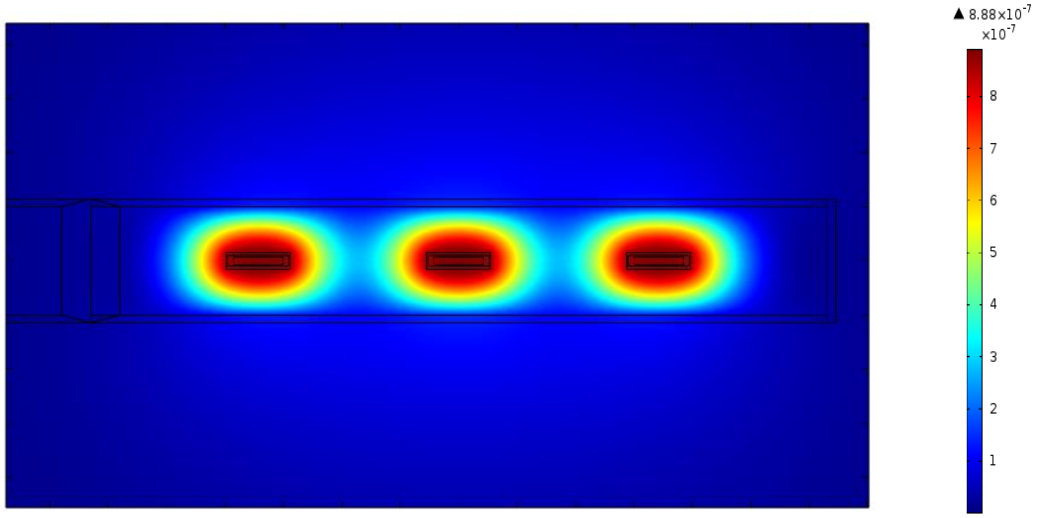
# 6th IGD-TP Exchange Forum (EF6)
# WG3 - CementOrganicsRadionuclidesInteractions - CORI

## TOPIC: Modelling, upscaling, application to PA
## Leader: KIT-INE → SCK CEN

KIT-INE

**London, November 3 - 4, 2015**



# Introduction

- One topic of interest in the framework of nuclear waste disposal is the understanding of the interactions of cement with radionuclides in the presence of organic components.

- **Modeling** of such interactions requires the coupling of
  - Chemical processes
  - Transport processes and
  - Mechanistic understanding.

*The aim of this WP is to provide a scientifically convincing integrated modelling approach, also including the important aspect of up-scaling, in support of PA interests.*

# Identified Tasks within modeling

- **Task 1. Reactive transport modelling**
- **Task 2. Upscaling** (based upon reference scenarios)
- **Task 3. Application to PA**

Excluded or included in other WP:

No TDB development but *TDB is a key requirement for modeling*: definition of an "overview on thermodynamic data" as deliverable and establishment of link to NEA-TDB frame.

Sorption modeling (including molecular dynamics) is included in the experimental studies as interpretation of the data.

# Groups to be involved

(Groups that have filled in the Questionnaire)

| No | Institution | Reactive transport | Upscaling | PA |
|---|---|---|---|---|
| 1 | KIT-INE | X | | |
| 2 | AMPHOS | X | | |
| 3 | JÜLICH | X | | |
| 4 | SCK CEN | X | | |
| 5 | CTU | X | | |
| 6 | U. BERN | | | |
| 7 | SUBATECH | | | |
| 8 | CEA | | | |

Not PA calculations. Application of the results to PA

# Link to the experimental work

- Modeling related with experimental results *are NOT part of this WP*

**Degradation of organics**

Modelling: Degradation rates

(SUBATECH, JULICH, PSI, KIT-INE, BRGM, SCK CEN)

**Organics / cementitious environment / Fe**

Modelling: Aqueous speciation, sorption, molecular dynamics

(SUBATECH, JULICH, PSI, KIT-INE, BRGM, SCK CEN, CTU)

**Organics / RN / cementitious environment**

Modelling: Aqueous speciation, sorption

(KIT-INE, AMPHOS, CTU, SUBATECH)

# Mobility of organics in cementitious environment and their interaction with Fe

## Outcomes from WP2

- ✓ Organics sorption models versus cement degradation
- ✓ Modelling of competitive effects between organics for sorption sites
- ✓ Reactive transfer models applied to hardened cement materials
- ✓ Organics-Iron interactions in cement porewater solutions: speciation model
- ✓ Organics-Iron interactions in cement systems: up-take models with respect to iron corrosion products and cement phases

## Focuses

- ✓ ISA and Phthalate interactions
- ✓ Iron steel corrosion under cementitious conditions and their interactions with dissolved organics species
- ✓ Reactive transfer of main organic species (from WP1) through cement components

# Task 1. Reactive transport modelling

*Partners involved:* ***KIT-INE, JÜLICH, AMPHOS, CTU, SCK-CEN***

This work includes the study of the concentration distribution of complexing agents in the repository as a function of time: diffusion of radionuclide in presence of organic species and organic migration behavior.

- The tools to be used will need to be discussed (from 1D to 3D modelling):

but between them we can include *PHREEQC, OpenGeoSys-Gem, COMSOL*, COMSOL-PhreeqC coupling (iCP)

# SCK contribution CORI WP5
# Task 1 – Reactive transport modelling

- Modelling of experiments done by SCK•CEN (part of WP2)
- Using
  - Pore-scale models (lattice Boltzmann)
  - Continuum models
- Possibility to assist other research groups to calibrate parameters if needed
  - Global search algorithm
  - Correlation and uncertainties estimates (posterior pdf)
  - Using Markov Chain Monte Carlo techniques

# Task 1. Reactive transport modelling

## Contributions of JUELICH

- **Reactive transport modelling:**
  - Coupled reactive transport simulations of the migration behaviour and distribution of selected organics and radionuclides in repository systems with time, e.g.
    - simulation of radionuclide release from cemented Spent Ion Exchange Resins (SIER) and radionuclide migration behaviour in cemented wastes
    - simulation of radionuclide migration through cementitious backfill and barriers in the presence of organics

  → application of input information from CORI (degradation products, kinetic rates) and (interaction of organics with RN and cements; retention mechanisms and parameters)

  → Tools: COMSOL-PhreeqC coupling (iCP) (within the HPC environment if required)

*Guido Deissmann, Natalia Shcherbina and Dirk Bosbach*

# Task 3. Upscaling

## Work in the literature

Physics and Chemistry of the Earth 70–71 (2014) 114–126

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce

### Reactive transport modelling of organic complexing agents in cement stabilized low and intermediate level waste

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ARTICLE INFO

*Article history:*
Available online 28 November 2013

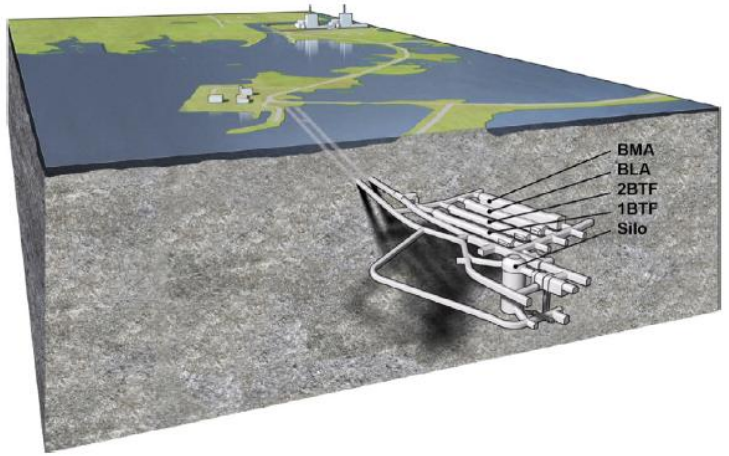
*Keywords:*
Low and intermediate-level waste
Complexing agents
NTA
Cellulose
Isosaccharinic acid
SFR 1

ABSTRACT

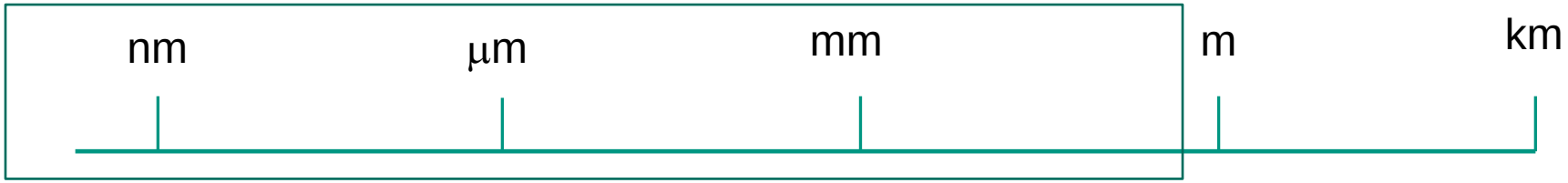
The Swedish final repository for short-lived radioactive waste (SFR 1) is located at Forsmark in Sweden. It holds low and intermediate-level operational waste from the Swedish nuclear power plants, as well as industrial, research-related, and medical waste. A variety of low molecular weight organic compounds are present in the waste or in its matrix. Such compounds can also be formed by chemical degradation of organic macromolecules. These organics can ligate to metal atoms forming stable complexes and also adsorb to the surface of cement, thereby influencing the net release of radionuclides from the repository. This motivates the study of the concentration distribution of complexing agents in the repository as a function of time. The following paper reports the results of mass transport modelling, describing the transport of complexing agents through the cementitous matrix in the rock vault for intermediate-level waste in the SFR 1 repository. Nitrilotriacetate (NTA) and isosaccharinate (ISA) have been investigated, where the former is considered to be non-sorbing and non-reacting, while the latter is produced from cellulose degradation and adsorbs strongly to cement. The 3D model considers advection, diffusion, and sorption of solvated species in cement pore water over a time period of 20,000 years. The model accounts

*Recent work published*

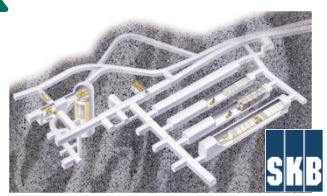
The Swedish final repository for short-lived radioactive waste.

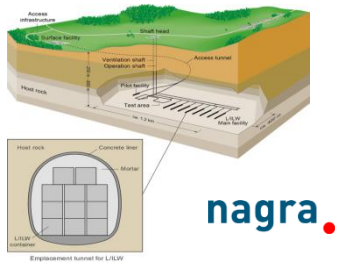


# Task 2. Upscaling
(based upon reference scenarios)



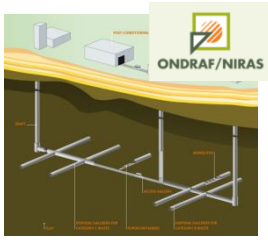

*Link with experiments performed in CORI*

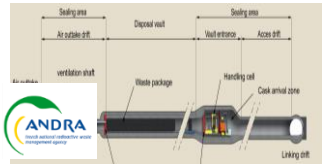



To define reference scenarios (still not decided)

- For the upscaling work it is needed to define a reference case and to work in the model from different scales looking which are the parameters needed.
- Define who will be interested

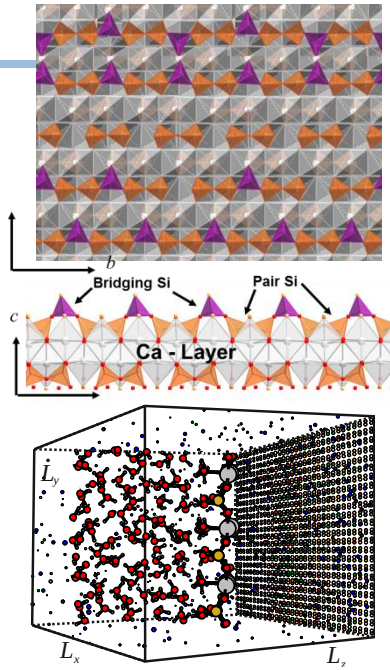


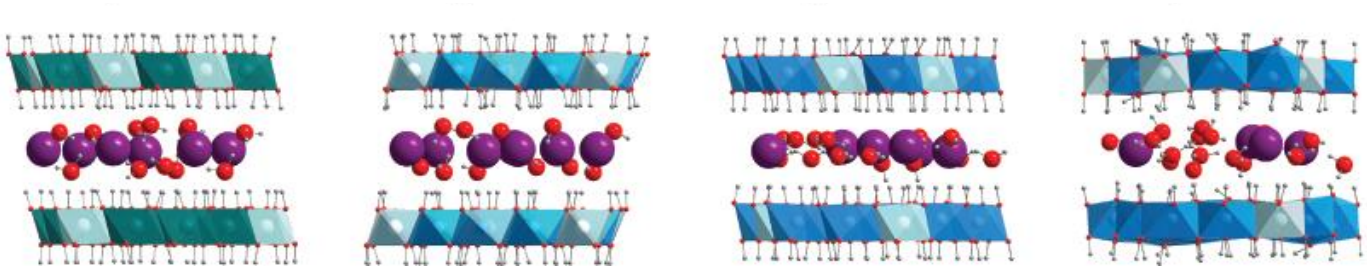



# Multiscale molecular simulations of ions and organics with cement minerals

UNIVERSITÄT BERN

- Intensive molecular simulations studies of surface properties and stability of C-S-H/C-A-S-H and AFm/AFt phases in wide range of pH conditions *(Churakov et al., 2009, 2010 Cem. Conc. Res.)*
- Combined classical and ab initio modelling of surface protolysis reactions and surface titration at wide range on pH conditions *(Churakov et al., 2014, JPCC)*
- Molecular dynamics studies of radionuclide Interaction with cement phases (*Aimoz et al., 2012a,b, JPCC;ES&T*)
- Atomistic simulations of organics interaction with water ( e.g. cellulose stability, *Kulasinski et al., 2014a,b, Nano Lett., Celllul.* )

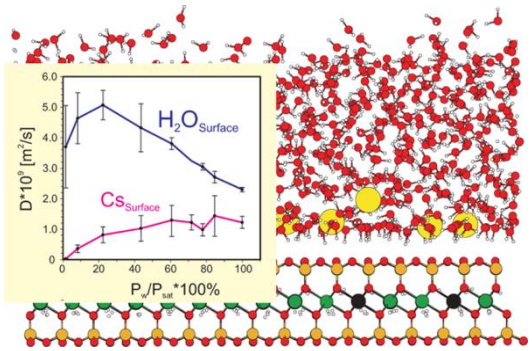


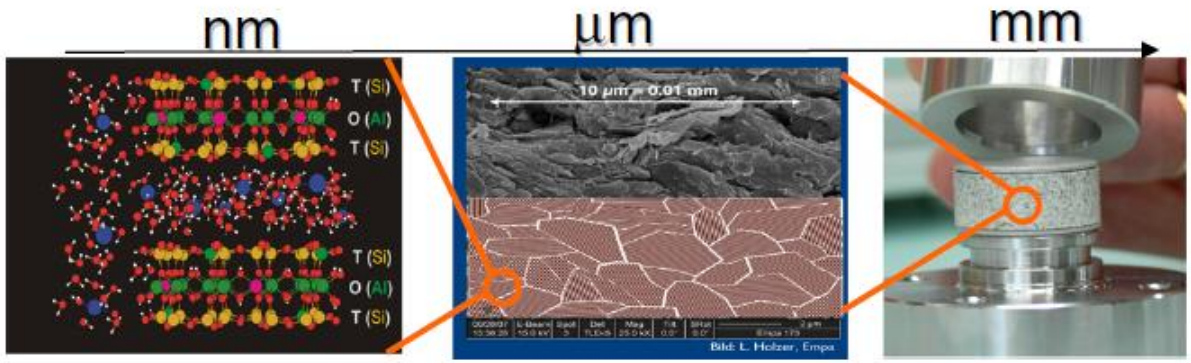



# Upscaling of molecular transport parameters in porous materials

UNIVERSITÄT BERN

- Diffusion in poly-mineral clay mineral clay matrix and upscaling of molecular diffusion coefficients *(Churakov et al., 2014, Appl. Clay Sci.; Churakov and Gimmi 2011, JPC)*
- Classical and molecular dynamics simulations of ions diffusion in confined media. (*Churakov, 2013 ES&T, Churakov Kosakowski 2010 Phyl. Mag.)*



# SCK contribution CORI WP5 Task 2 - Upscaling

- What is the extent and the lifetime of the organic plume ?
- Reactive Transport modelling: from labscale to medium to large scale
- Spatial & temporal upscaling
  - Experimental scales (cm, WP2 & 3) → waste-package/engineered barrier (m) → repository scale (100s of m)
  - Kinetics vs Equilibrium approach
  - Effect on RN transport
- Sensitivity Analysis
    - Model and parameter uncertainty (deterministic & stochastic)
      - lifetime of organics & org-RN complexes
      - Sorption/diffusion of organics & org-RN complexes
    - Influence of concrete composition, type of organics,…

→ Model reduction/abstraction → upscaling towards PA-models

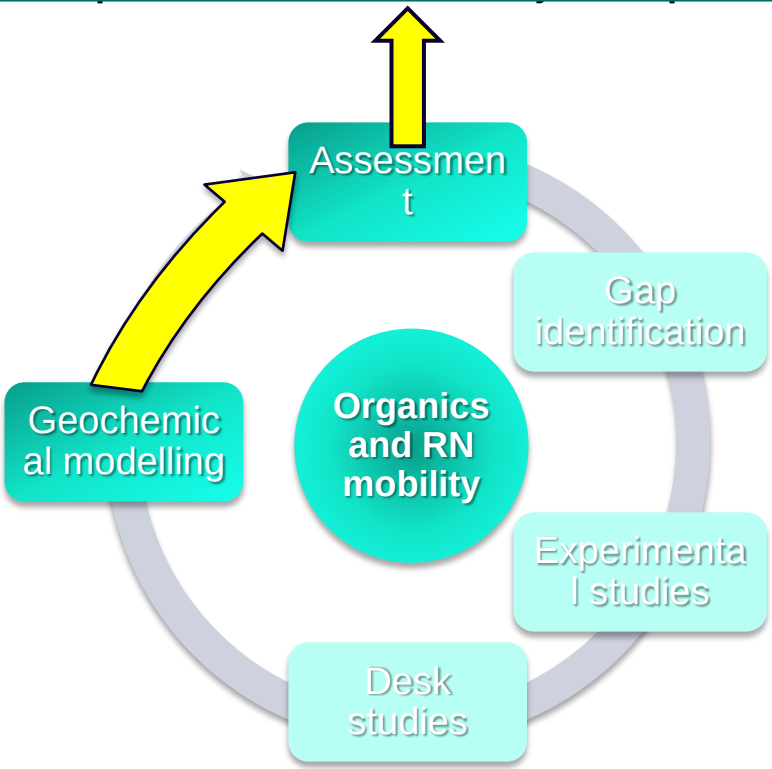
# Up-scaling modelling

- ✓ Use outcomes from others WPs of CORI to an integrated process
- ✓ Define conceptual model from waste degradation to organics sensitivity cases
- ✓ Assess organics effect to radionuclide mobility through cementitious systems (waste packages, backfill and structures)
- ✓ Rank priorities within organic inventories and define conceptual models
- ✓ Define threshold effects and help in defining correcting factors versus PA parameters (i.e. Kd and SL)

- ✓ Numerical modelling to be applied from reactive transfer models to disposal designs / inventories. Need of a project positioning on this regard.

**Evaluation of the influence of organics on RN mobility**
**under cementitious conditions.**

**Competition with Fe&other major components**

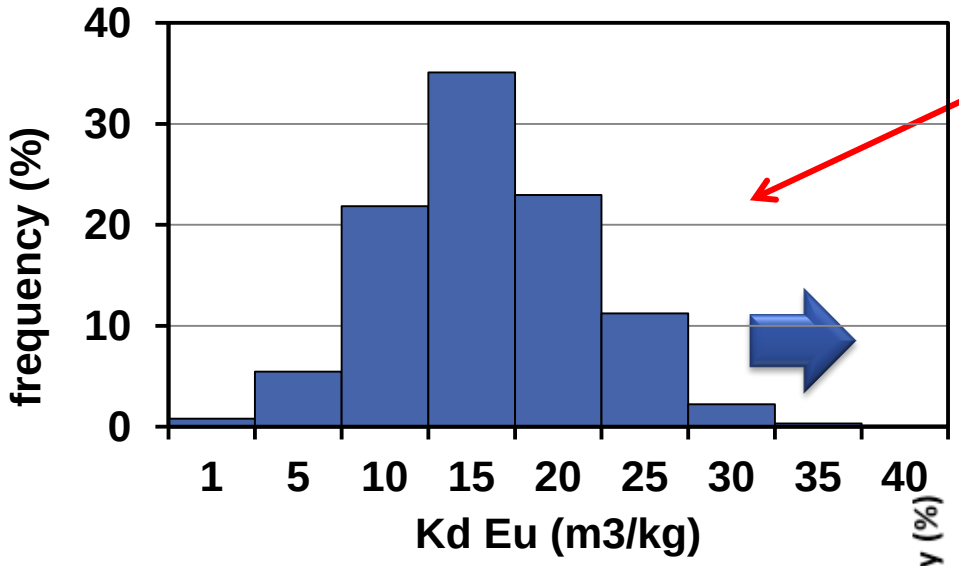



- Application of experimental and desk studies to evaluate the influence of organics on RN mobility under cementitious conditions
  - Using existing modelling tools
  - **Developing tailored tools *(next slide)***

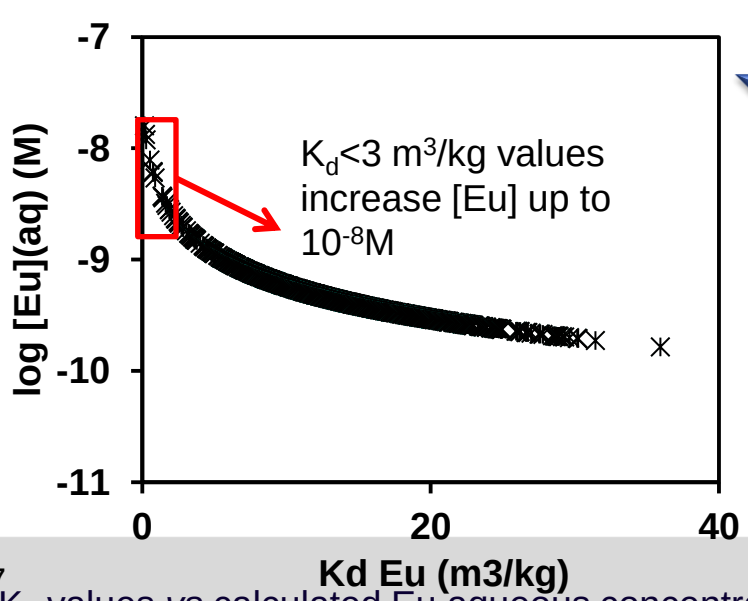
*Microsoft Excel tool:*
*Influence of organic ligands on the sorption of radionuclides on cement-based materials*

# Application: MonteCarlo simulations

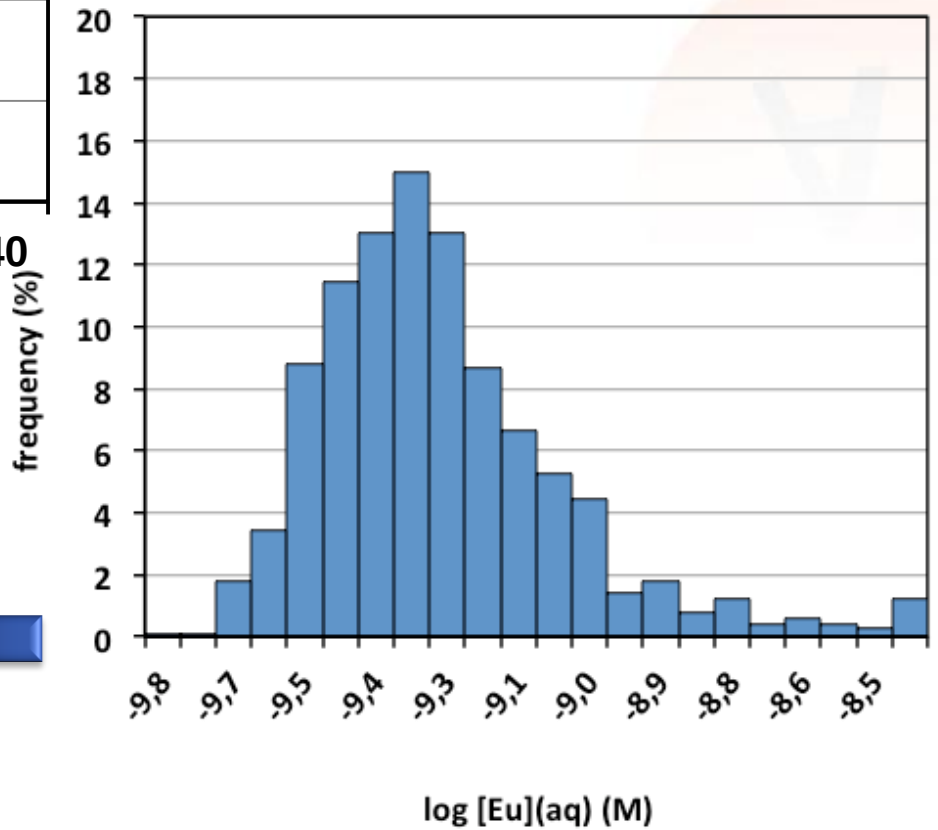
- Results obtained for a full **range of sorption** values




Gaussian distribution




$K_d$ values *vs* calculated Eu aqueous concentrations




Calculated Eu aqueous concentration using the Monte-Carlo simulation.

# Task 4. Application to PA

PA assessment calculations **will not be done within the project**, but the project results will be integrated in the PA of the different countries.

Linking the scientific work with the application of its results in PA

- Definition of the boundary conditions for applications e.g.
  - Organics inventories in different countries, identification of relevant organics in PA
  - Geometries

- Evaluation/integration of the scientific results of the project to the use in the PA

# SCK contribution CORI WP5 Task 3

- Is it possible/needed to go beyond the rather "static" sorption reduction / solubility enhancement approach that is currently use ?
- Upscaling to PA
  - Translation of reactive transport models in simplified PA models (input Task 2)
  - Use of surrogate models/model abstraction/model reduction
- Generic Application for demonstration purposes
  - PA – exercise with the resulting models → goal is to
    - Scope the impact on resulting (normalized) dose curves of the upscaled/simplified model.
    - Assess the sensitivities and uncertainties associated with the model, its parameters and their values.
    - Assess the impact of uncertainties in inventories/geometry/etc…
  - Frame 'threshold values/correction factors' in relation to uncertainties