Solubility

SSM preliminary review of Sr-Site

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National Nuclear Laboratory

Structure

- Underpinning chemical dataset (e.g. thermodynamic data for radionuclide solubility calculations)
- Solubility calculation approach and methodology (Simple Functions spreadsheet tool)
- Solubility ranges for assessment calculations

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- Co-precipitation of Ba(Ra)SO4

- Solubility ranges for assessment calculations

Thermodynamic data to calculate solubility limits

- SKB have extensively reviewed the thermodynamic data used in the Simple Functions spreadsheet. Reviews mainly based upon NEA TDB programme updates – data transfer spot checks OK **to date (in progress)**.

- Major review of Pb chemistry from the literature. However the review quotes an internal/non-public domain report which cannot be assessed **(yet!)**

- Previous reviewers for Sr-CAN noted that phosphate not considered…TR 11-01 says:

There will be a competition for phosphate between the iron together with its corrosion products and the components in the spent fuel. The total concentrations of phosphate in the Forsmark groundwaters are generally low and are therefore not expected to have any significant impact on the solubilities. Therefore, it is concluded that no additional studies of the effect of phosphate on the solubilities are required.

Is this consistent with pH, carbonate, sulphate etc, all of which are kept at *groundwater* values in solubility calcs but will also be affected by near field materials !

Thermodynamic data to calculate solubility limits

- Phosphate *can* affect radionuclide solubilities e.g assessment of generic Canadian spent fuel disposal facility: Pu solubilities in the presence of phosphate (Amphos21 study in 2010):

Table 38: Pu solid phases and concentration values (m) under the different selected conditions and using both databases.

	Equilibrated (eq)		Bentonite + C-steel insert (NF)	
	TC / SIT	YMP / PITZER	TC / SIT	YMP / PITZER
CR-10	$PuPO_4$ $5.12 \cdot 10^{-12}$ $PuO_2(am)$ $1.50 \cdot 10^{-8}$ $PuPO_4$* $8.24 \cdot 10^{-11}$ -***	$PuPO_4$ $9.27 \cdot 10^{-13}$ $PuO_2(am)$ $7.01 \cdot 10^{-8}$ -***	$PuPO_4$ $8.12 \cdot 10^{-13}$ $PuO_2(am)$ $9.10 \cdot 10^{-8}$ $PuPO_4$* $3.2 \cdot 10^{-10}$ $Pu(OH)_3$ $2.47 \cdot 10^{-8}$	$PuPO_4$ $4.26 \cdot 10^{-12}$ $PuO_2(am)$ $1.44 \cdot 10^{-5}$ $Pu(OH)_3$ $5.20 \cdot 10^{-6}$
SR-270	n.s.l.**	n.s.l	$Pu(OH)_3$ $4.50 \cdot 10^{-5}$	$Pu(OH)_3$ $3.15 \cdot 10^{-5}$

- Note that in the Canadian case solubilities *take into account the equilibration of groundwater with bentonite and the impact of steel inserts – Different concept in Sr-Site.*

Thermodynamic data to calculate solubility limits

- The SR-Can review said that Mg was not considered in deriving the solubilities of radionuclides. Main issue is that Mg may compete with rads for anions e.g. carbonates. Scoping calcs using PHREEQC and Forsmark groundwater chemistry using the default PHREEQC database as part of this review suggests that this perhaps has a lesser impact than other areas (1E-8 to 1E-9M of the species $MgCO_3^0$ produced e.g.)

  Mg+2 9.999e-05M
  MgCO3 4.485e-09M
  MgOH+ 3.946e-09M

- BUT SKB need to undertake and document this assessment themselves to clarify this issue.

Thermodynamic data to calculate solubility limits

- SKB have reviewed the potential for ionic strengths in groundwaters to be higher than appropriate for the Simple Functions spreadsheet… from TR 11-01:

> The treatment of *activity corrections* also represents an uncertainty to the current solubility assessment…
> …SIT…approach is still not implemented in the geochemical codes used and, therefore, the extended Debye-Hückel approach /Allard et al. 1997, pp 328–329/ has been used for activity corrections. The results obtained by using the extended Debye-Hückel approach are comparable with the ones obtained by the SIT for those cases where the comparison is possible. Higher ionic strength than 1 mole/dm3 would lead to an increased uncertainty in the obtained results.

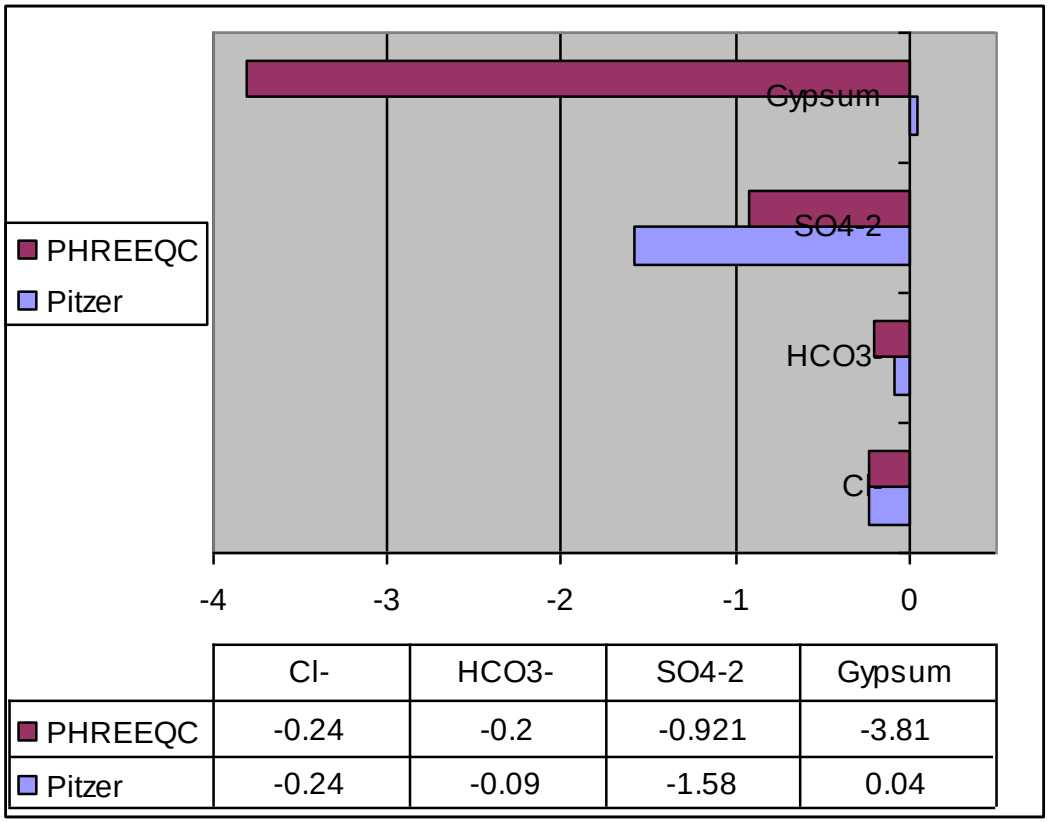
- Since 2010 PHREEQC now includes SIT modelling capability and a database e.g. from USGS website:

Version 2.17.0: February 25, 2010:Added Specific ion Interaction Theory (SIT) activity coefficient model as described in Grenthe, Ingmar, Plyasunov, A.V., and Spahiu, Kastriot, 1997, Estimations of medium effects on thermodynamic data, in Modelling in Aquatic Chemistry, Grenthe, Ingmar, and Puigdomenech, Inasi, eds, OECD Publications,

- This capability means that at least scoping calculations can be now undertaken to assess the impact of higher salinities on solubility (see next page).

Thermodynamic data to calculate solubility limits

- Simple Functions spreadsheet approach OK to 0.2M Ionic strength (I)
- Saline Laxemar groundwater at approx 1.7M I
- Difference between PITZER vs Davis:
- Gypsum SI – a big difference
- Log10(γ) values for SO4-2(aq)
- Need to assess effect?
- SIT much simpler that PITZER



	Cl-	HCO3-	SO4-2	Gypsum
PHREEQC	-0.24	-0.2	-0.921	-3.81
Pitzer	-0.24	-0.09	-1.58	0.04

Structure

- Underpinning chemical dataset (e.g. thermodynamic data for radionuclide solubility calculations)

- Co-precipitation of Ba(Ra)SO4

- Solubility ranges for assessment calculations

Radium co-precipitation

- Ra was shown to be a key risk dominating radionuclide in Sr-Can.
- In Sr-Site, *in some calculations,* SKB invoke radium incorporation into barite to produce a $Ba(Ra)SO_4$ co-precipitate that limits Ra solubility.
- This is probably the *first time* that co-precipitation has been invoked in safety case calculations.
- Why has this not been done to date? While co-precipitation is well known and used routinely for chemical separations:
  - It is conservative to neglect the phenomena,
  - Co-precipitation can be used as a term to lump together several phenomena including true matrix incorporation, surface precipitation, surface sorption, physical entrapment etc –rather like a Kd value.
  - Unlike solubility limits, there is no unique *thermodynamic model* for all aspects of co-precipitation.
  - Conversely, *empirical* co-precipitation distribution coefficients using total metal concentrations are regularly reported in the literature – which cannot be applied outside their experimental conditions.
  - Data for co-precipitation of most radionuclides onto key precipitates is lacking.

Radium co-precipitation

- Why do SKB think they can use radium co-precipitation in Sr-Site?
  - Ra incorporation into barites is a standard analytical separation tool. Probably the very first systematic co-precipitation study was reported for Ra into barites (Doerner and Hoskins, 1925). $Ba(Ra)SO_4$ is commonly found as precipitates in oil field pipe work and at mine tailings.
  - Barites is a relatively straightforward insoluble salt that does not precipitate as an amorphous/ non stoichiometric solid (compare this to tetravalent actinide or iron oxy-hydroxides).
  - Unlike the actinides, Ra is a simple ion in solution that forms very few complexes, does not readily hydrolyse and there are relatively few issues associated with the kinetics of sorption and precipitation.
  - Chemically Ra is very similar to Ba (ionic radii 1.48 Å compared to 1.35 Å), electronegativities similar etc, and should replace Ba in the barites crystal lattice with minimum structural disruption.

Radium co-precipitation

- Is the approach traceable transparent and plausible?

➢ Ra/Ba distribution coefficients for $Ba(Ra)SO_4$ use latest data and approaches, e.g. review by Zhu(in GCA, 2004).

➢ Barites is discussed as being at or near saturation in appropriate near field waters, which is needed for co-precipitation. But look the following:

Radium co-precipitation

- Field data correlation between Ra/Ba is weak (Retardation report R-10-48):

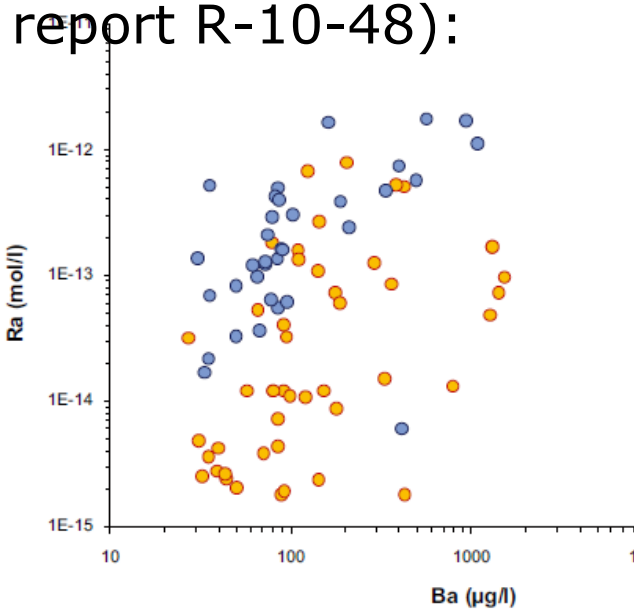


Figure A-6. Cross plot of measured Ra (mol/l) concentrations in g are taken from the Forsmark and Laxemar site investigation datab account of the weak correlation between these solutes.

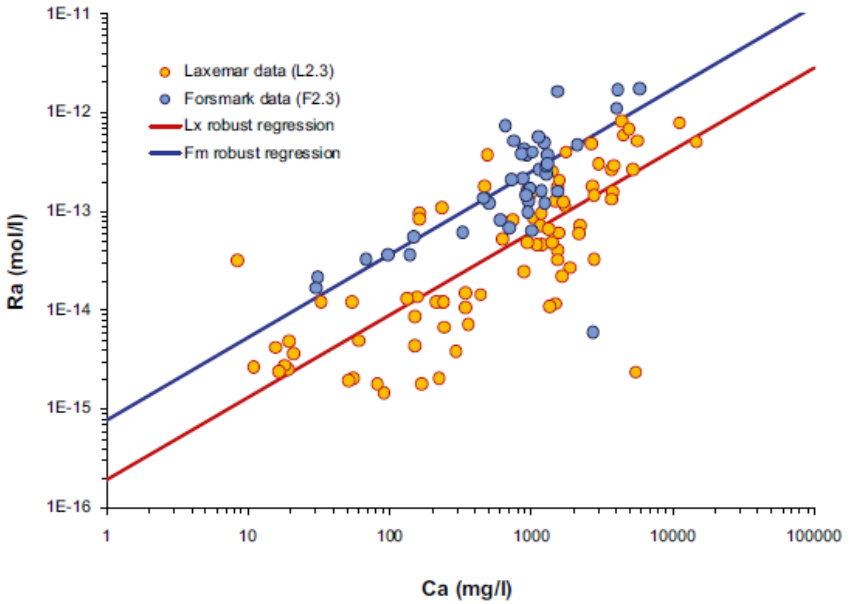


Figure A-7. Cross plot of measured Ra (mol/l) concentrations in groundwater versus Ca (mg/l) where data are taken from the Forsmark (Fm) and Laxemar (Lx) site investigation database. Power-law regression curves are shown for each site considered separately.

- Field correlation of Ra with Ca stronger !

Radium co-precipitation

- Because this is an area of conceptual uncertainty, *have appropriately conservative values been chosen* (present Ra solubility reduction factor of 1000)? Need to ensure that the 1000 factor reduction is conservative and robust.
- See dose calcs for the near field:.

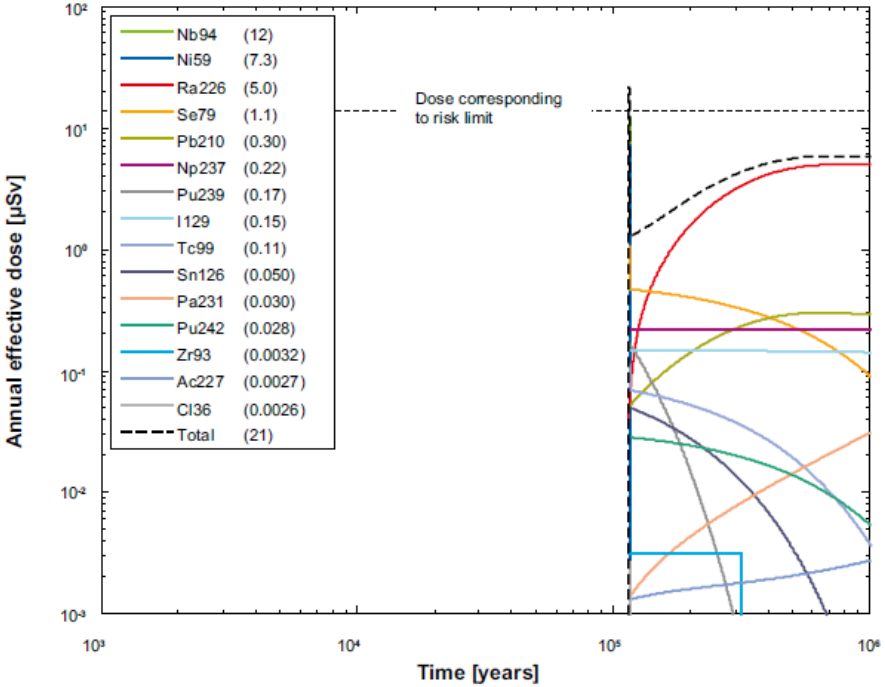


Figure 4-16. Near-field dose equivalent release for a deterministic calculation of the central corrosion case, including solubility limits in the near field. The legend is sorted by peak (in the one-million year period) of the annual effective dose. The values in brackets are peak dose in units of μSv.

- This suggests that for the *central corrosion* case the risk limit is between 1-2 orders of magnitude above *near field* risk values. Ra-226 is main contributor (from TR-10-50).
- Factor of 1000 is therefore important in the near field when solubility is included.

Radium co-precipitation

- Conceptual uncertainty is that sulphate could be consumed by microbes in the near field. SKB say sulphate reducing bacteria unlikely to be transported across the bentonite backfill. Concerning microbes they say: “However, it is highly unlikely that SRB’s will survive the radiation field in the vicinity of the fuel.” (TR-08-07).
- Careful: Many microbial varieties are found in the intensely radioactive fuel storage ponds at Sellafield ! (Victoria Evans PhD at Manchester University)

Indoor Pond (Sellafield Ltd.)

Structure

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Solubility ranges for assessment calculations

- Detailed in Appendix F of TR-10-50

Simple Functions spreadsheet used with @Risk software to generate solubility ranges.

Say "For each groundwater a set of 6,916 groundwater composition data were randomly chosen, as input data to the Simple Functions."

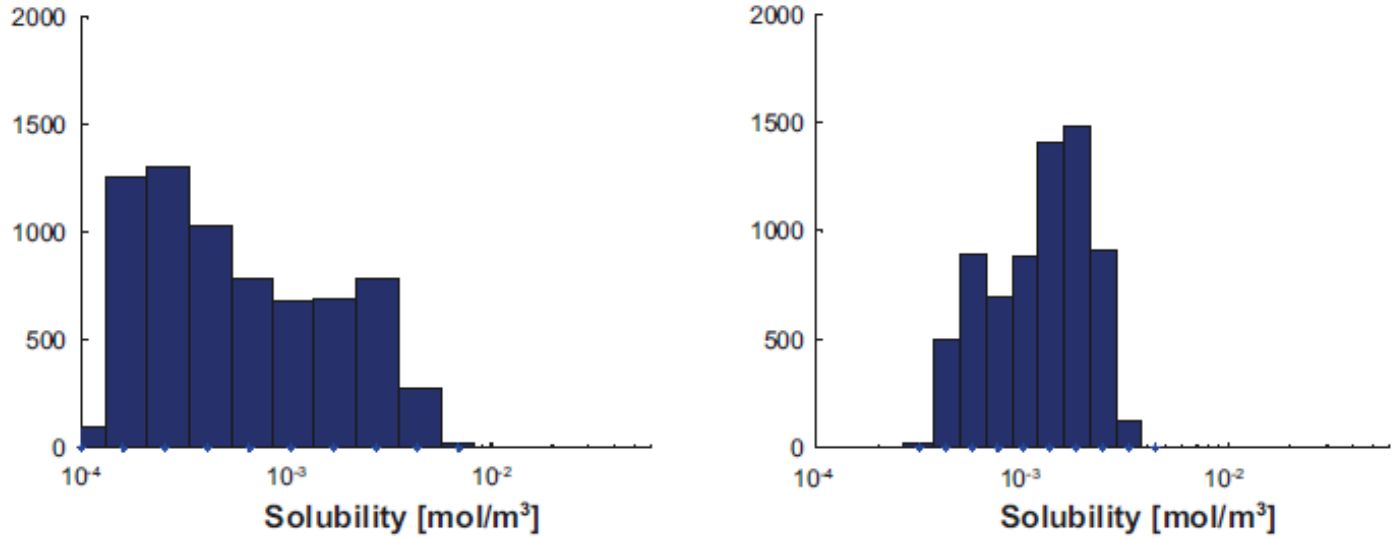
- The reader would be more informed if it could be explained what parameter values were actually changed e.g. Calcium was varied between x and y ppm etc. And why? One can imagine that uranium is sensitive to carbonate concentrations much more than to Cl.

- Why 6916 iterations in every single calculational case? A very precise number for some reason (2x2x7x13x19).

Solubility ranges for assessment calculations

- Detailed in Appendix F of TR-10-50

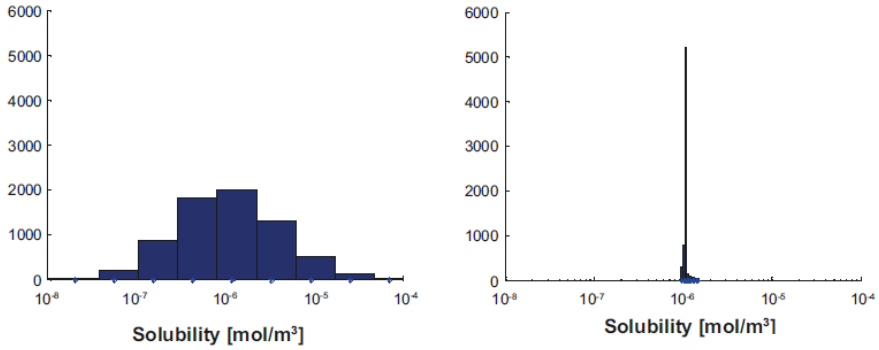
Most results were approx Normal distributions, but some were skewed:



- Radium under temperature conditions (LHS) skewed compared to permafrost conditions groundwater (RHS). No explanation of why this has occurred. Is this a real chemical effect or an error?

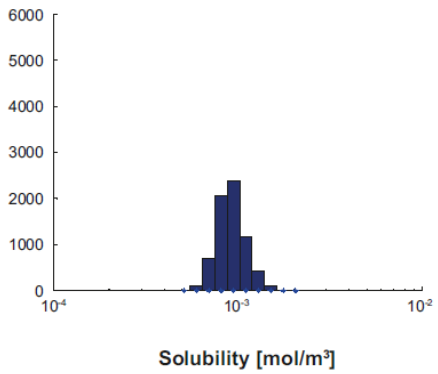
Solubility ranges for assessment calculations

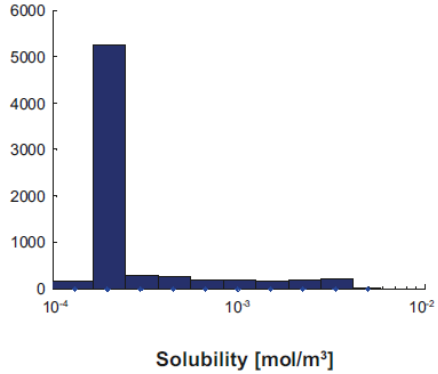
SKB also looked at the effect of uncertainty in thermodynamic data. The output looked like this for Np (comparing temperate water distributions (LHS) with thermodynamic uncertainty (RHS):



- Clearly groundwater composition induces more variation in solubility than thermodynamic data

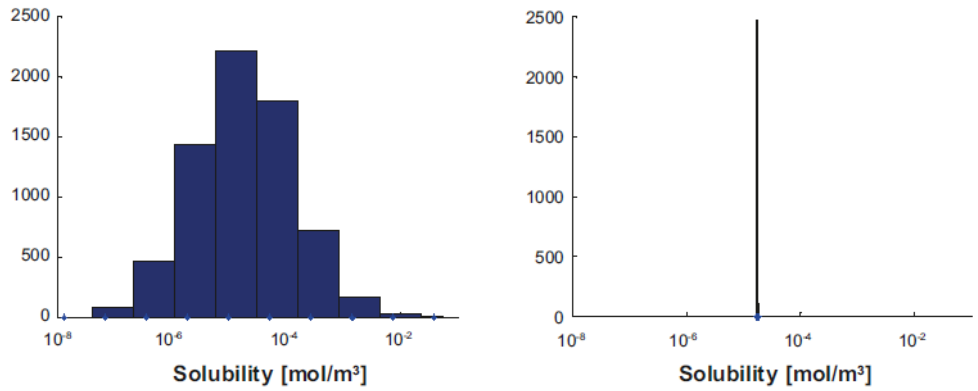
- Radium distributions very different…Why?





Solubility ranges for assessment calculations

SKB statement: "Since the uncertainty in thermodynamic data appears to have a larger impact on the solubility limits than variations in groundwater composition, *the choice of groundwater should be of less importance*."



- Actually, apart from Radium, *the opposite is true* (left are figures for Zr). Need to correct this statement.

- However the subsequent usage in the assessment is based upon solubility ranges as a result of groundwater uncertainties, which is the most likely inference.

Solubility ranges for assessment calculations

- Finally, solubility limits ranges are calculated given combinations of waters and a Monte Carlo sampling approach: TR-10-50 Appendix F says a combination of water compositions were sampled and Simple Functions/@risk run using:

25% of groundwater compositions representing the temperate climate, 25% representing the permafrost climate, 25% representing glacial climate and 25% representing submerged climate,

- This gives a broad range of values. Are these appropriate to represent the uncertainty caused by not having time dependent solubilities?