-bearing sediment, these values seem broadly consistent. The value reported by Kaplan (2016) is at the lower end of the range of K_d values reported for soils in the reviewed literature (Appendix A). It is considered reasonable to recommend a reference K_d at the lower end of the range owing to the possibility of bias in published values due to solubility control of aqueous Ag concentrations. Upper and Lower Guide: Lower Guide reflects uncertainty concerning reported K_d and whether these represent sorption or instead nano-particle precipitation. In view of this uncertainty, sensitivity calculations could consider the case where no sorption occurs. Upper Guide is in the same order of magnitude as the largest geometric means reported for sets of published data in the reviewed literature (Appendix A). Maximum K_d reported in this literature are an order of magnitude larger, but are not used here owing to the possibility that these reflect precipitation of Ag nanoparticles rather than sorption.
	Lake/river	1.0E-02	1.0E+00	0.0E+00	Reference: The same as for reference soil water conditions in fine, lower organic content soil/sediment because the available data do not justify specification of a different K_d value. Upper and Lower Guide: These are the same as for soil waters in fine, lower organic content soil/sediment since the available data do not justify specifying different values.
	River bed	0.0E+00	1.0E+00	0.0E+00	Reference: Ag is likely to be in a neutral species (Ag) and therefore probably sorb to a lesser extent than in the other reference water conditions considered (in which Ag is in the form of Ag^+). However, there are no reliable data on which to base a recommendation for a reference K_d, hence specify a value of zero. Upper and Lower Guide: These are the same as for soil waters in fine, lower organic content soil/sediment since the available data do not justify specifying different values.
	Aquifer	1.0E-02	1.0E+00	0.0E+00	Reference: The same as for reference soil water conditions in fine, lower organic content soil/sediment because the available data do not justify specification of a different K_d value. Upper and Lower Guide: These are the same as for soil waters in fine, lower organic content soil/sediment since the available data do not justify specifying different values.

Tab. 4-28: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, higher organic content	Soil	4.0E-02	1.0E+00	0.0E+00	Reference: For each reference water 4× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. This is based on a comparison between data for organic-rich soils and mineral soils (e.g. IAEA, 2010) and considering the reported strong sorption of Ag on organic materials (Jacobson et al. 2005). Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	4.0E-02	1.0E+00	0.0E+00	
	River bed	0.0E+00	1.0E+00	0.0E+00	
	Aquifer	4.0E-02	1.0E+00	0.0E+00	
Coarse, low-organic content	Soil	5.0E-03	1.0E+00	0.0E+00	Reference: For reference conditions, 0.5× K_d for soil water conditions in fine lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	5.0E-03	1.0E+00	0.0E+00	
	River bed	0.0E+00	1.0E+00	0.0E+00	
	Aquifer	5.0E-03	1.0E+00	0.0E+00	

4.30 Strontium (Sr)

Strontium (Sr) is an alkaline earth metal (Group 2, Period 5). Naturally, the element exists only in the +II oxidation state. Reflecting their similar ionic radii, Sr exhibits similar geochemical behaviour to Ca and often occurs as a trace or minor component of Ca-bearing minerals like calcite, aragonite, gypsum, anhydrite and Ca-plagioclase. Across the range of Eh and pH that is relevant to this work aqueous Sr is likely to be predominantly in the form of Sr^{2+} (Fig. 4-29). At pH greater than ~ 9, in atmosphere-equilibrated water, Sr could plausibly precipitate as strontianite ($SrCO_3$). However, this pH is higher than the pH of any Northern Swiss water that is considered by this work.

Similar to other alkaline earth elements Sr typically interacts with clay minerals predominantly by ion exchange reactions (Higgo 1988, Linklater et al. 2003). The element generally sorbs more strongly by this mechanism than Ca and Mg, but less strongly than Ra and Ba, reflecting the relative sizes of the divalent cations formed in solution by these elements; generally smaller divalent ions will tend to displace larger ones from a mineral's surfaces. However, available sorption data suggest that the difference between Ca and Sr sorption is small (Appendix A). Baeyens & Bradbury (2003) note that apparently the selectivity coefficient for Sr-Ca exchange on clays is close to unity and proposed the same K_d for both elements.

In addition to sorption by cation exchange on clay minerals Sr can also sorb to amorphous silica, clay minerals, Fe-oxides and Fe-oxyhydroxides by outer sphere surface complexation (Carroll et al. 2008, Wallace et al. 2012). It has also been reported by Boyer et al. (2018) that proteins in organic matter in wetland sediments can sorb Sr strongly and only partially reversibly. The same authors found that in contrast carbohydrates and lignin sorb Sr to a much lower degree. However, little evidence was found in the present review to justify recommendation of different K_d values for fine, lower organic content soil/sediment and fine, higher organic content soil/sediment.

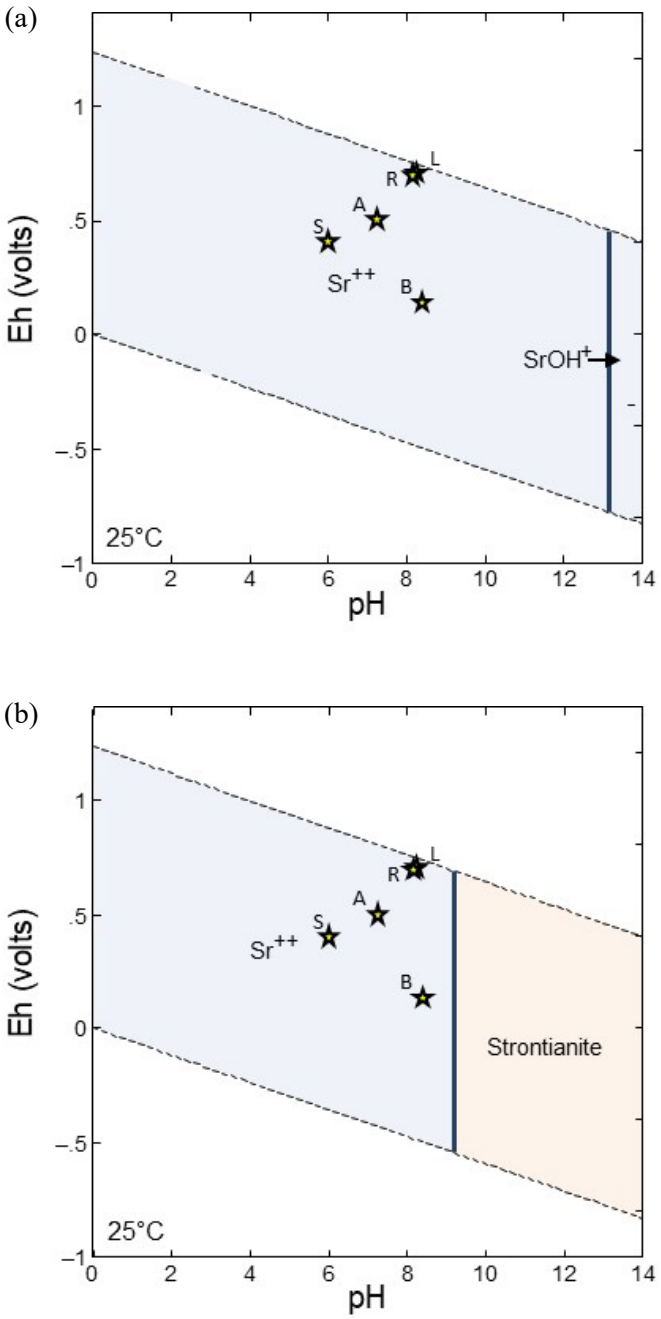

Fig. 4-29: Pourbaix diagrams for Sr at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Sr^{2+} = -6; (b) log *a* Sr^{2+} = -6, log pCO_2(g) = -3.5 (ambient atmospheric conditions). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Sr are given in Tab. 4-29.

Tab. 4-29: Recommended K_d values for Strontium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-02	1.0E+00	1.0E-04	Reference: 2 orders of magnitude less than value for Cs. This is consistent with reviewed data in which K_d values are generally 1 to 3 orders of magnitude smaller than for Cs which also sorbs by cation exchange (Appendix A). The K_d value is the same as for Ca, consistent with very similar sorption of Ca and Sr, as noted by Bradbury & Baeyens (2003). Upper and Lower Guide: Lower Guide is in the same order of magnitude as the smallest K_d reported in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the largest K_d reported in the reviewed literature (Appendix A). The available data do not justify specification of different Lower Guide and Upper Guide K_d for the different waters and soils/sediments.
	Lake/river	1.0E-02	1.0E+00	1.0E-04	
	River bed	1.0E-02	1.0E+00	1.0E-04	
	Aquifer	1.0E-02	1.0E+00	1.0E-04	
Fine, higher organic content	Soil	1.5E-02	1.0E+00	1.0E-04	Reference: For all reference conditions 1.5× the K_d for the corresponding reference conditions in fine, lower organic content soil/sediment. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide is in the same order of magnitude as the smallest K_d reported in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the largest K_d reported in the reviewed literature (Appendix A). The available data do not justify specification of different Lower Guide and Upper Guide K_d for the different waters and soils/sediments.
	Lake/river	1.5E-02	1.0E+00	1.0E-04	
	River bed	1.5E-02	1.0E+00	1.0E-04	
	Aquifer	1.5E-02	1.0E+00	1.0E-04	
Coarse, low-organic content	Soil	5.0E-03	1.0E+00	1.0E-04	Reference: For all reference conditions 0.5× the K_d for the corresponding reference conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the smallest K_d reported in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the largest K_d reported in the reviewed literature (Appendix A). The available data do not justify specification of different Lower Guide and Upper Guide K_d for the different waters and soils/sediments.
	Lake/river	5.0E-03	1.0E+00	1.0E-04	
	River bed	5.0E-03	1.0E+00	1.0E-04	
	Aquifer	5.0E-03	1.0E+00	1.0E-04	

4.31 Technetium (Tc)

Technetium (Tc) is a second-row transition metal from Group 7 and Period 5 of the periodic table. Across the range of pH relevant to natural waters Tc will have a +VII oxidation state under more oxidising conditions (Eh > 0 V at pH 8; Eh > 0.40 V at pH 4), the dominant aqueous species being TcO_4^- (Fig. 4-30a,b). Under more reducing conditions, the oxidation state will be +IV, with the speciation over the range of pH relevant to shallow groundwater and surface water in Northern Switzerland being dominated by electrically neutral $TcO(OH)_2$ (Fig. 4-30b). Conceivably, under reducing conditions, when Tc is in the +IV redox state, over this relevant pH range the aqueous concentration of Tc could be in equilibrium with a solid hydrous amorphous oxide phase, as shown in Fig. 4-30a. In such a case it would be inappropriate to model aqueous Tc concentrations using a sorption isotherm.

Sorption data for Tc under the conditions considered here are sparse. For the reducing conditions in the Opalinus Clay, in which Tc is in the Tc(IV) form, Bradbury & Baeyens (2003) used Th(IV) as an analogue, assigning Th(IV) K_d values to Tc(IV). However, as calculated with the PSI/Nagra thermodynamic database 2020v1-1, $TcO(OH)_2$ dominates the aqueous speciation of Tc(IV), whereas under similarly reducing conditions $Th(OH)_4$ dominates the aqueous speciation of Th(IV) (cf. Fig. 4-30 and Fig. 4-31). This difference in speciation suggests that Th(IV) may be unsuitable as an analogue of Tc(IV).

Under relatively oxidising conditions under which TcO_4^- dominates the aqueous speciation, sorption is reported to be low, with weak sorption at low pH on some minerals being due to surface complexation (Higgo 1988, Gu & Schulz 1991, Linklater et al. 2003). Under oxidising conditions, the behaviour of Tc has been reported to be like that of iodine, with retention associated with organic matter, Fe-oxyhydroxides, Fe-oxides and Al-oxides, and retention on layer silicates being negligible (Gu & Schulz 1991, Söderlund et al. 2011). However, Kaplan (2016) has reported sorption data for TcO_4^- that shows significant sorption on clayey sediment from Savannah River, U.S.A, albeit with small K_d values and at low pH. The relationship between pH and K_d for Tc sorption is ambiguous, with different sources reporting different relationships (Söderlund et al. 2011).

Higher sorption is reported for reducing conditions in which Tc is the +IV oxidation state (Lieser & Bauscher 1987, Higgo 1988, Linklater et al. 2003). However, these values must be treated with caution owing to the possible formation of insoluble phases under reducing conditions and the difficulty of measuring low concentrations of Tc in solution. It has been reported that the higher sorption under these reducing conditions is associated with complexation of Tc with organic matter.

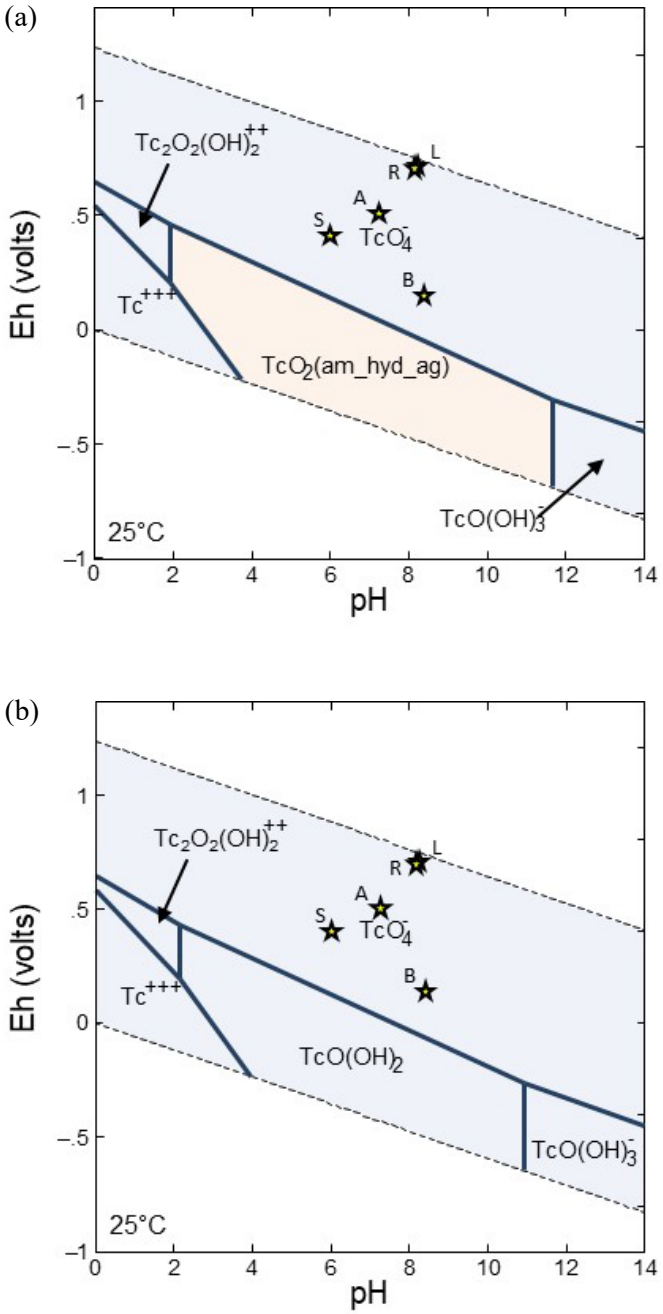

Fig. 4-30: Pourbaix diagrams for Tc at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* $TcO(OH)_2^-$ = -8; (b) log *a* $TcO(OH)_2^-$ = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Tc are given in Tab. 4-30.

Tab. 4-30: Recommended K_d values for Technetium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-03	1.0E+00	0.0E+00	Reference: Linklater et al. (2003) report K_d values for a range of materials, with values for Tc(VII) being generally < 1.0E-03 m^3/kg. Based on measurements of TcO_4^- sorption Kaplan (2016) recommended a K_d value of 2.0E-03 m^3/kg for clayey sediments from Savannah River, USA. Geometric means of K_d in several reviewed datasets are in the order of 1.0E-03 m^3/kg. Upper and Lower Guide: Lower Guide is consistent with some studies reporting negligible sorption (e.g. Krupka et al. 2004) and is appropriate for oxidising conditions in which Tc(VII) dominates. Upper Guide is in the same order of magnitude as the highest value reported for soils/sediments (Appendix A) and is appropriate for reducing conditions in which Tc(IV) dominates.
	Lake/river	1.0E-03	1.0E-02	0.0E+00	Reference: The same as for reference soil water conditions in fine, lower organic content soil/sediment because the available data do not justify specification of a different K_d value. The available data do not justify specification of different reference K_d for lake/river waters and river bed waters. Upper and Lower Guide: Lower Guide is consistent with some studies reporting negligible sorption (e.g. Krupka et al. 2004) and is appropriate for oxidising conditions in which Tc(VII) dominates. Upper Guide is an order of magnitude larger than the Reference K_d and is a reasonable estimate for use in sensitivity calculations that is not well-constrained by data. In both lake/river waters and river bed waters Tc(VII) will be the dominant oxidation state of Tc and therefore the Upper Guide should be less than the Upper Guide for soil waters and aquifer waters, some of which are sufficiently reducing for more strongly sorbing Tc(IV) to dominate. The available data do not justify different Lower Guide and Upper Guide values for lake/river waters and river bed waters.
	River bed	1.0E-03	1.0E-02	0.0E+00	
	Aquifer	1.0E-03	1.0E+00	0.0E+00	Reference: The same as for reference soil water conditions in fine, lower organic content soil/sediment because the available data do not justify specification of a different K_d value. Upper and Lower Guide: Lower Guide is consistent with some studies reporting negligible sorption (e.g. Krupka et al. 2004) and is appropriate for oxidising conditions in which Tc(VII) dominates. Upper Guide is in the same order of magnitude as the highest value reported for soils/sediments (Appendix A) and is appropriate for reducing conditions in which Tc(IV) dominates.

Tab. 4-30: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, higher organic content	Soil	4.0E-03	1.0E+00	0.0E+00	Reference: For all reference conditions 4× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment, based on reported enhanced sorption in organic-rich materials (Söderlund et al. 2011 and references therein), and the reported K_d values for organic soils (Appendix A). Larger K_d values in some publications are neglected because possibly they reflect reduction of Tc(VII) to Tc(IV) in the presence of organic matter, with consequent precipitation of a solid Tc-phase leading to over-estimates of K_d. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	4.0E-03	1.0E-02	0.0E+00	
	River bed	4.0E-03	1.0E-02	0.0E+00	
	Aquifer	4.0E-03	1.0E+00	0.0E+00	
Coarse, low-organic content	Soil	5.0E-04	1.0E+00	0.0E+00	Reference: For all reference conditions 0.5× the K_d values for the corresponding reference conditions in fine, lower organic content soil/sediment, Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	5.0E-04	1.0E-02	0.0E+00	
	River bed	5.0E-04	1.0E-02	0.0E+00	
	Aquifer	5.0E-04	1.0E+00	0.0E+00	

4.32 Thorium (Th)

Thorium (Th) is an actinoid (Period 7 of the periodic table). The element exists naturally only in the +IV oxidation state and progressively hydrolyses as pH increases (Fig. 4-31). In natural waters, Th may form complexes with fluoride, chloride, carbonate, nitrate, phosphate and sulphate (Higgo 1988). However, over most of the pH range relevant to soil waters in Northern Switzerland, and over the entire pH range of shallow groundwater and surface waters in Northern Switzerland, aqueous Th will be dominant in the form of the electrically neutral $Th(OH)_4$ species (Fig. 4-31). In soil waters with pH lower than about 5.5, the divalent cationic aqueous species $Th(OH)_2^{2+}$ could dominate. At pH > 5, amorphous $ThO_2(s)$ could be thermodynamically (meta)stable and buffer dissolved Th concentrations. If this, or a similar phase, were to be present, such that aqueous Th concentrations are solubility limited, then it would be inappropriate to model Th retention in the solid phase using a sorption isotherm.

It is reported that Th sorbs strongly to hematite, ilmenite, micas, and chlorite, but less strongly to calcite, feldspar, and quartz (Linklater et al. 2003). Sorption is little affected by the ionic strength of the solution and therefore probably sorbs through an inner-sphere surface complexation mechanism (Higgo 1988, Linklater et al. 2003). In contrast, pH affects sorption markedly, reflecting both, the pH-dependent change in speciation of aqueous Th and the pH-dependent change in charge at the surface of a solid phase. However, different authors have reported different variations in K_d with respect to pH. Higgo et al. (1988) and Linklater et al. (2003) report that sorption is generally lowest at pH < 2, where cations dominate the aqueous speciation of Th and solid surfaces are positively charged. These authors also report that as pH increases above pH 2, the K_d increases to a maximum at pH c. 5. In contrast, Bradbury & Baeyens (2003) concluded that under conditions relevant to the Opalinus Clay, the K_d would roughly double between pH 6.2 and pH 7.2, above which it would be constant at least to pH 7.8.

Reported K_d values for Th vary widely, mostly lying in the range 1.0E-02 m^3/kg to 1.0E+02 m^3/kg (Appendix A). However, values as high as 1.0E+04 m^3/kg have been reported by some authors (Linklater et al. 2003 and references therein).

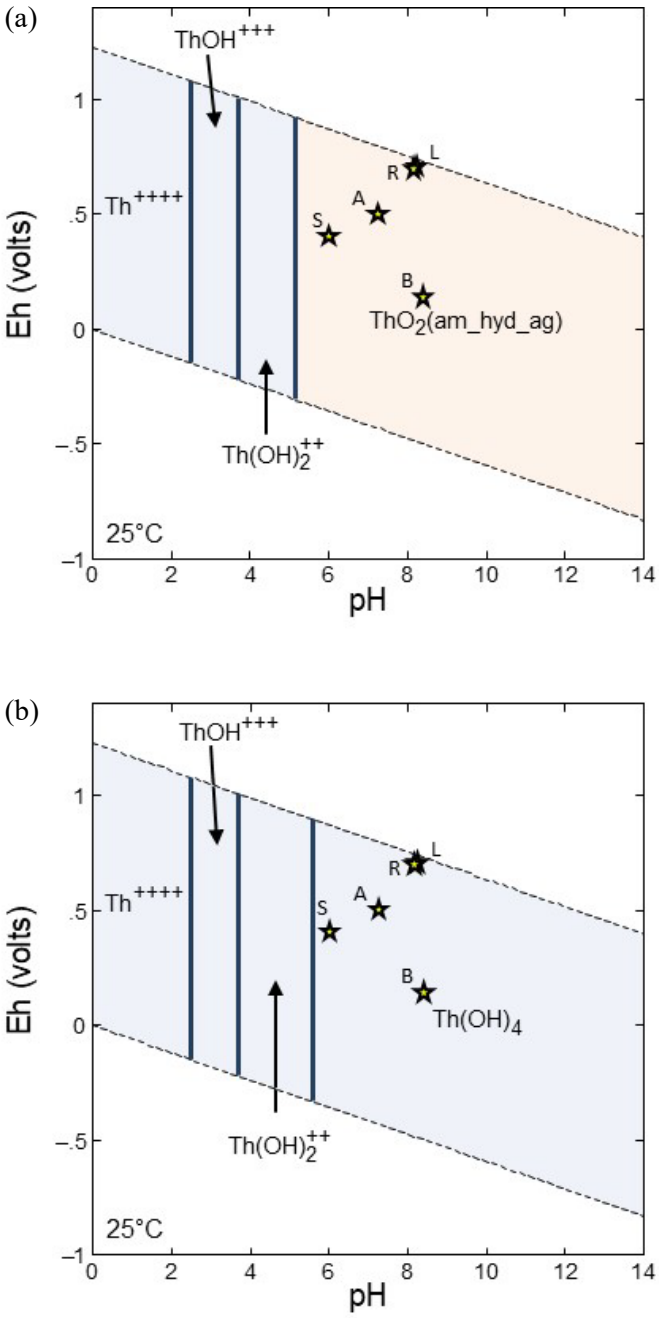

Fig. 4-31: Pourbaix diagrams for Th at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Th^{4+} = -8; (b) log *a* Th^{4+} = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Th are given in Tab. 4-31.

Tab. 4-31: Recommended K_d values for Thorium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	2.0E+00	1.0E+01	1.0E-02	Reference: The geometric means of sets of reviewed soil data are generally in the order of 1.0E+00 m^3/kg (Appendix A). Kaplan (2016) recommended a K_d for clayey sediment at Savannah River, U.S.A. of 2.0E+00 m^3/kg based on measurements of Zr sorption, taken as an analogue. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported for pH < 5 in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the geometric mean K_d reported for clay-rich sediments in the pH range 7-8 (Appendix A).
	Lake/river	2.0E+00	1.0E+02	1.0E-01	Reference: The same as for reference soil water in fine, lower organic content soil/sediment because the available data do not justify specification of different K_d values. Available data on pH dependency (Higgo 1988, Bradbury & Baeyens 2003) suggest that K_d values will not change significantly over the pH differences between reference soil water and the other reference water conditions. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported for pH > 6 in the reviewed literature; given the pH-dependence of K_d, a larger minimum value is expected than for soil waters, some of which have pH as low as 3.9. Upper Guide is in the same order of magnitude as the largest K_d reported for soil/sediment in the reviewed literature (Appendix A). The available data do not justify specification of different Lower Guide and Upper Guide values for lake waters, river bed waters and aquifer waters.
	River bed	2.0E+00	1.0E+02	1.0E-01	
	Aquifer	2.0E+00	1.0E+02	1.0E-01	
Fine, higher organic content	Soil	3.0E+00	1.0E+01	1.0E-02	Reference: For each reference water 1.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	3.0E+00	1.0E+02	1.0E-01	
	River bed	3.0E+00	1.0E+02	1.0E-01	
	Aquifer	3.0E+00	1.0E+02	1.0E-01	
Coarse, low-organic content	Soil	1.0E+00	1.0E+01	1.0E-02	Reference: For each reference water 0.5× the K_d for the corresponding reference water in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment, as the available data do not justify specification of different Lower Guide and Upper Guide K_d for the different soils/sediments.
	Lake/river	1.0E+00	1.0E+02	1.0E-01	
	River bed	1.0E+00	1.0E+02	1.0E-01	
	Aquifer	1.0E+00	1.0E+02	1.0E-01	

4.33 Tin (Sn)

Tin (Sn) is a metal (Group 14, Period 5 of the periodic table), which can have oxidation states of +II and +IV, although only the latter is predicted to be relevant to the natural shallow groundwaters and surface waters of Northern Switzerland (Fig. 4-32). In dilute aqueous solutions Sn will be strongly hydrolysed, with increasing hydrolysis as pH increases. Over most of the pH range relevant to these waters, aqueous Sn is likely to be predominantly in the form of electrically neutral $Sn(OH)_4$, but in waters towards the higher end of the relevant range, with pH > 8, the anionic species $Sn(OH)_5^-$ could be dominant (Fig. 4-32). All the reference water conditions plot in the field of aqueous $Sn(OH)_4$ predominance (Fig. 4-32). At pH lower than c. 8, cassiterite could be thermodynamically stable. Were it to form and provide a solubility limitation on Sn concentrations, it would be inappropriate to model the solid-aqueous distribution of Sn using a sorption isotherm.

Sorption data for Sn under relevant conditions are scarce. Tits & van Dorp (1999) considered Sn to have sufficiently similar chemical characteristics to those of Pb that the same K_d values could be recommended for both elements. Similarly, Kaplan (2016) used Pb as a chemical analogue for Sn when recommending K_d values for sediments from Savannah River, U.S.A. However, as calculated using the PSI/Nagra thermodynamic database 2020v1-1 the aqueous chemical speciation of Sn and Pb over relevant Eh and pH ranges are quite different (cf. Fig. 4-32 and Fig. 4-14). Hence the validity of this analogue is questionable.

Based on a literature review Linklater et al. (2003) concluded that Sn most likely sorbs strongly by a surface complexation mechanism, and in particular sorbs strongly to oxide/hydroxide surfaces. They also noted the possibility that unhydrolysed Sn might exchange for Ca^{2+} on clay minerals. There is evidence that Sn may form complexes with organic material and bind strongly to humic materials (Higgo 1988, Linklater et al. 2003).

The available data suggest that over the pH range relevant to the present work (pH 3.9 to pH 9) Sn sorption is likely to vary little. Bradbury & Baeyens (2003) considered that Sn sorption would not be significantly pH-dependent between pH 4 to c.9.5. Modelling reported in Bradbury & Baeyens (2009) suggest that sorption of Sn onto illite should be maximal at pH 7 – 9, but decreases sharply at higher pH owing to increasing hydrolysis of Sn.

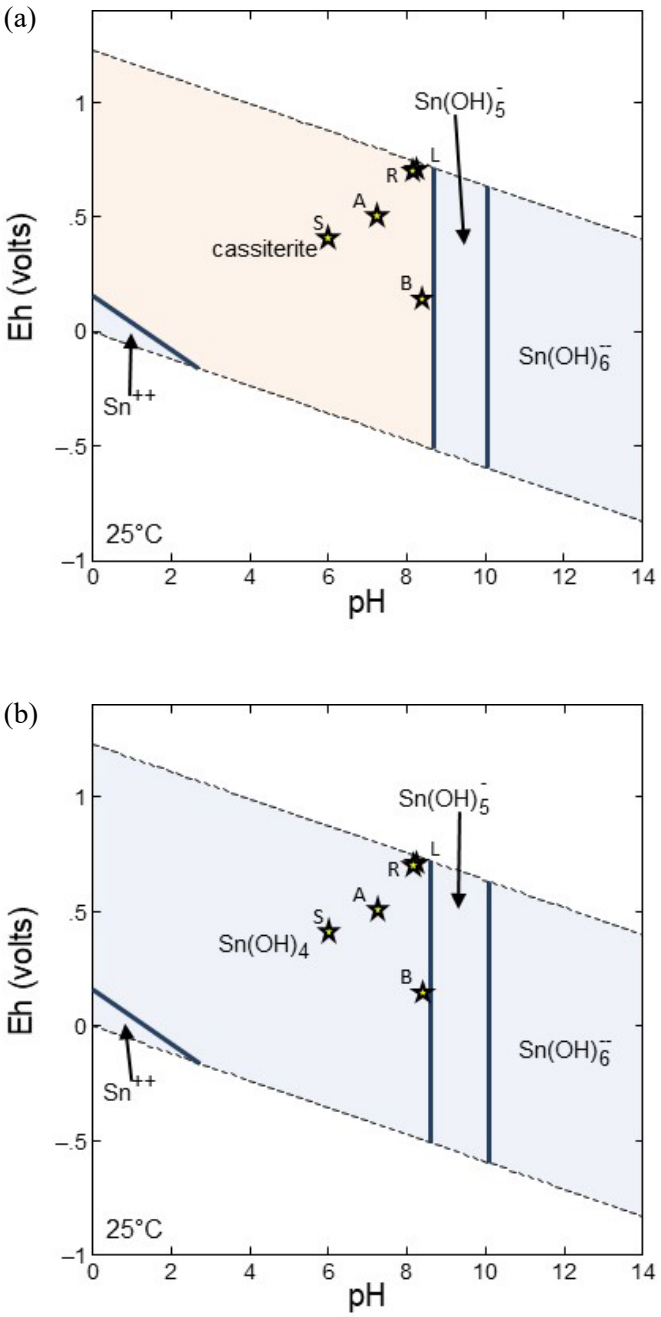

Fig. 4-32: Pourbaix diagrams for Sn at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Sn^{4+} = -8 (cassiterite is SnO_2); (b) log *a* Sn^{4+} = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Sn are given in Tab. 4-32.

Tab. 4-32: Recommended K_d values for Tin (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E-01	1.0E+03	1.0E-02	Reference: K_d values for clay soils and mineral soils in the reviewed compilations are typically in the order 1.0E-01 m^3/kg(Appendix A). Available data on pH dependency (Higgo 1988, Bradbury & Baeyens 2003) suggest that K_d will not change significantly over the unit differences between the difference reference waters. The available data do not justify the specification of different K_d for the different reference waters in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide is in the same order as the lowest K_d reported in the reviewed literature (Appendix A). Upper Guide is in the same order as the highest K_d reported in the reviewed literature (Appendix A). Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/ sediment. The data do not justify specification of different values for the different waters and soils/sediments.
	Lake/river	1.0E-01	1.0E+03	1.0E-02	
	River bed	1.0E-01	1.0E+03	1.0E-02	
	Aquifer	1.0E-01	1.0E+03	1.0E-02	
Fine, higher organic content	Soil	4.0E-01	1.0E+03	1.0E-02	Reference: For each reference condition 4× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment. Sn is known to bind strongly to organic matter (Higgo 1988, Linklater et al. 2003). In the reviewed literature reported K_d values for organic-rich materials are often around an order of magnitude greater than the reported K_d values for organic poor materials (e.g. IAEA (2010) give 1.60E+00 m^3/kg for organic soils, and 2.8E-01 m^3/kg for mineral soils), although the data show wide scatter (Appendix A). The available data do not justify the specification of different K_d for the different reference waters in fine, higher organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters and soils/sediments.
	Lake/river	4.0E-01	1.0E+03	1.0E-02	
	River bed	4.0E-01	1.0E+03	1.0E-02	
	Aquifer	4.0E-01	1.0E+03	1.0E-02	
Coarse, loworganic content	Soil	5.0E-02	1.0E+03	1.0E-02	Reference: For each reference condition 0.5× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment. The available data do not justify the specification of different K_d for the different reference waters in coarse, low-organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters and soils/sediments.
	Lake/river	5.0E-02	1.0E+03	1.0E-02	
	River bed	5.0E-02	1.0E+03	1.0E-02	
	Aquifer	5.0E-02	1.0E+03	1.0E-02	

4.34 Titanium (Ti)

Titanium (Ti) is a transition metal (Group 4, Period 4 of the periodic table). The element can occur in both the +II, +III and +IV oxidation states, but only +IV is relevant to soils, shallow groundwater and surface waters in Northern Switzerland. Over the entire relevant pH range Ti is predicted using the latest Nagra/PSI thermodynamic database 2020v1-1 to be present dominantly as the electrically neutral $TiO(OH)_2$ species (Fig. 4-33). Depending on the water composition, conceivably, a solid Ti-phase such as hydrated, amorphous titanium oxide (TiO_2(am,hyd)) could be thermodynamically (meta)stable over the same field as this neutral species. If this were to be the case, and aqueous Ti concentrations are solubility-controlled, then it would be inappropriate to model partitioning of Ti between solid and aqueous phases using a sorption isotherm.

Owing to its low solubility and a possible solubility control on aqueous concentrations, there are few data on Ti sorption in soils, sediments and rocks. It is noteworthy that TiO_2 nanoparticles of anthropogenic origin in natural waters and sediments have received increasing recognition as pollutants in recent years (Simonin et al. 2016, Zhao et al. 2019). These materials have been shown to be strong sorbents with respect to organic matter and heavy metals (Rosenfeldt et al. 2014, Zhao et al. 2019).

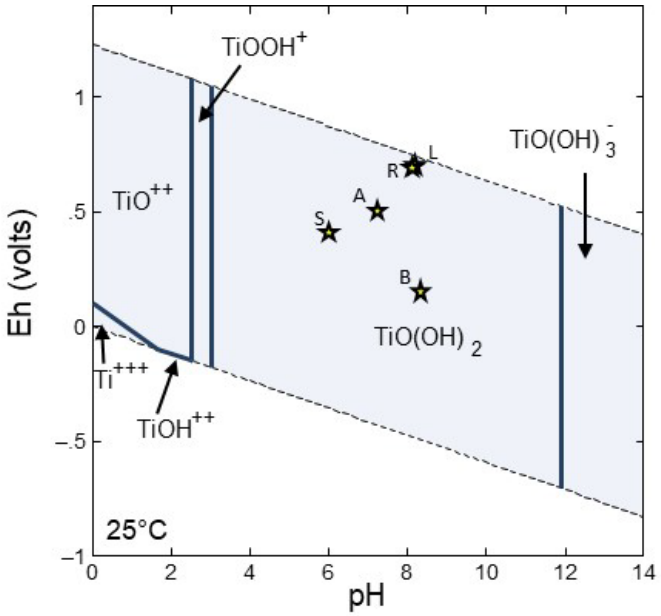

Fig. 4-33: Pourbaix diagrams for Ti at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

log *a* TiO^{2+} = -8. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Ti are given in Tab. 4-33.

Tab. 4-33: Recommended K_d values for Titanium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	0.0E+00	1.0E+03	1.0E-03	Reference: Limited data cover a very wide range of K_d values (Appendix A) and do not allow a reference K_d value to be assigned confidently. Therefore, Ti is treated as being non-sorbing. Upper and Lower Guide: Upper Guide and Lower Guide are in the same orders as the lowest and highest reported values in the reviewed literature (Appendix A). Data are insufficient to allow different Guide values to be specified for the different reference water conditions and soil/sediment types.
	Lake/river	0.0E+00	1.0E+03	1.0E-03	
	River bed	0.0E+00	1.0E+03	1.0E-03	
	Aquifer	0.0E+00	1.0E+03	1.0E-03	
Fine, higher organic content	Soil	0.0E+00	1.0E+03	1.0E-03	
	Lake/river	0.0E+00	1.0E+03	1.0E-03	
	River bed	0.0E+00	1.0E+03	1.0E-03	
	Aquifer	0.0E+00	1.0E+03	1.0E-03	
Coarse, low-organic content	Soil	0.0E+00	1.0E+03	1.0E-03	
	Lake/river	0.0E+00	1.0E+03	1.0E-03	
	River bed	0.0E+00	1.0E+03	1.0E-03	
	Aquifer	0.0E+00	1.0E+03	1.0E-03	

4.35 Uranium (U)

Uranium (U) is an actinoid (Period 7 of the periodic table). This element may exist in redox states +III, +IV, +V or +VI. However, under most conditions in nature the +III form readily oxidises to +IV and the +V form (UO_2^+) converts easily to the +IV and +VI forms. Therefore, in the natural surface waters of Northern Switzerland only the +VI oxidation state is relevant (Fig. 4-34). This oxidation state is also the dominant one throughout most of the Eh and pH ranges spanned by the soil waters of Northern Switzerland. However, the more reducing of these waters may have Eh < -0.10 V, in which case U(IV) would be the dominant form (Fig. 4-34). In the absence of carbonate, U progressively hydrolyses as pH increases (Fig. 4-34a). Accordingly at the lowest pH of shallow groundwaters (pH ~ 6) in the absence of carbonate, the univalent cationic species UO_2OH^+ is predicted to dominate, whereas in shallow groundwaters or surface waters with near-neutral pH, $UO_2(OH)_2$ would dominate and at still higher pH, $UO_2(OH)_3^-$ would dominate. When redox conditions are sufficiently oxidising for U(VI) species to dominate, in the presence of carbonate, as pH increases above ~ 6.5, neutral UO_2CO_3, then progressively more negatively charged carbonate species, $(UO_2)_2CO_3(OH_3)^-$ $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ dominate (Fig. 4-34b, Fig. 4-34c).

Both U(IV) and U(VI) are believed to sorb by surface complexation (Waite et al. 1994, Linklater et al. 2003). Depending on the pH, and the carbonate content, cationic, electrically neutral or anionic species are possible. This complexity of speciation makes it difficult to recommend K_d values for the different considered waters. Additionally, potentially under reducing conditions at pH > c.4.5 hydrated amorphous UO_2 (UO_2(am,hyd)) could be thermodynamically (meta)stable and act as a solubility-limiting phase (Fig. 4-34). If this phase, or a similar phase, forms such that aqueous U is solubility-limited, it would be inappropriate to model partitioning of U between solid and aqueous phases using a sorption isotherm.

Owing to its complex redox chemistry, couplings between different chemical processes need to be taken into account when evaluating U sorption. However, qualitatively, variations in sorption reflect several general principles affect the pH-dependence of sorption. U is believed to sorb dominantly via a surface complexation mechanism, which is pH dependent. Sorption is lowest at low-pH and increases to a maximum at near-neutral conditions, before decreasing again at higher pH (Linklater et al. 2003, Bradbury & Baeyens 2009, Crawford 2013). This behaviour reflects the pH-dependence of the charge on solid surfaces and the hydrolysis of U. At lowest pH, solid phases tend to have positive surface charges while the dissolved U is dominantly in cationic form. At near-neutral pH, the surface charge is negative, while aqueous U is still in cationic form. As pH increases further, firstly electrically neutral and then anionic species become dominant, which sorb less well to the progressively negatively charged surfaces of solid phases. Systematic sorption data for U(VI) as a function of pH and pCO_2 on a simple substrate (ferrihydrite) (Waite et al. 1994) show that sorption can vary by several orders of magnitude within a relatively narrow range of aqueous chemistry. In experiments with solutions of 1.0E-06 mol/kg U in equilibrium with the atmosphere and either 0.001 mol/kg Fe or 0.02 mol/kg Fe as ferrihydrite, sorption of U increased from near zero at pH 3.5 to almost 100% at pH 5.5, remaining constant between pH 5 and pH 8 and then falling again to nearly zero between pH 8 and 9. Increasing pCO_2 by 25× from atmospheric levels resulted in the decrease in sorption with increasing pH shifting by about 1 pH unit towards more acidic values; U sorption decreased from 100% at pH c. 7 to about zero at pH c. 8. Linklater et al. (2003) reported data for sorption of U(VI) on hematite and volcaniclastic rock that suggests K_d would decrease by about an order of magnitude for an increase in log pCO_2 from -3.5 to -1.6 (all other conditions being kept constant).

U(IV) sorption is generally expected to be much stronger than U(VI) sorption (Linklater et al. 2003). Different minerals sorb U to different extents. Fe-oxide, Fe-oxyhydroxide, clay minerals and zeolites are reported to sorb U particularly strongly, whereas calcite, feldspar and quartz sorb U relatively weakly (Linklater et al. 2003).

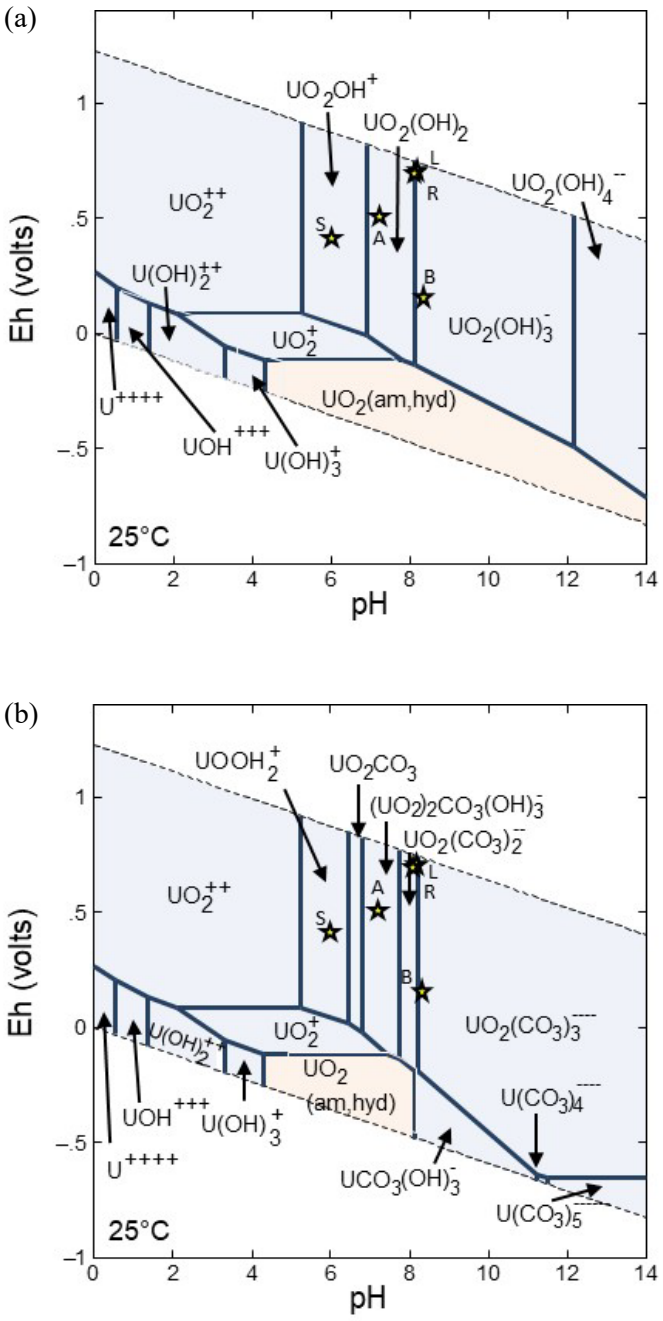

Fig. 4-34: Pourbaix diagrams for U at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log a UO22+- = -8; (b) log a UO22+- = -8, log pCO2(g) = -3.5 (ambient atmospheric conditions); (c) log a UO22+ = -8, log a HCO3 = -3.5 (equivalent to 3.5 mg/L, the highest reported concentration in shallow aquifer waters, resulting in log pCO2(g) = -1.6 at pH 6 and -6.1 at pH 8.25). Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

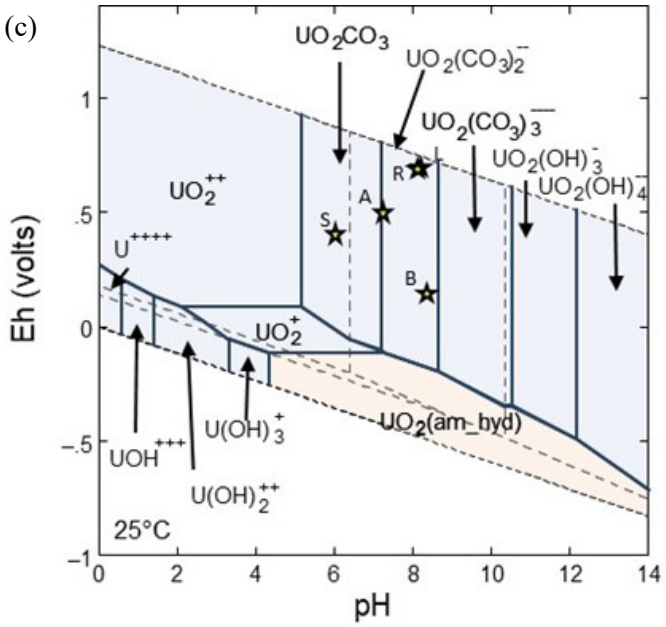

Fig. 4-34: Cont.

Recommended K_d values for U are given in Tab. 4-34.

Tab. 4-34: Recommended K_d values for Uranium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	1.0E+00	1.0E+02	1.0E-04	Reference: Published K_d for U in soils and sediments show considerable variability (Appendix A). In most cases U(VI) data are presented, reflecting the relative difficulty of measuring K_d for U(IV). Most geometric mean values for the different datasets are in the order of 1.0E+00 m^3/kg, including several studies for which pH is relevant (pH 5 – 7; e.g. Ramírez-Guinart et al. 2020). Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported for pH < 5 in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the highest K_d reported in the reviewed literature for Th(IV) (excluding one outlier K_d = 1.0E+04 m^3/kg), taken as an analogue for U(IV) (Appendix A). Lower Guide is appropriate for the lowest-pH most oxidising soil water, in which U(VI) dominates. Upper Guide is appropriate for the highest-pH, most reducing soil water in which U(IV) dominates.
	Lake/river	1.0E+00	1.0E+01	1.0E-03	Reference: Same as the K_d for reference soil water conditions in fine, lower organic content soil/sediment. Published data (e.g. Waite et al. 1994) suggest little change in K_d over the difference in pH between the reference soil water (pH 6) and of reference Lake/river water and reference river bed water (pH of both c. 8). The available data do not justify specification of different K_d for reference Lake/river water and reference river bed water conditions. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the smallest K_d reported for water with pH > 7 in the reviewed literature (Appendix A). The Lower Guide is an order of magnitude greater than the Lower Guide for soil waters in fine, lower organic content soil/sediment, consistent with the lowest pH of the lake/river waters and river bed waters being > 3 units higher than the lowest pH of soil waters (lowest pH 6.25 and 3.9 respectively). Upper Guide is an order of magnitude greater than the Upper Guide for soil waters in fine, lower organic content soil/sediment, recognising that U(VI) will dominate in lake/river, river bed and aquifer waters; U(VI) sorbs less strongly than U(IV). The available data do not justify specification of different Lower Guide and Upper Guide values for lake/river waters and river bed waters.
	River bed	1.0E+00	1.0E+01	1.0E-03	

Tab. 4-34: Cont.

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Aquifer	1.0E-01	1.0E+01	1.0E-03	Reference: Order of magnitude smaller than the K_d for reference soil water in fine, lower organic content soil/sediment. This considers the likely higher carbonate content in the aquifer water compared to the other waters and the relationship between carbonate content and K_d reported in published literature (e.g. Waite et al. 1994, Linklater et al. 2003). Upper and Lower Guide: Same as the Lower Guide and Upper Guide for soil waters, lake/river waters and river bed waters. The available data do not justify specification of different Lower Guide and Upper Guide values for these waters.
Fine, higher organic content	Soil	4.0E+00	1.0E+02	1.0E-04	Reference: For each reference condition 4× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment. This considers the greater quantity of solid phases on which sorption may occur in the fine, higher organic content soil/sediment (see Chapter 4.1). Published K_d values for U in soils/sediments are often c. 1 order of magnitude higher in organic-rich, compared to organic-poor materials (Appendix A). The available data do not justify specification of different K_d for the different reference waters in fine, higher organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters in different soils/sediments.
	Lake/river	4.0E+00	1.0E+01	1.0E-03	
	River bed	4.0E+00	1.0E+01	1.0E-03	
	Aquifer	4.0E-01	1.0E+01	1.0E-03	
Coarse, low-organic content	Soil	5.0E-01	1.0E+02	1.0E-04	Reference: For each reference condition 0.5× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment). The available data do not justify specification of different K_d for the different reference waters in coarse, low-organic content soil/sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	5.0E-01	1.0E+01	1.0E-03	
	River bed	5.0E-01	1.0E+01	1.0E-03	
	Aquifer	5.0E-02	1.0E+01	1.0E-03	

4.36 Zirconium (Zr)

Zirconium (Zr) is a transition metal (Group 4, Period 5 of the periodic table). The element occurs only in the +IV oxidation state. Throughout the range of pH relevant to soils, shallow groundwaters and surface waters in Northern Switzerland, aqueous Zr will be dominated by the neutral species $Zr(OH)_4$ (Fig. 4-35a). However, over the same range of pH, plausibly the solid phase baddeleyite (ZrO_2) could be thermodynamically stable (Fig. 4-35b). If this, or another Zr-bearing phase, places a solubility limit on aqueous Zr concentrations, it would be inappropriate to model partitioning of Zr between the aqueous and solid phase using a sorption isotherm.

Tits & van Dorp (1999) pointed out that Zr has a similar atomic radius and ionisation energies to those of Th. In view of this similarity and the similar redox chemistries of these elements it is reasonable to suppose that they will have generally similar sorption characteristics. It has also been suggested that Zr should sorb in a similar fashion to Sn, again based on the similar redox chemistry of Sn and Zr, and their similar atomic radii and ionisation energies (Crawford 2013). The aqueous speciation of each of Zr, Th and Sn is such that all the reference water compositions considered here plot within the fields of neutral hydroxo-species (c.f Fig. 4-35, Fig. 4-31 and Fig. 4-32). However, $Zr(OH)_4$ is the dominant Zr-species over all ranges of Swiss water conditions considered (Fig. 2-10). In contrast, the positive species $Th(OH)_2^{2+}$ dominates Th speciation over much of the field of reference soil water conditions, while the $Sn(OH)_5^-$ dominates Sn speciation over some of the fields of reference lake water, aquifer water and river bed water conditions. These differences suggest that Th and Sn are not good analogues for Zr across the full ranges of relevant water conditions.

Zr is thought to sorb by a surface complexation mechanism and therefore its sorption is likely to be pH-dependent (Higgo 1988, Linklater 2003, Crawford 2013). However, there is little data with which to judge the magnitude of this pH-dependence. Presumably sorption will be lower under low-pH and high-pH conditions than under near-neutral conditions.

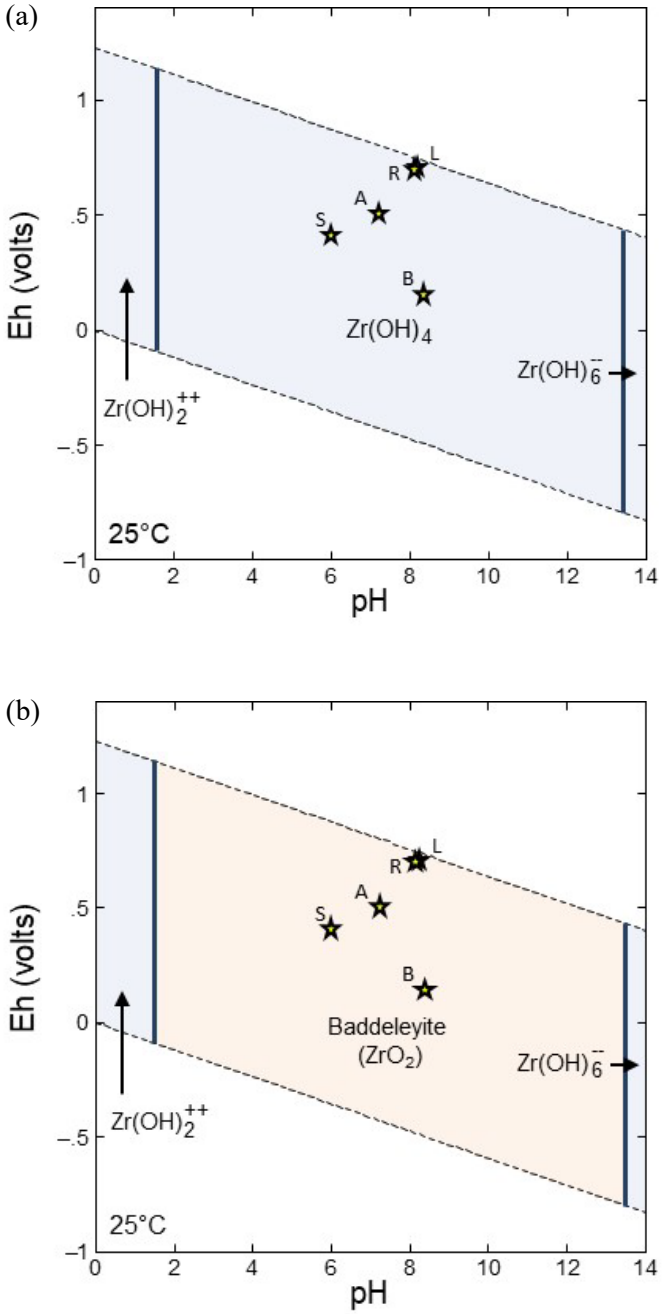

Fig. 4-35: Pourbaix diagrams for Zr at 25 °C, 1 bar (PSI/Nagra thermodynamic database 2020v1-1)

(a) log *a* Zr^{4+} = -10; (b) log *a* Zr^{4+} = -9. Reference conditions are shown by yellow stars: L = lake water; R = river water; A = aquifer water; S = soil water; B = river bed water.

Recommended K_d values for Zr are given in Tab. 4-35.

Tab. 4-35: Recommended K_d values for Zirconium (m^3/kg)

Material	Water	Reference	Upper guide	Lower guide	Justification
Fine, lower organic content	Soil	2.0E+00	1.0E+01	1.0E-03	Reference: The geometric means of sets of reviewed soil data are generally in the order of 1.0E+00 m^3/kg (Appendix A). Kaplan (2016) recommended a K_d for clayey sediment at Savannah River, U.S.A. of 2.0E+00 m^3/kg based on measurements of Zr sorption. The available data do not justify specification of different reference K_d for the different reference water conditions in fine, lower organic content soil/sediment. Upper and Lower Guide: Lower Guide is in the same order of magnitude as the lowest K_d reported in the reviewed literature (Appendix A). Upper Guide is in the same order of magnitude as the highest K_d in the reviewed literature (Appendix A). The available data do not justify different Lower Guide and Upper Guide values for the different waters in fine, lower organic content soil/sediment.
	Lake/river	2.0E+00	1.0E+01	1.0E-03	
	River bed	2.0E+00	1.0E+01	1.0E-03	
	Aquifer	2.0E+00	1.0E+01	1.0E-03	
Fine, higher organic content	Soil	3.0E+00	1.0E+01	1.0E-03	Reference: For each reference condition 1.5× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment. There is no clear evidence that sorption on organic-rich materials would be higher than on organic-poor, but otherwise similar materials (Appendix A). The available data do not justify specification of different K_d for the different reference water conditions in fine, higher organic content soil/ sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	3.0E+00	1.0E+01	1.0E-03	
	River bed	3.0E+00	1.0E+01	1.0E-03	
	Aquifer	3.0E+00	1.0E+01	1.0E-03	
Coarse, low-organic content	Soil	1.0E+00	1.0E+01	1.0E-03	Reference: For each reference condition 0.5× the K_d for the corresponding reference condition in fine, lower organic content soil/sediment. The available data do not justify specification of different K_d for the different reference water conditions in coarse, lower organic content soil/ sediment. Upper and Lower Guide: Lower Guide and Upper Guide are the same as specified for each water in fine lower organic content soil/sediment. The data do not justify specification of different values for the different waters.
	Lake/river	1.0E+00	1.0E+01	1.0E-03	
	River bed	1.0E+00	1.0E+01	1.0E-03	
	Aquifer	1.0E+00	1.0E+01	1.0E-03	

5 Conclusions

This report recommends values for K_d for 35 elements, to be used in Nagra's SGT E3 biosphere modelling using the SwiBAC model. The K_d values are given for three soil/sediment types:

1. fine grained, lower organic content (clay content ≥ 30 vol.-%, organic matter content < 5 wt.-%)
2. fine grained, higher organic content (clay content ≥ 30 vol.-%, organic matter content ≥ 5 wt.-%)
3. coarse low-organic content (clay content < 30 vol.-% and organic matter content < 5 wt.-%)
    a. For each soil/sediment type three K_d values are given in Chapter 4:"a "Reference" value; "a "Lower Guide" value, and
    b. "n "Upper GuideE value.

The "ReferenceK_d" is considered to be a plausible value for the K_d in Northern Swiss soils, river sediments and lake sediments. The "ReferenceK_d" is suitable for use in "base case" biosphere models implemented in SwiBAC. The "Lower Guide" and "Upper Guide" values in contrast are likely to lie towards the lower end and upper end, respectively, of the natural ranges of K_d values in these Northern Swiss environments. These "Lower Guide" and "Upper Guide" values are appropriate for use in sensitivity calculations carried out with the SwiBAC model.

The recommended K_d values are *consistent* with published K_d values experimentally determined under conditions that are broadly similar that are to those in the biosphere of Northern Switzerland. That is, as far as could be ascertained, the published K_d values were obtained using soils/sediments and waters that are as close as possible to those found in the areas being considered by Nagra in SGT E3. However, none of the K_d values were measured on these Northern Swiss soils/sediments in the presence of actual coexisting waters. Inevitably, there is uncertainty as to the applicability of the published experimental K_d values to the biosphere of Northern Switzerland. To mitigate this, the following approach was taken:

- K_d values are recommended from within the published ranges of values so that differences in K_d between different soils and sediments are consistent with the theoretical understanding of sorption,
- K_d values are recommended so that differences in K_d under different conditions (e.g. Eh and pH) are consistent with differences in the chemical speciation of the element under the different conditions, as determined using the latest PSI/Nagra thermodynamic database 2020v1-1.
- A wide range is specified between "Lower Guide" and "Upper Guide" K_d values, to bracket the overall envelope arising from uncertainty in available data and its applicability, and variability in sorption.

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7 Glossary

Term	Abbr.	Definition	German
Adsorption	-	Here, a surface process that results in transfer of a molecule from an aqueous solution to solid surface.	
Anion	-	A negatively charged ion.	
Aqueous species	-	A single element or combination of elements in solution in water. The element or combination of elements may be neutrally charged, negatively charged or positively charged.	
Aquifer	-	A rock formation or sediment layer that is water-bearing and permeable.	
Cation	-	A positively charged ion.	
Cation Exchange Capacity	CEC	A measure of how many aqueous cations can be retained on the negatively charged surfaces of solid phases. Usually measured in either milli-equivalents/100 gramme (meq/100 g) or centi-mole charge/kilogramme (cmolc/kg).	
Clay		Soft, unconsolidated sediment consisting predominantly of clay minerals (> 75%) and with grain size < 2 μm.	Ton
Complexation	-	The combination of individual atom groups, ions or molecules to create one large ion or molecule.	
Gravel	-	Unconsolidated sediment with grain size 2 mm to 64 mm.	
Groundwater	-	Water below the ground surface that is free to flow by advection, provided that a head gradient exists to drive flow.	
High Level Waste	HLW	High-level radioactive waste	
Isotherm	-	The relationship between the concentration of an element in aqueous solution (the sorbate) and the concentration of the element on the surfaces of a solid (the sorbent) at equilibrium. In this report the relationship is a linear one, represented by a simple ratio of the elements concentration on the solid phase to its concentration in the aqueous phase.	
Intermediate Level Waste	ILW	Intermediate-level radioactive waste	

Term	Abbr.	Definition	German
Karst	-	A landscape with distinctive hydrology and landforms that arise when the underlying rock is particularly soluble (in the present report this refers to limestone).	
Low Level Waste	LLW	Low-level radioactive waste	
Porewater	-	Water within the pores of rocks or sediments. In fine grained rocks and compacted sediment it is water mainly bound to the solid phases present, in which case the water moves only by diffusion through connected micropores.	
Sand	-	Unconsolidated sediment with grain size 62 μm to 2 mm.	
Sediment	-	Unconsolidated granular material that has been transported by and deposited from moving water or air.	
Silt	-	Unconsolidated sediment with grain size 4 μm to 62 μm.	
Soil	-	Unconsolidated material composed of minerals, organic matter, living organisms, gas, and water.	
Sorbate	-	Here, a chemical species that becomes attached to solid surfaces of a sorbent, or which is attracted to the solid surfaces of the sorbent and remains in the close proximity thereof.	
Sorbent	-	Here, a solid that has surfaces onto which aqueous species may become attached or to which aqueous species are attracted and remain in the close proximity thereof.	
Surface complexation	-	Here, sorption by means of chemical bonding between an aqueous species and a site at the surface of a solid phase.	
Sorption	-	Here, removal of a compound from solution by attachment to a solid phase, or by being held by electrostatic forces in close proximity to the solid phase.	
Thermodynamic database	-	A database of thermodynamic data that describe equilibria between different chemical species and phases. A thermodynamic database is used to support geochemical calculations.	

App. A: Summary compilation of K_d values

This appendix presents the compiled K_d values obtained from published literature in Tab. A-1. The references given in this table are listed below the table.

Tab. A-1: Compilation of published K_d values

Element	Data Source	Material/ environment	Values (L/kg)	Notes
Ac	Andra (2005)	Callovo-Oxfordian Clay (COx)	5.0E+04	Reference value
	Bradbury & Baeyens (2003)	Opalinus Clay (Am data) (ref pH 7.24, same value used for bounding pH values of 6.3 and 7.8)	pH 7.24 (ref): 1.7E+04; pH 6.3: 1.2E+03; pH 7.8: 6.3E+04	Values for reference pH and bounding pH
	IAEA (2010)	All Soils	1.7E+03 (4.5E+02 to 5.4E+03)	GM, range
	IAEA (2010)	Mineral soils	1.2E+03 (4.5E+02 to 2.4E+03)	GM, range
	IAEA (2010)	Organic soils	5.40E+03	n = 1
	Gil-García et al. (2009)	Sand soil	4.50E+02	n = 1
	Gil-García et al. (2009)	Loam soil	1.50E+03	n = 1
	Gil-García et al. (2009)	Clay soil	2.40E+03	n = 1
	Kaplan (2016)	Sandy sediment (trivalent cation group value)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (trivalent cation group value)	9.0E+03	Best estimate
	Krupka et al. (2004)	Sand sequence (Am data cited)	3.0E+02 (6.0E+01 to 1.3E+03)	Best estimate, range
	Sakamoto et al. (2002)	Japanese soils pH 6.5 to 7.9	6.0E+03 to 1.8E+04	Range
Ag	Gil-García et al. (2009)	All soils	3.8E+02 (3.6E+01 to 1.5E+04)	GM, range
	Gil-García et al. (2009)	Sand soil	1.3E+02 (3.6E+01 to 7.0E+02)	GM, range
	Gil-García et al. (2009)	Loam sol	1.2E+02	n = 1
	Gil-García et al. (2009)	Clay Soil	1.8E+02	n = 1
	IAEA (2010)	All Soils	3.8E+02 (3.6E+01 to 1.5E+04)	GM, range
	IAEA (2010)	Mineral soils	1.4E+02 (3.6E+01 to 7.0E+02)	GM, range
	IAEA (2010)	Organic soils	9.7E+03 (4.4E+03 to 1.5E+04)	GM, range
	Kaplan (2016)	Sandy sediment (SRS data 10.6 ± 2.5 L/kg)	1.0E+01	Best estimate
	Kaplan (2016)	Clayey sediment (SRS data 33.8 ± 13 L/kg)	3.0E+01	Best estimate
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	2.6E+03 (GM); 2.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	2.1E+03 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	8.0E+02 (GM); 3.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	2.9E+03 (GM); 2.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Kyziol-Kominska et al. (2020)	Montmorillonite	7.0E+02	Estimated from experimental Langmuir isotherms
	Kyziol-Kominska et al. (2020)	Kaolinite	4.0E+01	Estimated from experimental Langmuir isotherms
	Kyziol-Kominska et al. (2020)	Ferrihydrite	1.5E+03	Estimated from experimental Langmuir isotherms
	USEPA (2005)	Ag (I) soil/soil water	4.0E+02 (1.0E+01 to 3.2E+04)	Mean, range
Al	Kaplan (2016)	Sandy sediment (Crapse et al.2004)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (Crapse et al. 2004)	1.0E+03	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	2.6E+03 to 1.1E+04 (GM 4.3E+03)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	5.4E+03 (GM); 2.6E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	3.4E+05 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.5E+05 (GM); 1E+04 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	6.4E+03(GM); 1.4E+03 (GSD)	GM, GSD (variation in soil depths)
Am	Andra (2005)	Callovo-Oxfordian (COx) clay	5.0E+04	Reference value
	Bradbury & Baeyens (2003)	Opalinus Clay (ref pH 7.24, same value used for bounding pH values of 6.3 and 7.8)	pH 7.24: 1.7E+04; pH 6.3: 1.2E+03; pH 7.8: 6.3E+04	Values for reference pH and bounding pH
	IAEA (2010)	All soils	2.6E+03 (5.0E+01 to 1.1E+05)	GM, range
	IAEA (2010)	Sand soil	1.0E+03 (6.7E+01 to 3.7E+04)	GM, range
	IAEA (2010)	Loam and clay soil	4.3E+03 (5.0E+01 to 4.8E+04)	GM, range
	IAEA (2010)	Organic soil (pH 3 – 5), ≥ 20% organic matter	2.5E+03 (2.1E+02 to 1.1E+05)	GM, range
	Kaplan (2016)	Sandy sediment (SRS trivalent ion data, Ce Eu)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (SRS trivalent ion data, Ce Eu)	9.0E+03	Best estimate
	Krupka et al. (2004) (citing Routson et al. 1977, Sheppard et al. 1976)	Sand sequence (Hanford)	3E+02 (6.0E+01 to 1.3E+03)	Best estimate (range)
	Linklater et al. (2003) (citing Higgo 1988)	Sandstone	4.4E+02 to 5.8E+02	Range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Linklater et al. (2003) (citing Berry et al. 1987)	Darley Dale Sandstone	6.6E+02 to 1.2E+04	Range
	Ramírez-Guinart et al. (2020b)	Organic soil (Am + analogue data)	4.5E+03 (GM); 2.7E+00 (GSD); 1.3E+03 (5th); 1.5E+04 (95th)	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020b)	Mineral soil: clay (Am + analogue data)	5.6E+04 (GM); 5.7E+00 (GSD); 2.8E+02 (5th); 3.9E+05 (95th)	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020b)	Mineral soil: loam (Am + analogue data)	1.9E+04 (GM); 3.4E+00 (GSD); 2.7E+03 (5th); 9.1E+04 (95th)	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020b)	Mineral soil: sand (Am + analogue data)	4.9E+03 (GM); 5.1E+00 (GSD); 2.2E+02 (5th); 3.7E+04 (95th)	GM, GSD, 5th and 95th centiles
	Rumynin & Nikulenkov (2014)	Quaternary sediments (sandy loam sediment/soil)	3.0E+04 (1.2E+04 to 7.7E+04)	Mean, range
C	Bradbury & Baeyens (2003)	Opalinus Clay (C-14, considering isotopic exchange)	pH 7.24: 1.6E+00; pH 6.3: 1.3E-01; pH 7.8: 6.0E+00	Values for reference pH and bounding pH
	Kaplan (2016)	Sandy sediment (SRS data, carbonate mineral solubility not expected to control concentration K_d = 8.6 L/kg after 6 months, noting slow sorption kinetics)	1.0E+01	Best estimate
	Kaplan (2016)	Clayey sediment (SRS data, carbonate mineral solubility not expected to control concentration K_d = 372 L/kg after 6 month, noting slow sorption kinetics)	4.0E+02	Best estimate
	Krupka et al. (2004)	Sand sequence (C-14)	5.0E+00 (5.0E-01 to 1.0E+03)	Best estimate, range
Ca	Bradbury & Baeyens (2003)	Opalinus Clay (ref pH 7.24, same value used for bounding pH values of 6.3 and 7.8)	pH 7.24: 1.1E+00; pH 6.3: 9.3E-01; pH 7.8: 1.1E+00	
	IAEA (2010)	All soils	8.0E+00 (7.0E-01 to 1.1E+02)	GM, range
	IAEA (2010)	Mineral soils	7.0E+00 (7.0E-01 to 8.9E+01)	GM, range
	IAEA (2010)	Organic soils	1.1E+02	n = 1
	Kaplan (2016)	Sandy sediment (Ca grouped with Sr)	5.0E+00	Best estimate
	Kaplan (2016)	Clayey sediment (Ca grouped with Sr)	2.0E+01	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	1.3E+02 (2.4E+01 to 4.6E+02)	GM, range
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	4.4E+01 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Sheppard et al. (2011)	Clay till (pH 8.1)	2.6E+02 (GM); 2.5E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.8E+02 (GM); 3.2E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	2.4E+02 (GM); 2.0E+03 (GSD)	GM, GSD (variation in soil depths)
Cf	Kaplan (2016)	Sandy sediment (trivalent cation group value)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (trivalent cation group value)	9.0E+03	Best estimate
Cl	Bradbury & Baeyens (2003)	Opalinus Clay	0.0E+00	Reference value
	Gil-García et al. (2009)	All soil	3.0E-01 (4.0E-02 to 1.2E+00)	GM, range
	Gil-García et al. (2009)	Sand soil	5.0E-01 (1.0E-01 to 1.1E+00)	GM, range
	Gil-García et al. (2009)	Loam soil	4.0E-01 (4.0E-02 to 9.0E-01)	GM, range
	Gil-García et al. (2009)	Clay Soil	2.0E-01 (6.0E-02 to 9.0E-01)	GM, range
	Gil-García et al. (2009)	Organic Soil	1.0E-01 to 1.2E+00	Range, n = 2
	Heuel-Fabianek (2014)	Sand soil	8.0E-01	Reference value
	Heuel-Fabianek (2014)	Silt soil	2.5E-01	Reference value
	Heuel-Fabianek (2014)	Clay Soil	4.4E+00	Reference value
	Heuel-Fabianek (2014)	Organic soil	1.1E+01	Reference value
	IAEA (2010)	soil	3.0E-01 (4.0E-02 to 1.2E+00)	GM, range
	Krupka et al. (2004)	Sand sequence (Cl specific data not cited, expected to behave as dissolved anionic species)	0.0E+00 (0.0+00 to 6.0E-01)	Best estimate, range
	Kaplan (2016)	Sandy sediment	1.0E+00	Best estimate, based on measurements
	Kaplan (2016)	Clayey sediment	8.0E+00	Best estimate, based on measurements
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments (native Cl)	3.6E-02 to 4.1E+01 (5.2E+00)	Range, GM
	Söderlund et al. (2011) (citing Sheppard et al. 2004)	Organic litter	8.3E+01 to 5.7E+03 (2.0E+03)	Range, GM
	Söderlund et al. (2011) (citing Sheppard et al. 2006)	Organic soil	1.1E+01	Discrete value
	Söderlund et al. (2011) (citing IAEA 2009)	Organic soil	1.5E+02	GM
	Söderlund et al. (2011) (citing Kashparov 2005)	Organic soil (Ukraine)	1.2E+00	Discrete value
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Organic soil	7.0E-01	Mean
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Clay	2.0E-01	GM

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Loam	4.0E-01	Discrete value
	Söderlund et al. (2011) (citing Sheppard et al. 2006)	Loam	4.0E-01	Discrete value
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Sand	5.0E-01	GM
	Söderlund et al. (2011) (citing Sheppard et al. 2006)	Sand soil	8.0E-01	Discrete value
	Söderlund et al. (2011) (citing Kashparov et al. 2005)	Mineral soil (Ukraine)	0.0E+00	Discrete value
	Söderlund et al. (2011) (citing IAEA 2009)	Mineral soil	1.4E+00	GM
Cm	Andra (2005)	Callovo-Oxfordian Clay (COx)	5.0E+04	Reference value
	Bradbury & Baeyens (2003)	Opalinus Clay (Am data)	pH 7.24 (ref): 1.7E+04; pH 6.3: 1.2E+03; pH 7.8: 6.3E+04	Values for reference pH and bounding pH
	Gil-García et al. (2009)	All soil	9.3E+03 (1.9E+02 to 5.2E+04)	GM, range
	Gil-García et al. (2009)	Sand soil	3.4E+03 (1.9E+02 to 3.1E+04)	GM, range
	Gil-García et al. (2009)	Loam soil	1.9E+04 (6.8E+03 to 5.2E+04)	GM, range
	Gil-García et al. (2009)	Clay Soil	5.4E+03	n = 1
	Gil-García et al. (2009)	Organic Soil	7.4E+03 (5.1E+03 to 1.2E+04)	GM, range
	IAEA (2010)	All soils	9.3E+03 (1.9E+02 to 5.2E+04)	GM, range
	Kaplan (2016)	Sandy sediment (trivalent ions grouped together, Ce and Eu data cited, Cm specific data not considered)	1.0E+03	
	Kaplan (2016)	Clayey sediment (trivalent ions grouped together, Ce and Eu data cited, Cm specific data not considered)	9.0E+03	
	Krupka et al. (2004)	Sand sequence (Am data cited)	3.0E+02 (6.0E+01 to 1.3E+03)	Best estimate, range
Co	Kaplan (2016)	Sandy sediment	4.0E+01	Best estimate
	Kaplan (2016)	Clayey sediment	1.0E+02	Best estimate
	Krupka and Serne (2002) (citing Gee and Campbell,1980)	Sandy sediment, low % clay and silt, synthetic groundwater	2.75E+03 to 1.11E+04 (4.23E+03)	Range (GM)
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	1.0E+02 to 1.1E+03 (5.0E+02)	Range (GM) (variation in sample depth)
	Sheppard et al. (2011)	Clay till (pH 8.1)	1.3E+04 to 4.2E+04 (2.2E+04)	Range (GM) (variation in sample depth)

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	5.6E+02 to 1.9E+05 (2.0E+04)	Range (GM) (variation in sample depth)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	6.0E+02 to 4.0E+03 (1.5E+03)	Range (GM) (variation in sample depth)
Cs	Bradbury & Baeyens (2003)	Opalinus Clay	5.5E+02	Values for ref pH and pH range
	Bugai et al. (2019)	Sand (Chernobyl Exclusion Zone)	2.7E+01 to 1.1E+03	Range
	Bugai et al. (2019)	Loam/clay (Chernobyl Exclusion Zone)	2.1E+02 to 8.3E+03	Range
	IAEA (2010)	All soils	1.2E+03 (4.3E+00 to 3.8E+05)	GM, range
	IAEA (2010)	Sand soil (pH 3.5 – 6.5), ≥ 65% sand, 18% Organic matter	5.3E+02 (9.6E+00 to 3.5E+04)	GM, range
	IAEA (2010)	Loam and clay soil	3.7E+02 (3.9E+01 to 3.8E+05)	GM, range
	IAEA (2010)	Organic soil (pH 3 – 5), ≥ 20% organic matter	2.7E+02 (4.3E+00 to 9.5E+04)	GM, range
	Kaplan (2016)	Sandy sediment	1.0E+01	Best estimate
	Kaplan (2016)	Clayey sediment	5.0E+01	Best estimate
	Krupka et al. (2004) (citing Routson et al. 1978, Serne et al. 1993)	Sand sequence (Hanford)	2E+03 (5E+02 to 4E+03)	Best estimate (range)
	Kumar et al. (2019) (citing Thibault et al. 1990)	Soil (compiled report)	8.2E+01 to 1.4E+04	Range
	Kumar et al. (2019) (citing Sanchez et al. 2002)	Soil (compiled report)	2.5E+02 to 1.7E+05	Range
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Soil (compiled report)	1E+04 to 1.2E+05	Range
	Kumar et al. (2019) (citing Serne et al. 1993)	Sediment (groundwater)	6.9E+02 to 3.12E+03	Range
	Kumar et al. (2019) (citing Shimada et al. 1996)	Soil (compiled report)	1.0E+01 to 2.0E+03	Range
	Kumar et al. (2019) (citing Mollah & Ullah 1998)	soil (groundwater)	1.278E+03 to 2.156E+03	Range
	Kumar et al. (2019) (citing Gil-García et al. 2009)	Soil (report considering texture organic matter)	4.0E+00 to 3.75E+05	Range
	Linklater et al. (2003) (citing Higgo 1988)	Sandstone	5.1E+01 to 8.9E+3	Range
	Linklater et al. (2003) (citing Berry et al. 1987)	Darley Dale Sandstone	1.1E+01	Discrete value
	Linklater et al. (2003) (citing Stenhouse 1995)	Marl	4E+02 to 6.9E+03	Range
	Ramírez-Guinart et al. (2020a)	Clay + loam (long-term data, > 1 y–) - note shorter term values ~ 1 OM lower (sorption only?)	3.0E+04 (GM); 2.6E+00 (GM); 8.0E+03 (5th); 2.2E+05 (95th)	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020a)	Sand (long-term data, > 1 y)	2.0E+04 (GM); 2.7E+00 (GSD); 3.7E+03 (5th); 9.4E+04 (9th)	GM, GSD, 5th and 95th centiles

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Ramírez-Guinart et al. (2020a)	Organic (> 90%) (long-term data, > 1 y)	3.7E+02 (GM); 2.4E+00 (GSD); 1.1E+02 (5th); 1.6E+03 (95th)	GM, GSD, 5th and 95th centiles
	Rumynin and Nikulenkov (2014)	Quaternary sandy loam sediments/soil	4.0E+03 (1.5E+03 to 7.8E+03)	Mean, range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	2.1E+04 to 1.2E+05 (3.8E+04)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	3E+04 (GM); 3.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	4.6E+05 (GM); 1.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.7E+05 (GM); 3.8E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	4.5E+03 (GM); 2.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Söderlund et al. (2011) (citing Holgersson 2009)	Peat	1.4E+01 to 3.8E+03	Range
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Organic	2.7E+01	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Organic	5.5E+03	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Loam	3.5E+03	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	Sand	5.3E+02	GM
	Söderlund et al. (2011) (citing Kamei-Ishikawa et al. 2008)	Japanese paddy soil (pH 5.8 – 6.8)	2.3E+03 (2.7E+01 to 1.7E+04)	GM?, range
	Söderlund et al. (2011) (citing Kamei-Ishikawa et al. 2008)	Japanese upland soil (pH 5.8 – 6.8)	3.9E+03 (3.6E+01 to 3.6E+04)	GM?, range
	Krupka et al. (1999)	Soil (min to max clay content content)	1.0E+01 to 2.67E+04	Range (geometric mean)
Fe	IAEA (2010)/Gil-García et al. (2009)	All soils	8.8E+02 (2.2E+02 to 4.9E+03)	GM, range
	IAEA (2010)/Gil-García et al. (2009)	Sand soil (pH 3.5 – 6.5), ≥ 65% sand, < 18% Organic matter	3.2E+02 (2.2E+02 to 4.2E+02)	GM, range
	IAEA (2010)/Gil-García et al. (2009)	Loam soil (pH 4 – 6), 2 – 6.5% organic matter	8.9E+02 (2.9E+02 to 2.2E+03)	GM, range
	IAEA (2010)/Gil-García et al. (2009)	Clay soil	1.6E+03 (1.2E+03 to 2.2E+03)	GM, range
	IAEA (2010)/Gil-García et al. (2009)	Organic soil	1.4E+03 (5.2E+02 to 4.9E+03)	GM, range
	JAEA (2021) SDB	Soil (multiple sources)	1.5E+02 to 3.5E+03	Range
	JAEA (2021) SDB	Sandstone (multiple sources)	5.0E+00 to 5.0E+02	Range
	Kaplan (2016)	Sandy sediment (SRS sediment value of 400 ml/g)	2.0E+02	Best estimate

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Kaplan (2016)	Clayey sediment (SRS sediment value of 400 ml/g)	4.0E+02	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	4.9E+03 to 1.6E+05 (GM 2.5E+04)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	8.1E+03 (GM); 5.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	2.6E+05 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.0E+05 (GM); 1.1E+04 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.2E+04 (GM); 19.E+03 (GSD)	GM, GSD (variation in soil depths)
Ho	Bradbury & Baeyens (2003)	Opalinus Clay (Eu analogue)	pH 7.24: 6.0E+04; pH 6.3: 5.0E+03; pH 7.8: 5.0E+04	Values for reference pH and bounding pH
	IAEA (2010)	All soils	9.3E+02 (2.4E+02 to 3.0E+03)	GM, range
	IAEA (2010)	Mineral soil	6.3E+02 (2.4E+02 to 1.3E+03)	GM, range
	IAEA (2010)	Organic soil	3.0E+03	(n = 1)
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	1.8E+03 to 3.7E+04 (GM 7.7E+03)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	1.7E+03 (GM); 2.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	3.7E+04 (GM); 1.2E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	2.1E+04 (GM); 6.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.1E+04 (GM); 1.6E+03 (GSD)	GM, GSD (variation in soil depths)
Hg	Debure et al. (2020)	Albian Tégulines Clay (iron-rich) oxidised	1.0E+02	Reported
	Debure et al. (2020)	Albian Tégulines Clay (iron-rich) reduced	1.2E+03	Reported
	IAEA (2010)	Soil (note that n = 1)	6.3E+03	Discrete value (n = 1)
	Kaplan (2016)	Sandy sediment (SRS site-specific data)	8.0E+02	Best estimate
	Kaplan (2016)	Clayey sediment	1.0E+03	Best estimate
	Lyon et al. (1997)	Hg(II) in soil	3E+03 to 3.5E+04	Range (median)
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	3.3E+03 (GM); 2.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	5.0E+03 (GM); 2.2E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.9E+03 (GM); 2.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.0E+04 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)
	USEPA (2005)	Soil	4E+03 (1.6E+02 to 6.31E+05)	Mean, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
I	IAEA (2010)	All soils	6.9E+00 (1.0E-02 to 5.8E+02)	GM, range
	IAEA (2010)	Mineral soil	7.0E+00 (1.0E-02 to 5.4E+02)	GM, range
	IAEA (2010)	Organic Soil	3.2E+01 (8.5E+00 to 5.8E+02)	GM, range
	IAEA (2010)	OM < 2	2.3E+00 (1.0E-02 to 5.7E+01)	GM, range
	IAEA (2010)	2 ≥ OM < 5	9.1E+00 (6.0E-01 to 5.4E+02)	GM, range
	IAEA (2010)	OM ≥ 5	2.3E+01 (2.0E+00 to 5.8E+02)	GM, range
	Kaplan (2016)	Sandy sediment (SRS data discussed, iodide values noted for three loamy sediments considered between sand and clay, range from 0.5 to 33.7 L/kg; iodate range from 3.5 to 60.9 L/kg).	1.0E+00	Best estimate
	Kaplan (2016)	Clayey sediments (SRS data discussed, noting iodide values for three loamy sediments considered between sand and clay, range from 0.5 to 33.7 L/kg; iodate range from 3.5 to 60.9 L/kg).	3.0E+00	Best estimate
	Krupka et al. (2004)	Sand sequence (based on Hanford site data)	2.5E-01 (0.0E+00 to 1.5E+01)	Best estimate, range
	Linklater et al. (2003) (citing Higgo 1988)	Argillite (oxic)	2.0E+00 to 6.0E+00	Range
	Linklater et al. (2003) (citing Stenhouse 1995)	Sediments (oxic)	1.0E-01 to 4.0E+01	Range
	Linklater et al. (2003) (citing Fukui et al. 1996)	Soil (I^-)	6.0E-01 to 2.5E+00	Range
	Linklater et al. (2003) (citing Fukui et al. 1996)	Soil (IO_3^-)	8.0E-01 to 2.0E+01	Range
	Yuanfang & von Gunten (1988)	Argillaceous rock formations at Wellenberg (excluding Valanginian Marl)	3.0E-01 to 1.0E+00	Range
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	2.4E+02 (GM); 2.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	2.3E+02 (GM); 1.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.5E+02 (GM); 2.2E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	3.3E+02 (GM); 1.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Söderlund et al. (2011) (citing Bird & Schwartz 1996)	I^-, organic sediment anoxic conditions	3.0E+01	Discrete value

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Söderlund et al. (2011) (citing Bird & Schwartz 1996)	IO_3^-, organic sediment, oxic conditions	4.6E+01	Discrete value
	Söderlund et al. (2011) (citing Vidal et al. 2009)	I^-, organic sediment	3.6E+01	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	IO_3^-, organic sediment	7.7E+00	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	I^- clay	6.8E+00	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	I^- loam soil	6.5E+00	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	IO_3^-, loam soil	8.9E+00	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	I^-, sand	3.6E+00	GM
	Söderlund et al. (2011) (citing Vidal et al. 2009)	IO_3^-, sand	3.6E+00	GM
	Söderlund et al. (2011) (citing Holgersson 2009)	I^- clay (Sweden)	0.0E+00 to 1.9E+01	Range
	Söderlund et al. (2011) (citing Holgersson 2009)	Peat (Sweden)	0.0E+00 to 3.8E+01	Range
	Söderlund et al. (2011) (citing IAEA 2009)	I^- clay soil	1.1E+01	GM
	Söderlund et al. (2011) (citing Sheppard et al. 2009)	Simpevarp Clay gyttja	2.9E+00 to 8.8E+00	Range
Mo	Bradbury & Baeyens (2003)	Opalinus Clay (Mo[VI]) (ref pH 7.24, same value used for bounding pH values of 6.3 and 7.8)	pH 7.24: 1.7E+01; pH 6.3: 3.2E+01; pH 7.8: 1.2E+01	Values for reference pH and bounding pH
	IAEA (2010)	All soils	4.0E+01 (7.0E+00 to 1.3E+02)	GM, range
	Kaplan (2016)	Sandy sediments (considered with Nb, Se, Te)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediments (considered with Nb, Se, Te)	1.0E+03	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	7.0E+01 to 6.8E+03 (8.1E+02)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	5.1E+03 (GM); 3.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	1.3E+02 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	2.1E+02 (GMN); 2.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	4.8E+02 (GM); 2.1E+03 (GSD)	GM, GSD (variation in soil depths)
	USEPA (2005)	Soil Mo(VI)	2.0E+01 (4.0E-01 to 5.0E+02)	Mean, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
Nb	Bradbury & Baeyens (2003)	Opalinus clay 4 m^3/kg based on lower values reported for sediments (data from Legoux et al. 1992)	4.00E+03	Best estimate
	Gil-García et al. (2009) (see IAEA 2010)	All soil	1.5E+03 (1.6E+02 to 8.4E+03)	GM, range
	Gil-García et al. (2009)	Sand soil	1.6E+02 to 1.9E+02	Range
	Gil-García et al. (2009)	Loam soil	2.5E+03 (5.4E+02 to 8.4E+03)	GM, range
	Gil-García et al. (2009)	Clay Soil	2.4E+03 (9.0E+02 to 4.7E+03)	
	Gil-García et al. (2009)	Organic Soil	2.0E+03	n = 1
	IAEA (2010)	All soils	1.5E+03 (1.6E+02 to 8.4E+03)	GM, range
	IAEA (2010)	Sand soil	1.7E+02 (1.6E+02 to 1.9E+02)	Arithmetic mean (n = 2), range
	IAEA (2010)	Loam + clay soil	2.5E+03 (5.4E+02 to 8.4E+03)	GM, range
	IAEA (2010)	Organic Soil	2.0E+03	n = 1
	Kaplan (2016)	Sandy and clayey sediment, based on sorption of selenate to SRS soil, lack of data noted as well as complexity of speciation and variability in data (citing Söderlund et al. 2015)	1.00E+03	Best estimate
	Linklater et al. (2003) (citing Higgo 1988)	Clayey sand (Swiss data)	1.0E+01 to 3.6E+03	Range
	Linklater et al. (2003) (citing Higgo 1987)	Marine sediment	1.0E+03 to 1.0E+06	Range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	1.7E+03 to 1.4E+04 (1.0E+04)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, pH 4.8)	1.2E+04 (GM); 4.3E+03 (GSD)	GM, GSD
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	6.7E+04 (GM); 1.4E+03 (GSD)	GM, GSD
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	3.1E+04 (GM); 6.4E+03 (GSD)	GM, GSD
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	4.1E+03 (GM); 1.4E+03 GSD)	GM, GSD
Ni	Bradbury & Baeyens (2003)	Opalinus Clay	pH 7.24: 9.3E+02; pH 6.3: 2.9E+02; pH 7.8: 1.9E+03	Values for reference pH and bounding pH
	Gil-García et al. (2009) (see IAEA 2010)	All soils	2.8E+02 (3.0E+00 to 7.3E+03)	GM, range
	Gil-García et al. (2009)	Sand soil	1.3E+02 (3.0E+00 to 7.3E+03)	GM, range
	Gil-García et al. (2009)	Loam soil	1.8E+02 (8.0E+00 to 1.2E+03)	GM, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Gil-García et al. (2009)	Clay soil	9.3E+02 (2.5E+2 to 3.2E+03)	GM, range
	Gil-García et al. (2009)	Organic soil	1.1E+03 (4.1E+2 to 5.0E+03)	GM, range
	IAEA (2010)	All soils	2.8E+02 (3.0E+00 to 7.2E+03)	GM, range
	IAEA (2010)	Sand + Loam soil	1.4E+02 (3.0E+00 to 7.2E+03)	GM, range
	IAEA (2010)	Clay + Organic soil	9.8E+02 (2.5E+02 to 5.0E+03)	GM, range
	IAEA (2010)	pH < 5	1.4E+01 (3.0E+00 to 4.8E+01)	GM, range
	IAEA (2010)	5 ≤ pH < 6.5	5.8E+01 (7.0E+00 to 1.1E+03)	GM, range
	IAEA (2010)	pH ≥ 6.5	8.2E+02 (4.0E+01 to 7.2E+03)	GM, range
	Kaplan (2016)	Sandy sediment (SRS sandy sediment Ni K_d = 7 ± 2 mL/g at pH 5.3)	7.0E+00	Best estimate
	Kaplan (2016)	Clayey sediment (SRS clayey sediment Ni K_d = 30 ± 1 mL/g at pH 5.3)	3.0E+01	Best estimate
	Krupka et al. (2004) (citing Serne et al. 1993, Serne & Relyea 1981)	Sand sequence (Hanford)	3.0E+02 (5.0E+01 to 2.5E+03)	Best estimate (range)
	Linklater et al. (2003) (citing Berry et al. 1990)	St Bees Sandstone	1.8E+03 to 4.2E+03	Range
	Linklater et al. (2003) (citing Berry et al. 1990)	Eden Shale	4.0E+03 to 6.1E+03	Range
	Linklater et al. (2003) (citing Berry et al. 1990)	Fulbeck Clay (mudrock)	1.1E+03 to 3.3E+03	Range
	Linklater et al. (2003) (citing Berry et al. 1988b)	Elstow Clay (mudrock)	1.3E+03 to 2.5E+03	Range
	Linklater et al. (2003) (citing Berry et al. 1988b)	Killingholme Clay	7E+02 to 1.7E+03	Range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	4.5E+02 to 3.8E+03 (GM 9.8E+02)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	4.6E+02 (GM); 1.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	4.5E+03 (GM); 1.6E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	5.1E+03 (GM); 4.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.8E+03 (GM); 1.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Allison & Allison (2005)	Soil	7.9E+02, (1.0E+01 to 6.3E+03)	Mean, range
	Usman (2008)	Egyptian soil	7.9E+00 to 3.8E+02	Range of soils supported my mineralogical analysis

Element	Data Source	Material/ environment	Values (L/kg)	Notes
Np	Bradbury & Baeyens (2003)	Opalinus Clay (Th analogue)	pH 7.24 to 7.8: 5.5E+04; pH 6.3 2.2E+04	Values for reference pH and bounding pH
	Gil-García et al. (2009)	All soils	3.6E+01 (1.3E+00 to 1.2E+03)	GM, range
	Gil-García et al. (2009)	Sand soil	1.4E+01 (3.0E+00 to 1.1E+02)	GM, range
	Gil-García et al. (2009)	Loam soil	2.3E+01 (1.3E+00 to 1.2E+02)	GM, range
	Gil-García et al. (2009)	Clay soil	2.0E+01 to 5.5E+01	Range
	Gil-García et al. (2009)	Organic soil	8.1E+02 (5.0E+02 to 1.2E+03)	GM, range
	IAEA (2010)	All soils	3.5E+01 (1.3E+00 to 1.2E+03)	GM. Range
	IAEA (2010)	Mineral soil	2.0E+01 (1.3E+00 to 1.2E+02)	GM. Range
	IAEA (2010)	Organic soil	8.1E+02 (5.0E+02 to 1.2E+03)	GM. Range
	Kaplan (2016)	Sandy sediment (SRS specific data 4.26 ± 0.24 L/kg) Np considered mostly as Np(V) with little tendency to reduce even under most strongly reducing conditions expected.	3.0E+00	Best estimate
	Kaplan (2016)	Clayey sediment (SRS data: 9.05 ± 0.61 L/kg). Np considered mostly as Np(V) with little tendency to reduce even under most strongly reducing conditions expected	9.0E+00	Best estimate
	Linklater et al. (2003) (citing Berry et al. 1987)	Darley Dale Sandstone (aerobic conditions)	1.0E+01 to 3.4E+01	Range
	Linklater et al. (2003) (citing Higgo 1988)	Sandstone (Rockwell International Lab.) (anaerobic cond.)	1.9E+03 to 3.0E+03	Range
	Linklater et al. (2003) (Berry et al. 1990)	Mercia Mudstone (anaerobic cond.)	1.4E+02 to 3.1E+03	Range
Pa	Gil-García et al. (2009)	All soils	2.0E+03 (5.4E+02 to 6.6E+03)	GM, range
	Gil-García et al. (2009)	Sand soil	5.4E+02	n = 1
	Gil-García et al. (2009)	Loam soil	1.8E+03	n = 1
	Gil-García et al. (2009)	Clay soil	2.7E+03	n = 1
	Gil-García et al. (2009)	Organic soil	6.6E+03	n = 1
	Andra (2005)	Callovo-Oxfordian Clay (COx)	1.0E+03	Reference value
	Bradbury & Baeyens (2003)	Opalinus Clay (based on London Clay data from Berry et al. 1988a)	5.0E+03	Values for reference pH and bounding pH
	IAEA (2010)	All soils	2.0E+03 (5.4E+02 to 6.6E+03)	GM, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	IAEA (2010)	Mineral soil	1.4E+03 (5.4E+02 to 2.7E+03)	GM, range
	IAEA (2010)	Organic soil	6.6E+03	n = 1
	Kaplan (2016)	Sandy sediment (Pa grouped with Np(V))	3.0E+00	Best estimate
	Kaplan (2016)	Clayey sediment (Pa grouped with Np(V))	9.0E+00	Best estimate
	Sakamoto et al. (2002)	Japanese soils pH 6.2 to 8.9	7.0E+02 to 5.2E+04	Range
Pb	Andra (2005)	Callovo-Oxfordian (COx) clay	1.6E+02	Range
	Bradbury & Baeyens (2003)	Opalinus clay	pH 7.24: 2.7E+03; pH 6.3: 8E+02; pH 7.8: 6.7E+03	Values for reference pH and bounding pH
	IAEA (2010)	All soils	2E+03 (2.5E+01 to 1.3E+05)	GM, range
	IAEA (2010)	Sand Soil	2.2E+02 (2.5E+01 to 1.3E+03)	GM, range
	IAEA (2010)	Loam + Clay soil	1.3E+04 (3.6E+03 to 1.3E+05)	GM, range
	IAEA (2010)	Organic Soil	2.5E+03 (8.8E+02 to 1E+04)	GM, range
	Krupka et al. (2004) (citing Rhoads et al. 1994)	Sand sequence (Hanford)	1.0E+04 (8.0E+03 to 8.0E+04)	Best estimate (range)
	Kaplan (2016)	Sandy sediment (based on measurements below solubility limit)	2.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (based on measurements below solubility limit)	5.0E+03	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	2E+03 to 4.4E+04 (GM 9.6E+03)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	4.5E+03 (GM); 2.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till (pH 8.1)	1.5E+05 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	4.8E+04 (GM); 7.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.9E+04 (GM); 1.9E+03 (GSD)	GM, GSD (variation in soil depths)
	USEPA (2005)	Soil	5.0E+03 (5.0E+00 to 1.0E+05)	Mean, range
	Usman (2008)	Egyptian soils	1.09E+02 to 4.61E+02	Range
	Vandenhove et al. (2009)	all soils	2.1E+03 (GM); 1E+01(GSD), 2.5E+01 to 1.28E+05	GM, GSD, range
	Vandenhove et al. (2009)	Sand soil	2.2E+02 (GM); 4.0E+00 (GSD); 2.5E+01 to 1.35E+03	GM, GSD, range
	Vandenhove et al. (2009)	Loam soil	1.0E+04 (GM); 3.0E+00 (GSD); 3.6E+03 to 4.3E+04	GM, GSD, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Vandenhove et al. (2009)	Clay soil	5.4E+03 to 1.28E+05	GM, GSD, range
	Vandenhove et al. (2009)	Organic soil	2.5E+03 (GM); 3.0E+00 (GSD); 8.8E+02 to 1.03E+05	GM, GSD, range
Pd	Gil-García et al. (2009)	All soils	1.8E+02 (5.5E+01 to 6.7E+02)	GM, range
	Gil-García et al. (2009)	Sand soil	5.5E+01 to 1.3E+02	Range
	Gil-García et al. (2009)	Loam soil	1.8E+02	n = 1
	Gil-García et al. (2009)	Clay soil	2.7E+02	n = 1
	Gil-García et al. (2009)	Organic soil	6.7E+02	n = 1
	Bradbury & Baeyens (2003) (Pb analogue)	Opalinus clay (based on sorption data for Pb, noting that Pd sorption likely to be stronger still)	5.0E+03	Values for reference pH and bounding pH
	IAEA (2010)	All soils	1.8E+02 (5.5E+01 to 6.7E+02)	GM, range
	IAEA (2010)	Mineral soil	1.4E+02 (5.5E+01 to 2.7E+02)	GM, range
	IAEA (2010)	Organic soil	6.7E+02	n = 1
	Kaplan (2016) (Ni analogue)	Sandy sediment (SRS sandy sediment Ni K_d = 7 ± 2 mL/g at pH 5.3)	7.0E+00	Best estimate
	Kaplan (2016) (Ni analogue)	Clayey sediment (SRS clayey sediment Ni K_d = 30 ± 1 mL/g at pH 5.3)	3.0E+01	Best estimate
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	4.3E+02, 9.6E+02 (n = 2)	n = 2
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	4.6E+03 (n =1)	n = 1
Po	Bradbury & Baeyens (2003)	Opalinus Clay (SeO_3^{2-} used as analogue for PoO_3^{2-})	pH 7.24: 1.8E+02; pH 6.3: 7.0E+01; pH 7.8: 2.8E+02	Values for reference pH and bounding pH
	IAEA (2010)	All soils	2.1E+02 (1.2E+01 to 7.0E+03)	GM, range
	IAEA (2010)	Mineral soil	1.9E+02 (1.2E+01 to 7.0E+03)	GM, range
	IAEA (2010)	Organic soil	6.6E+03	n = 1
	Kaplan (2016)	Sandy soil (grouped as divalent soft metal along with Pb and Sn). Pb data cited.	2.0E+03	Best estimate
	Kaplan (2016)	Clay soil (grouped as divalent soft metal along with Pb and Sn). Pb data cited.	5.0E+03	Best estimate
	Maity et al. (2011)	Soil (in the vicinity of a uranium mine in Taiwan)	1.4E+04 to 7.5E+03	Range
	Vandenhove et al. (2009)	All soils	1.8E+02 (1.2E+01 to 7.0E+03)	GM, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Vandenhove et al. (2009)	Sand soil	1.0E+02 (1.7E+01 to 7.0E+03)	GM, range
	Vandenhove et al. (2009)	Loam soil	2.3E+02 (1.2E+01 to 1.8E+03)	GM, range
Pu	Andra (2005)	Callovo-Oxfordian (COx) clay	9.0E+02	Reference value
	Bradbury & Baeyens (2003)	Opalinus clay, Pu(III) expected, Am(III) used an analogue	pH 7.24: 2.26E+04; pH 6.3: 1.1E+03; pH 7.8: 7.52E+04	Values for reference pH and bounding pH
	Bugai et al. (2019)	Sand *batch data* (Chernobyl Exclusion Zone)	5.0E+01 to 6.7E+02	Range
	Bugai et al. (2019)	Sand *in situ data* (Chernobyl Exclusion Zone)	7.0E+00 to 4.7E+02	Range
	Bugai et al. (2019)	Loam/clay *batch data* (based on data from Chernobyl Exclusion Zone)	2E+02 to 6.1E+03	Range
	IAEA (2010)	All soils	7.4E+02 (3.2E+01 to 9.6E+03)	Geometric mean and range
	IAEA (2010)	Sand soil	4E+02 (3.3E+01 to 6.9E+03)	Geometric mean and range
	IAEA (2010)	Loam + Clay soil	1.1E+03 (1E+02 to 9.6E+03)	Geometric mean and range
	IAEA (2010)	Organic soil	7.6E+02 (9.0E+01 to 3.0E+03)	Geometric mean and range
	Kaplan (2016)	Sandy sediment (best estimate based on SRS data, Pu IV)	7.0E+02	Best estimate
	Kaplan (2016)	Clayey sediment best estimate based on SRS data, Pu IV)	6.0E+03	Best estimate
	Krupka et al. (2004) (citing Rhoads et al. 1994)	Sand sequence (Hanford) (PuV, VI)	1.5E+02 (5.0E+01 to 2.0E+03)	Best estimate (range)
	Linklater et al. (2003) (citing Bond & Linklater 2001)	Sherwood Sandstone (sandstone and shale)	1.0E+04 to 1.6E+05	Range
	Linklater et al. (2003) (citing Bond & Linklater 2001)	Borrowdale Volcanic Group (different material to soil/sediment, but referenced because provides an example of very high Pu sorption)	1.0+06	Best estimate
	Linklater et al. (2003) (citing Higgo 1987)	Sandstone (non-reducing) (Rockwell International Laboratory data)	8.1E+01 to 5.2E+02	Range
	Linklater et al. (2003) (citing Higgo 1987)	Sandstone (reducing) (Rockwell International Laboratory data)	4.15E+02 to 2.97E+03	Range
	Rumynin & Nikulenkov (2014)	Quaternary sediments (sandy loam sediment/soil)	1.9E+04 (3.0E+03 to 3.9E+04)	Mean, range
Ra	Andra (2005)	Callovo-Oxfordian Clay (COx)	1.0E+03	Reference values

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Bradbury & Baeyens (2003)	Opalinus Clay (Sr analogue)	pH 7.24: 7.6E-01; pH 6.3: 6.9E-01; pH 7.8: 7.6E-01	Values for reference pH and bounding pH
	IAEA (2010)	All soils	2.5E+03 (1.2E+01 to 9.5E+05)	GM, range
	IAEA (2010)	Sand + Loam	1.9E+03 (1.2E+01 to 1.2E+05)	GM, range
	IAEA (2010)	Clay soil	3.8E+04 (7.0E+02 to 9.5E+05)	GM, range
	IAEA (2010)	Organic soil	1.3E+03 (2.0E+02 to 2.4E+03)	GM, range
	Kaplan (2016)	Sandy sediment (SRS site-specific data 30 ± 0.3 L/kg)	3.0E+01	Best estimate
	Kaplan (2016)	Clayey sediment (SRS site-specific data 185 ± 26 L/kg)	2.0E+02	Best estimate
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Sand soil	5.7E+01 to 2.1E+04	Range
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Silty soil	1.26E+03 to 5.3E+05	Range
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Clayey soil	6.96E+02 to 5.6E+04	Range
	Kumar et al. (2019) (citing Sakamoto et al. 2000)	Sandy soil	1.9E+02 to 2.3E+04	Range
	Kumar et al. (2019) (citing Sakamoto et al. 2000)	Loamy soil	2.8E+02 to 1.2E+04	Range
	Kumar et al. (2019) (citing Sheppard et al. 2006)	Soil	3.0E+01 to 2.0E+02	Range
	Kumar et al. (2019) citing (IAEA 2009)	Soil	1.1E+03 to 3.8E+04	Range
	Kumar et al. (2019) (citing Meier et al. 1994)	Sandy sediment (pH 6 – 9)	6.7E+00 to 2.6E+01	Range
	Linklater et al. (2003) (citing Berry et al. 1991, Baston et al. 1993]	London Clay	1.4E+02 to 3.6E+03	Range
	Linklater et al. (2003) (citing Bond and Linklater 2001]	Sherwood Sandstone Group (sandstone + shale)	8.0E+00 to 9.9E+03	Range
	Linklater et al. (2003) (citing Higgo 1988)	Soils	1.7E+02 to 7.9E+05	Range
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, acidic, pH 4.8)	8.70+02 to 6.4E+03 (2.6E+03)	Range (GM) (variation in sample depth)
	Sheppard et al. (2011)	Clay till (pH 8.1)	2.4E+03 to 2.8E+04 (8.7E+03)	Range (GM) (variation in sample depth)
	Sheppard et al. (2011)	Glacial clay (pH 7 – 8)	1.9E+03 to 2.2E+04 (5.5E+03)	Range (GM) (variation in sample depth)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	5.5E+02 to 5.4E+03 (2.0E+03)	Range (GM) (variation in sample depth)
	Vandenhove et al. (2009)	Sand soil	3.1E+03 (4.9E+01 to 4.0E+04)	GM, range
	Vandenhove et al. (2009)	Loam soil	1.1E+03 (1.2E+01 to 1.2E+05)	GM, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Vandenhove et al. (2009)	Clay soil	3.8E+04 (6.7E+02 to 9.5E+05)	GM, range
Sn	Bradbury & Baeyens (2003)	Opalinus Clay (assumed to be HSe^-)	0.00E+00	Values for reference pH and bounding pH
	IAEA (2010)	All soil	2.0E+02 (4.0E+00 to 2.1E+03)	Geometric mean and range
	IAEA (2010)	Sand soil	5.6E+01 (4.0E+00 to 1.6E+03)	Geometric mean and range
	IAEA (2010)	Loam + Clay	2.2E+02 (1.2E+01 to 2.1E+03)	Geometric mean and range
	IAEA (2010)	Organic Soil	1.0E+03 (2.3E+02 to 1.8E+03)	Arithmetic mean and range n = 2
	Kaplan (2016)	SeO_4^{2-} sorption to sandy sediment (up to pH 6.7, note sorption decreases with increasing pH)	1.0E+03	Best estimate
	Kaplan (2016)	SeO_4^{2-} sorption to clayey sediment (considers measured SRS data at pH up to 6.7)	1.0E+03	Best estimate
	Krupka et al. (2004)	Sand sequence (Hanford)	7.0E+00 (3.0E+00 to 1.5E+01)	Best estimate, range
	Linklater et al. (2003) (citing Bond & Linklater 2001)	Sherwood Sandstone (sandstone, shal–) - anaerobic conditions (NSARP data)	2.6E+02 to 4.2E+05	Range
	Linklater et al. (2003) (Higgo 1988)	selenite in soil	< 1.0E+00 to 5.2E+01	Range
	Linklater et al. (2003) (Higgo 1988)	selenate in soil	< 9.0E+00 to 7.3E+01	Range
	Linklater et al. (2003) (Higgo 1988)	sandstone (aerobic conditions) (Rockwell International Lab data)	2.0E+00 to 4.7E+00	Range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	1.0E+01 to 1.4E+02 (GM 3.5E+01)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	1.4E+03 (GM); 2.5E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	8.6E+02 (GM); 1.4E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	8.9E+02 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	cultivated peat (pH 5.9 – 6.0)	1.7E+03 (GM); 1.5E+03 (GSD)	GM, GSD (variation in soil depths)
	USEPA (2005)	Se(IV) soil	2.0E+01 (5.0E-01 to 2.5E+02)	Mean and range
Si	Gil-García et al. (2009)	All soils	1.3E+02 (3.3E+01 to 4.0E+02)	GM, range
	Gil-García et al. (2009)	Sand soil	3.3E+01	n = 1
	Gil-García et al. (2009)	Loam soil	1.1E+02	n = 1
	Gil-García et al. (2009)	Clay soil	2.8E+02	n = 1
	Gil-García et al. (2009)	Organic soil	4.0E+02	n = 1

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Heuel-Fabianek (2014)	Sand soil	3.50E+01	Reference value
	Heuel-Fabianek (2014)	Silt soil	1.10E+02	Reference value
	Heuel-Fabianek (2014)	Clay Soil	1.80E+02	Reference value
	Heuel-Fabianek (2014)	Organic soil	4.00E+02	Reference value
	IAEA (2010)	All soil	1.3E+02 (3.3E+01 to 4.0E+02)	GM, range
	IAEA (2010)	Mineral soil	8.7E+01 (3.3E+01 to 1.8E+02)	GM, range
	IAEA (2010)	Organic soil	4.00E+02	n = 1
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	4.1E+02 (GM); 1.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	4.4E+02 (GM); 1.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	1.9E+02 (GM); 2.6E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	8.3E+01 (GM); 2.3E+03 (GSD)	GM, GSD (variation in soil depths)
Sm	Gil-García et al. (2009)	All soils	9.3E+02 (2.4E+02 to 3.0E+03)	GM, range
	Gil-García et al. (2009)	Sand soil	2.4E+02	n = 1
	Gil-García et al. (2009)	Loam soil	8.1E+02	n = 1
	Gil-García et al. (2009)	Clay soil	1.3E+03	n = 1
	Gil-García et al. (2009)	Organic soil	3.0E+03	n = 1
	Bradbury & Baeyens (2003)	Opalinus Clay (Eu analogue)	pH 7.24: 6.0E+04; pH 6.3: 5.0E+03; pH 7.8: 5.0E+04	Values for reference pH and bounding pH
	IAEA (2010)	All soil	9.3E+02 (2.4E+02 to 3.0E+03)	GM, range
	IAEA (2010)	Mineral soil	6.3E+02 (2.4E+02 to 1.3E+03)	GM, range
	IAEA (2010)	Organic soil	3.0E+03	n = 1
	Kaplan (2016)	Sandy sediment (trivalent ions grouped together, Ce and Eu data cited)	1.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (trivalent ions grouped together, Ce and Eu data cited)	9.0E+03	Best estimate
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	1.3E+03 to 6.3E+04 (7.1E+03)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	2.0E+03 (GM); 2.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	5.7E+04 (GM); 1.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	2.8E+04 (GM); 7.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.3E+04 (GM); 1.6E+03 (GSD)	GM, GSD (variation in soil depths)

Element	Data Source	Material/ environment	Values (L/kg)	Notes
Sn	Gil-García et al. (2009)	All soils	1.6E+03 (1.3E+02 to 3.1E+04)	GM, range
	Gil-García et al. (2009)	Sand soil	1.3E+02 to 1.7E+02	Range
	Gil-García et al. (2009)	Loam soil	4.5E+02	n = 1
	Gil-García et al. (2009)	Clay soil	6.7E+02	n = 1
	Gil-García et al. (2009)	Organic soil	1.6E+03	n = 1
	Bradbury & Baeyens (2003)	Opalinus Clay	1.1E+05 (pH 6.3 to 7.8)	Reference values whole pH range
	IAEA (2010)	All soil	1.6E+03 (1.3E+02 to 3.1E+04)	GM, range
	IAEA (2010)	Mineral soil	2.8E+02 (1.3E+02 to 6.7E+02)	GM, range
	IAEA (2010)	Organic soil	1.60E+03	n = 1
	Kaplan (2016)	Sandy sediment (Pb, So and Sn considered in same group, Pb data cited)	2.0E+03	Best estimate
	Kaplan (2016)	Clayey sediment (Pb, So and Sn considered in same group, Pb data cited)	5.0E+03	Best estimate
	Krupka et al. (2004) (citing Serne et al. 1993, Serne & Relyea 1981)	Sand sequence (Hanford) based on Ni data	3.0E+02 (5.0E+01 to 2.5E+03)	Best estimate (range)
	Nakamaru & Uchida (2008)	Japanese agricultural soils	1.2E+04 (1.3E+02 to 1.6E+06)	GM, range
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	5.3E+03 (GM); 1.5E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	4.9E+03 (GM); 1.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	1.1E+04 (GM); 2.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	4.8E+03 (GM); 4.5E+03 (GSD)	GM, GSD (variation in soil depths)
	USEPA (2005)	Sn(II) soil	5.0E+02 (1.3E+02 to 1.0E+04)	Mean, range
Sr	Bradbury & Baeyens (2003)	Opalinus Clay (based on Ca, assumes Ca-Sr selectivity coefficient of 1)	pH 7.24: 1.1E+00; pH 6.3: 9.3E-01; pH 7.8: 1.1E+00	Values for reference pH and bounding pH
	Bugai et al. (2019)	Sand in situ (Chernobyl Exclusion Zone)	2.0E-01 to 2.2E+01	Range
	Bugai et al. (2019)	Loam/clay batch method (Chernobyl Exclusion Zone)	4.5E+00 to 7.7E+01	Range
	Kaplan (2016)	Sandy sediment (SRS data: 5 ± 1 L/kg at pH 5.3)	5.00E+00	Best estimate
	Kaplan (2016)	Clayey sediment (SRS data: 17 L/kg at pH 5.3)	2.00E+01	Best estimate
	Krupka et al. (2004)	Sand sequence (Hanford)	1.4E+01 (5.0E+00 to 2.0E+02)	Best estimate, range
	IAEA (2010)	All soils	5.2E+01 (4.0E-01 to 6.5E+03)	GM, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	IAEA (2010)	Sand soil	2.2E+01 (4.0E-01 to 2.4E+03)	GM, range
	IAEA (2010)	Loam + Clay + Organic	6.9E+01 (2.0E+00 to 6.5E+03)	GM, range
	Rumynin & Nikulenkov (2014)	Quaternary sediments (sandy loam sediment/soil)	3.4E+01 (1.6E+01 to 7.0E+01)	Mean, range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	3.0E+01 to 1.3E+03 (1.6E+02)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich organic matter, pH 4.8)	7.8E+01 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	2.0E+02 (GM); 2.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	2.5E+02 (GM); 2.9E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	2.7E+02 (GM); 2.0E+03 (GSD)	GM, GSD (variation in soil depths)
Tc	Gil-García et al. (2009)	All soils	2.0E-01 (1.0E-02 to 1.1E+01)	GM, range
	Gil-García et al. (2009)	Sand soil	4.0E-02 (1.0E-02 to 1.0E-01)	GM, range
	Gil-García et al. (2009)	Loam soil	7.0E-02 (1.0E-02 to 9.0E-01)	GM, range
	Gil-García et al. (2009)	Clay soil	9.0E-02 (2.0E-02 to 1.0E+00)	GM, range
	Gil-García et al. (2009)	Organic soil	3.0E+00 (9.0E-01 to 1.1E+01)	GM, range
	Bradbury & Baeyens (2003)	Opalinus clay (Th analogue)	pH 7.24 to 7.8: 5.5E+04; pH 6.3: 2.2E+04	Values for reference pH and bounding pH
	IAEA (2010)	All soil	2.3E-01 (1.0E-02 to 1.1E+01)	GM, range
	IAEA (2010)	Mineral soil	6.3E-02 (1.0E-02 to 1.2E+00)	GM, range
	IAEA (2010)	Organic soil	3.1E+00 (9.2E-01 to 1.1E+01)	GM, range
	Kaplan (2016)	Sandy sediment (numerous SRS references cited, median value adopted)	0.6	Best estimate
	Kaplan (2016)	Clayey sediment (numerous SRS references cited, median value adopted)	2	Best estimate
	Krupka et al. (2004)	Sand sequence (Hanford) (TcO_4^- speciation, note max cited value reported for Hanford is 2.8 L/kg)	0.0E+00 (0.0+00 to 6.0E-01)	Best estimate, range
	Lieser & Bauscher (1987)	Sediments, Tc(VII) and Tc(IV)	1.0E-01 to 1.0E+03	Range (minimum for Tc(VII), maximum for Tc(IV))

Element	Data Source	Material/ environment	Values (L/kg)	Notes
Th	Andra (2005)	Callovo-Oxfordian clay	8.0E+03	Reference value
	Bradbury & Baeyens (2003)	Opalinus clay (values based on Lauber et al. 2000)	pH 7.24 to 7.8 5.5E+04; pH 6.3 2.2E+04	Values for ref pH and pH range
	IAEA (2010)	All soil	1.9E+03 (1.8E+01 to 2.5E+05)	Geometric mean and range
	IAEA (2010)	Mineral soil	2.6E+03 (3.5E+01 to 2.5E+05)	Geometric mean and range
	IAEA (2010)	Organic soil	7.3E+02 (1.8E+01 to 8.0E+04)	Geometric mean and range
	IAEA (2010)	pH < 5	1.3E+03 (1.8E+01 to 1.0E+05)	Geometric mean and range
	IAEA (2010)	5 ≤ pH < 8	3.3E+03 (1.3E+02 to 2.5E+05)	Geometric mean and range
	IAEA (2010)	pH ≥ 8	3.1E+02 (3.5E+01 to 3.2E+04)	Geometric mean and range
	Kaplan (2016)	Sandy sediment (based on Zr data for SRS sediment)	9.0E+02	Best estimate
	Kaplan (2016)	Clayey sediment (based on Zr data for SRS sediment)	2.0E+03	Best estimate
	Kumar et al. (2019) (citing USEPA 1999)	Soil	2.07E+02 to 1.3E+07	Range
	Kumar et al. (2019) (citing IAEA 2009)	Soil	7E+02 to 3.8E+04	Range
	Kumar et al. (2019) (citing Sheppard et al. 2009)	Soil	1.3E+03 to 3.4E+04	Range
	Kumar et al. (2019) (citing IAEA 2009)	Soil	1.8E+01 to 2.5E+05	Range
	Linklater et al. (2003) (citing Bond & Linklater 2001)	Sherwood Sandstone (sandstone and shale)	5.2E+01 to 1.1E+04	Range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	5.5E+03 to 2.5E+05 (GM 2.5E+04)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, pH 4.8)	5.0E+03 (GM); 3.3E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	7.2E+04 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	2.5E+04 (GM); 6.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	6.2E+03 (GM); 1.5E+03 (GSD)	GM, GSD (variation in soil depths)
	Vandenhove et al. (2009)	All soil	1.9E+03 (GM); 1.0E+01 (GSD); 1.9E+01 to 2.5E+05	GM, GSD, range
	Vandenhove et al. (2009)	Sand soil	7.0E+02 (GM); 1.1E+01 (GSD); 3.5E+01 to 1.0E+05 (range)	GM, GSD, range
	Vandenhove et al. (2009)	Loam soil	1.8E+04 (GM); 4.0E+00 (GSD); 5.0E+03 to 2.5E+05 (range)	GM, GSD, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Vandenhove et al. (2009)	Clay soil	4.5E+03 (GM); 3.0E+00 (GSD); 8.0E+02 to 2.4E+04 (range)	GM, GSD, range
	Vandenhove et al. (2009)	Organic soil	7.3E+02 (GM); 4.4E+01 (GSD); 1.9E+01 to 8.0E+04 (range)	GM, GSD, range
	Vandenhove et al. (2009)	Soil (pH 3 – 5)	1.3E+03 (GM); 1.5E+01 (GSD); 1.9E+01 to 1.02E+04 (range)	GM, GSD, range
	Vandenhove et al. (2009)	Soil (pH 5 – 8)	3.26E+03 (GM); 8.0E+00 (GSD); 1.0E+02 to 1.0E+05 (range)	GM, GSD, range
	Vandenhove et al. (2009)	Soil (pH 8 – 10)	3.1E+02 (GM); 7.0E+00 (GSD); 3.5E+01 to 3.2E+04	GM, GSD, range
Ti	Heuel-Fabianek (2014)	Sand soil	3.3E+02	Reference value
	Heuel-Fabianek (2014)	Silt Soil	1.1E+00	Reference value
	Heuel-Fabianek (2014)	Clay soil	1.7E+00	Reference value
	Heuel-Fabianek (2014)	Organic soil	4.0E+00	Reference value
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, pH 4.8)	3.5E+04 (GM); 6.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	2.8E+05 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	1.5E+05 (GM); 9.1E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.2E+04 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
U	Andra (2005)	Callovo-Oxfordian clay	8.0E+03	Reference value
	Bradbury & Baeyens (2003)	U(IV) values based on Th analogy (noting limitations of data given by Berry et al. (1989), Berry et al. (1991), Baston et al. (1991), Baston et al. (1992)).	pH 7.24: 2.05E+04; pH 6.3: 5.5E+02; pH 7.8: 4.82E+04	Values for reference pH and bounding pH
	IAEA (2010)	All soil	2.0E+02 (7.0E-01 to 6.7E+04)	GM, range
	IAEA (2010)	Mineral soil	1.8E+02 (7.0E-01 to 6.7E+04)	GM, range
	IAEA (2010)	Organic soil	1.2E+03 (3.3E+02 to 7.6E+03)	GM, range
	IAEA (2010)	pH < 5	7.1E+01 (7.0E-01 to 6.7E+03)	GM, range
	IAEA (2010)	5 ≤ pH < 7	7.4E+02 (2.6E+00 to 6.7E+04)	GM, range
	IAEA (2010)	pH ≥ 7	6.5E+01 (9.0E-01 to 6.2E+03)	GM, range
	Kaplan (2016)	Sandy sediment (considers measured SRS data)	3.0E+02	Best estimate

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Kaplan (2016)	Clayey sediment (considers measured SRS data)	4.0E+02	Best estimate
	Krupka et al. (2004)	Sand sequence (Hanford) (site specific data, speciation not given - oxidising?)	1.0E+00 (1.0E-01 to 4.0E+00)	Best estimate (range)
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Sandy soil	4.6E+01 to 3.95E+05	Reported range
	Kumar et al. (2019) (citing Sheppard & Thibault 1990)	Clayey soil	3.0E-02 to 2.2E+03	Reported range
	Kumar et al. (2019) (citing McKinley & Scholtis 1993)	Soil/sediment	2.0E+01 to 1.7E+03	Reported range
	Kumar et al. (2019) (citing Erikson et al. 1993)	Soil + tap water (batch measurement) pH 6.8 to 8	5.4E+01 to 4.38E+03	Reported range
	Kumar et al. (2019) (citing Serkiz & Johnson 1994)	Soil + pore water (in situ, pH 3 to 6.7)	1.2E+00 to 3.4E+04	Reported range
	Linklater et al. (2003) (citing Bond & Linklater 2001)	U(VI) Sherwood Sandstone Group (sandstone, shale)	<1.0E+00 to 3.8E+03	Range
	Linklater et al. (2003) (citing Bond & Linklater 2001)	U(IV) Sherwood Sandstone Group (sandstone, shale)	1.00E+04	Single recommended value
	Linklater et al. (2003) (citing Berry et al. 1990, Berry et al. 1989, Baston et al. 1991)	U(VI) London Clay (different studies, range water to solid ratios)	1E+02 to 2.9E+04	Range
	Linklater et al. (2003) (citing Berry et al. 1989, Baston et al. 1991)	U(IV) London Clay	4.3E+03 to > 1E+04	Range
	Ramírez-Guinart et al. (2020a)	Mineral soil (OM < 20%)	2.2E+02 (GM); 8.7E+00 (GSD); 5th 2.4E+00; 95th 6.6E+03	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020a)	Organic (OM ≥ 20%)	1.1E+03 (GM); 6.4E+00 (GSD); 5th 3.3E+01; 95th 1.9E+04	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020a)	Soil pH < 5	2.0E+02 (GM); 7.8E+00 (GSD); 5th 3.5E+00, 95th 3.3E+03	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020a)	Soil ≥5 pH < 7	1.0E+03 (GM); 5.2E+00 (GSD); 5th 8.3E+01, 95th 1.5E+04	GM, GSD, 5th and 95th centiles
	Ramírez-Guinart et al. (2020a)	Soil pH ≥ 7	1.0E+02 (GM); 9.5E+00 (GSD); 5th 1.3E+00, 95th 3.7E+03	GM, GSD, 5th and 95th centiles
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	6.1E+02 to 4.4E+04 (GM 4.0E+03)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, pH 4.8)	3.1E+03 (GM); 2.2E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Clay till, average pH of 8.1 (clay 17% of mineral fraction)	7.7E+04 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	4.2E+02 (GM); 4.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (pH 5.9 – 6.0)	1.5E+04 (GM); 1.7E+03 (GSD)	
	USEPA (1999)	Soils	pH 5: 2.5E+01 to 1.6E+5; pH 6: 1.0E+02 to 1.0E+06; pH 8: 4 E-01 to 2.5E+05	Range (pH dependant)
	Vandenhove et al. (2009)	All soils	2.0E+02 (GM); 1.2E+01 (GSD); 7.0E-01 to 6.66E+04	GM, GSD, range
	Vandenhove et al. (2009)	Sand soil	1.1E+02 (GM); 1.2E+01 (GSD); 7.0E-01 to 6.66E+04	GM, GSD, range
	Vandenhove et al. (2009)	Loam soil	3.1E+02 (GM); 1.2E+01 (GSD); 9.0E-01 to 3.87E+04	GM, GSD, range
	Vandenhove et al. (2009)	Clay soil	2.8E+01 (GM); 7.0E+00 (GSD); 3.0E+00 to 4.8E+02	GM, GSD, range
	Vandenhove et al. (2009)	Organic soil	1.2E+03 (GM); 6.0E+00 (GSD); 3.3E+01 to 7.6E+03	GM, GSD, range
	Vandenhove et al. (2009)	pH < 5	7.1E+01 (GM); 1.1E+01 (GSD); 7.0E-01 to 6.7E+03	GM, GSD, range
	Vandenhove et al. (2009)	5 ≤ pH < 7	7.4E+02 (GM); 8.0E+00 (GSD); 2.6E+00 to 6.66E+04	GM, GSD, range
	Vandenhove et al. (2009)	pH ≥ 7	6.8E+01 (GM); 8.0E+00 (GSD); 9.0E-01 to 6.16E+03	GM, GSD, range
Zr	Gil-García et al. (2009)	All soils	4.1E+02 (2.0E+00 to 1.0E+04)	GM, range
	Gil-García et al. (2009)	Sand soil	3.2E+01 (2.0E+00 to 6.0E+02)	GM, range
	Gil-García et al. (2009)	Loam soil	2.2E+03 to 8.1E+03	Range
	Gil-García et al. (2009)	Clay soil	3.3E+03 to 1.0E+04	Range
	Gil-García et al. (2009)	Organic soil	3.3E+03 to 1.0E+04	Range
	Bradbury & Baeyens (2003)	Opalinus Clay (Sn analogue used given lack of data)	pH 7.24: 1.09E+04; pH 6.3: 3.97E+04; pH 7.8: 4.7E+03	Values for reference pH and bounding pH
	IAEA (2010)	All soil	4.1E+02 (2.0E+00 to 1.0E+04)	Mean, range
	IAEA (2010)	Sand soil	3.2E+01 (2.0E+00 to 6.0E+02)	Mean, range
	IAEA (2010)	Loam + clay soil	5.0E+03 (2.2E+03 to 1.0E+04)	Mean, range
	IAEA (2010)	Organic soil	3.7E+03 (2.3E+01 to 7.3E+03)	Mean, range

Element	Data Source	Material/ environment	Values (L/kg)	Notes
	Kaplan (2016)	Sandy sediment (measured SRS data considered, but noted as being problematic)	9.0E+02	Best estimate
	Kaplan (2016)	Clayey sediment (measured SRS data considered, but noted as being problematic)	2.0E+03	Best estimate
	Krupka et al. (2004) (citing Rhodes 1957)	Sand sequence (Hanford)	1.0E+03 (4.0E+01 to 2.5E+03)	Best estimate (range)
	Linklater et al. (2003) (citing Higgo 1987)	Marine sediment	1.0E+02 to 1.0E+04	Range
	Linklater et al. (2003) (citing Higgo 1988)	Clayey sand (aerobic conditions)	6E+00 to 2.8E+03	Range
	Sheppard et al. (2009)	Forsmark and Laxemar-Simpevarp soils/sediments	3.2E+02 to 7.5E+02 (GM 5.2E+02)	Range, GM
	Sheppard et al. (2011)	Clay gyttja (rich in organic matter, pH 4.8)	9.4E+02 (GM); 4.0E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	clay till, average pH of 8.1 (clay 17% of mineral fraction)	5.2E+03 (GM); 1.7E+03 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Glacial clay, pH 7 – 8 (clay 35 – 56% mineral fraction)	6.9E+03 (GM); 1.1E+04 (GSD)	GM, GSD (variation in soil depths)
	Sheppard et al. (2011)	Cultivated peat (5.9 – 6.0)	2.4E+03 (GM); 1.8E+03 (GSD)	GM, GSD (variation in soil depths)

GM: Geometric mean
GSD: Geometric Standard Deviation

References App. A

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App. B: Comparison of new K_d compilation with the old one

The conditions for which the new K_d values are recommended are compared with the conditions for which Tits & van Dorp (1999) recommended K_d values in Tab. B-1. The K_d values recommended by Tits & van Dorp (1999) are then compared with the ranges of values compiled from the literature in the present study, in Fig. B-1, Fig. B-2, and Fig. B-3. The recommended "Reference" K_d values produced by this study are compared with those recommended by Tits & van Dorp (1999) in Tab. B-1.

Tab. B-1: Comparison between the conditions considered in the previous compilation of K_d values in Tits & van Dorp (1999) and the conditions considered in this work to support the SGT3 biosphere assessment

Parameter	**Assumed range in Tits & van Dorp (1999)**	**Justification in Tits & van Dorp (1999)**	**Revision for this work**	**Justification for the revision**
pH	7 to 8	In the reference Swiss biosphere soils contain carbonate minerals which buffer pH	4 to 9.5	Range of pH identified in review of soil and surface waters in Northern Switzerland
Redox (Eh)	Reducing conditions	Most redox-sensitive elements sorb more strongly under reducing conditions.	-300 mV to +850 mV (Note all the reference water compositions considered are relatively oxidising, > 130 mV)	Some waters/environments will be clearly oxidising (in contact with the air). In a biosphere model it is not necessarily conservative to assume reducing conditions which results in greater sorption of most redox-sensitive elements.
Sesquioxide content	Neglected in assigning K_d	Little generic and no site-specific information	Neglected, as for (Tits & van Dorp 1999)	As for (Tits & van Dorp 1999)
Ionic strength, element concentrationsetc.	Not taken into account in assigning K_d	Little generic and no site-specific information	For ranges of inorganic ligand (Cl^-, HCO_3, SO_4) concentrations will not result in significant changes to speciation	In the dilute waters relevant to the study significant complexing not expected.

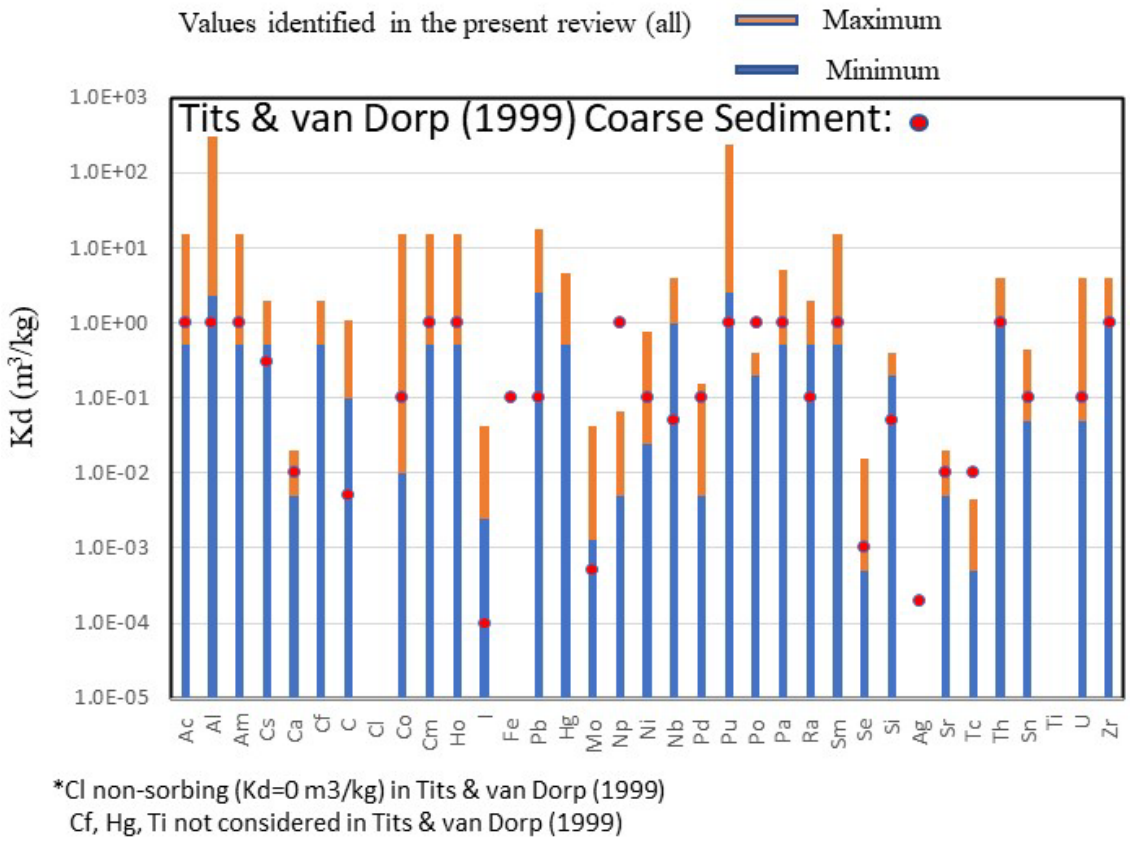

Fig. B-1: Comparison between K_d values recommended for coarse sediments in Tits & van Dorp (1999), and ranges of K_d for coarse, low-organic content soil/sediment identified in the review reported here

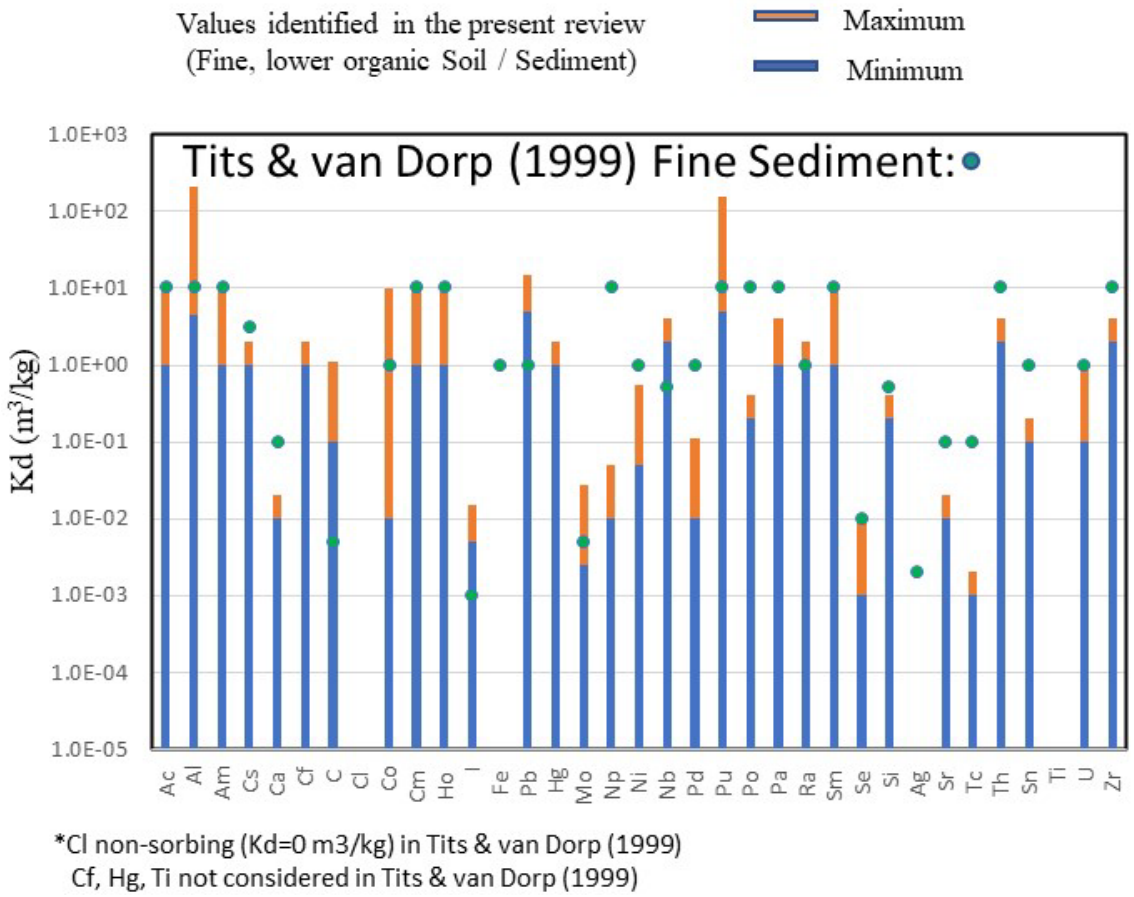

Fig. B-2: Comparison between K_d values recommended for fine sediment in Tits & van Dorp (1999), and ranges of K_d for fine, lower organic content soil/sediment identified in the review reported here

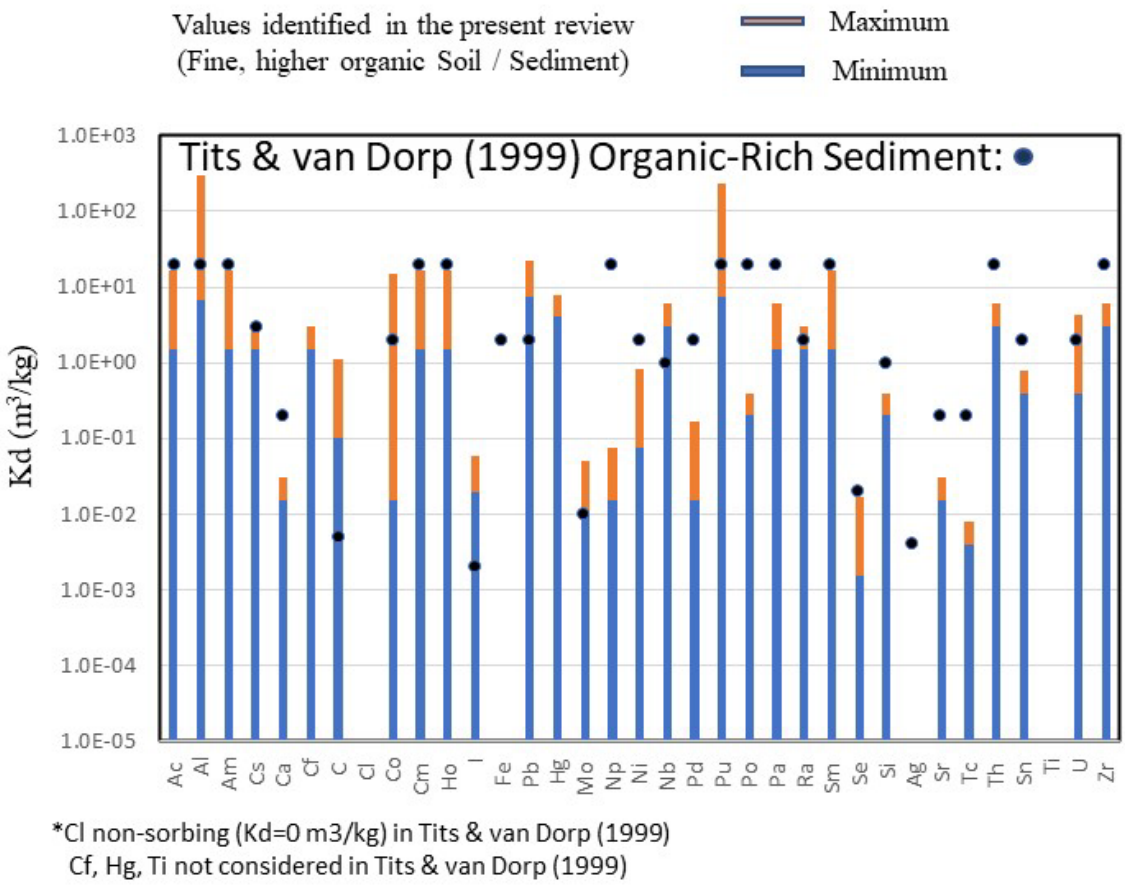

Fig. B-3: Comparison between K_d values recommended for organic-rich sediments in Tits & van Dorp (1999), and ranges of K_d for fine, higher organic soil/sediment identified in the review reported here

Tab. B-2: Compilation of recommended reference K_d values for each considered reference water in each soil/sediment type, compared with recommended K_d values in the earlier compilation of Tits & van Dorp (1999)

		Recommended reference soil water values (m^3/kg)			**Recommended reference lake/river water walues** (m^3/kg)			**Recommended reference river bed water values** (m^3/kg)			**Recommended reference aquifer water values** (m^3/kg)			**Tits & van Dorp (1999)** (m^3/kg) **(red indicates element included in new compilation, but not in the old one)**		
		Course	**Fine lower organic**	**Fine higher organic**	**Course**	**Fine lower organic**	**Fine higher organic**	**Course**	**Fine lower organic**	**Fine higher organic**	**Course**	**Fine lower organic**	**Fine higher organic**	**Course**	**Fine**	**Organic**
Actinium	Ac	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E+00	1.00E+01	2.00E+01
Aluminium	Al	2.25E+00	4.50E+00	6.75E+00	1.00E+02	2.00E+02	3.00E+02	1.00E+02	2.00E+02	3.00E+02	1.00E+02	2.00E+02	3.00E+02	1.00E+00	1.00E+01	2.00E+01
Americium	Am	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E+00	1.00E+01	2.00E+01
Caesium	Cs	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	3.00E-01	3.00E+00	3.00E+00
Calcium	Ca	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	1.00E-02	1.00E-01	2.00E-01
Californium	Cf	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E-10	1.00E-10	1.00E-10
Carbon	C	1.00E-01	1.00E-01	1.00E-01	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	5.00E-03	5.00E-03	5.00E-03
Chlorine	Cl	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.00E-10	1.00E-10	1.00E-10
Cobalt	Co	5.00E-01	1.00E-02	1.50E-02	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	2.50E-01	5.00E-01	7.50E-01	1.00E-01	1.00E+00	2.00E+00
Curium	Cm	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E+00	1.00E+01	2.00E+01
Holmium	Ho	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E+00	1.00E+01	2.00E+01
Iodine	I	2.50E-03	5.00E-03	2.00E-02	5.00E-03	1.00E-02	4.00E-02	2.50E-03	5.00E-03	2.00E-02	2.50E-03	5.00E-03	2.00E-02	1.00E-04	1.00E-03	2.00E-03
Iron	Fe	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	None – insoluble	1.00E-01	1.00E+00	2.00E+00
Lead	Pb	2.50E+00	5.00E+00	7.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	2.50E+00	5.00E+00	7.50E+00	1.00E-01	1.00E+00	2.00E+00
Mercury	Hg	5.00E-01	1.00E+00	4.00E+00	5.00E-01	1.00E+00	4.00E+00	5.00E-01	1.00E+00	4.00E+00	5.00E-01	1.00E+00	4.00E+00	1.00E-10	1.00E-10	1.00E-10
Molybdenum	Mo	5.00E-03	1.00E-02	4.00E-02	1.30E-03	2.50E-02	1.00E-02	1.30E-03	2.50E-03	1.00E-02	2.50E-03	5.00E-03	2.00E-02	5.00E-04	5.00E-03	1.00E-02
Neptunium	Np	5.00E-03	1.00E-02	1.50E-02	2.00E-02	4.00E-02	6.00E-02	2.00E-02	4.00E-02	6.00E-02	1.00E-02	2.00E-02	3.00E-02	1.00E+00	1.00E+01	2.00E+01
Nickel	Ni	2.50E-02	5.00E-02	7.50E-02	2.50E-01	5.00E-01	7.50E-01	2.50E-01	5.00E-01	7.50E-01	2.50E-01	5.00E-01	7.50E-01	1.00E-01	1.00E+00	2.00E+00
Niobium	Nb	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	5.00E-02	5.00E-01	1.00E+00
Palladium	Pd	5.00E-02	1.00E-01	1.50E-01	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	2.50E-02	5.00E-02	7.50E-02	1.00E-01	1.00E+00	2.00E+00

		Recommended reference soil water values (m^3/kg)			Recommended reference lake/river water walues (m^3/kg)			Recommended reference river bed water values (m^3/kg)			Recommended reference aquifer water values (m^3/kg)			Tits & van Dorp (1999) (m^3/kg) (red indicates element included in new compilation, but not in the old one)		
		Course	Fine lower organic	Fine higher organic	Course	Fine lower organic	Fine higher organic	Course	Fine lower organic	Fine higher organic	Course	Fine lower organic	Fine higher organic	Course	Fine	Organic
Plutonium	Pu	2.50E+00	5.00E+00	7.50E+00	2.50E+01	5.00E+01	7.50E+01	2.50E+01	5.00E+01	7.50E+01	7.50E+01	1.50E+02	2.30E+02	1.00E+00	1.00E+01	2.00E+01
Polonium	Po	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	1.00E+00	1.00E+01	2.00E+01
Protactinium	Pa	5.00E-01	1.00E+00	1.50E+00	1.50E+00	3.00E+00	4.50E+00	1.50E+00	3.00E+00	4.50E+00	1.30E+00	2.50E+00	3.80E+00	1.00E+00	1.00E+01	2.00E+01
Radium	Ra	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	5.00E-01	1.00E+00	1.50E+00	1.00E-01	1.00E+00	2.00E+00
Samarium	Sm	5.00E-01	1.00E+00	1.50E+00	5.00E+00	1.00E+01	1.50E+01	5.00E+00	1.00E+01	1.50E+01	1.50E+00	3.00E+00	4.50E+00	1.00E+00	1.00E+01	2.00E+01
Selenium	Se	5.00E-03	1.00E-02	1.50E-02	5.00E-04	1.00E-03	1.50E-03	5.00E-03	1.00E-02	1.50E-02	5.00E-04	1.00E-03	1.50E-03	1.00E-03	1.00E-02	2.00E-02
Silicon	Si	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	2.00E-01	5.00E-02	5.00E-01	1.00E+00
Silver	Ag	5.00E-03	1.00E-02	4.00E-02	5.00E-03	1.00E-02	4.00E-02	0.00E+00	0.00E+00	0.00E+00	5.00E-03	1.00E-02	4.00E-02	2.00E-04	2.00E-03	4.00E-03
Strontium	Sr	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	5.00E-03	1.00E-02	1.50E-02	1.00E-02	1.00E-01	2.00E-01
Technetium	Tc	5.00E-04	1.00E-03	4.00E-03	5.00E-04	1.00E-03	4.00E-03	5.00E-04	1.00E-03	4.00E-03	5.00E-04	1.00E-03	4.00E-03	1.00E-02	1.00E-01	2.00E-01
Thorium	Th	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	1.00E+01	2.00E+01
Tin	Sn	5.00E-02	1.00E-01	4.00E-01	5.00E-02	1.00E-01	4.00E-01	5.00E-02	1.00E-01	4.00E-01	5.00E-02	1.00E-01	4.00E-01	1.00E-01	1.00E+00	2.00E+00
Titanium	Ti	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.00E-10	1.00E-10	1.00E-10
Uranium	U	5.00E-01	1.00E+00	4.00E+00	5.00E-01	1.00E+00	4.00E+00	5.00E-01	1.00E+00	4.00E+00	5.00E-02	1.00E-01	4.00E-01	1.00E-01	1.00E+00	2.00E+00
Zirconium	Zr	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	2.00E+00	3.00E+00	1.00E+00	1.00E+01	2.00E+01