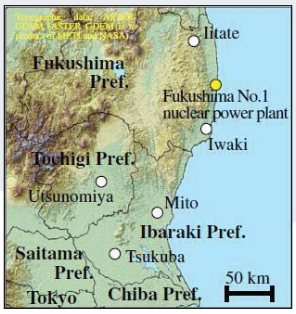

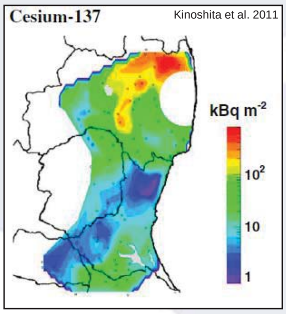

Cesium behavior in subsurface materials

sorption - desorption - migration

Cs Workshop Fukushima Recovery
Fukushima/Japan
September 30 - October 3, 2013

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Outline

1. Motivation / Overview
2. Observations & Database
3. Modeling Approaches
4. Some Illustrations
5. Relevance for Fukushima & brief Outlook

Motivation: Movement & Fate of Cs in Fukushima Soils

Distribution after deposition (main sinks)

- focus on various clay minerals
- based on chemical reasoning & direct evidence

Which Cs behavior to expect

- availability
- transport through soil to aquifer
- mobility in extraction procedures

Overview: Cs Immobilization in Soils and other Subsurface materials

Main Sinks (what can be expected, e.g. Sposito 1981)

- Based on aqueous chemistry (Cs^+ ion), ion exchange expected to be most important
- Solids with substantial negative charge at circumneutral pH
  → clays and other phyllosilicates, possibly some organic matter
  → especially illite and similar minerals: ionic radius of (dehydrated) Cs^+ ion
- Metal oxides, carbonates, feldspars etc. of minor importance

Main Chemical Factors influencing Immobilization

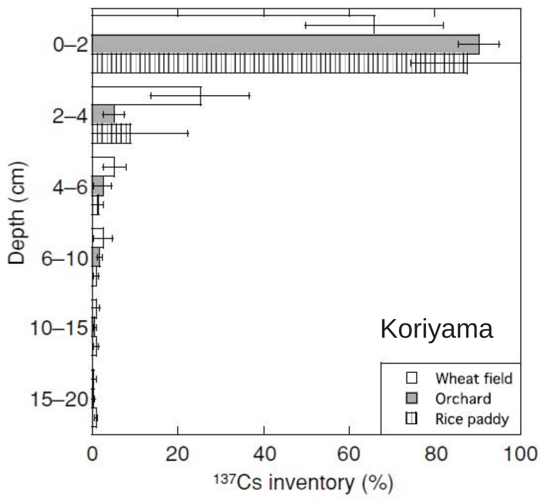
- Amount of phyllosilicates (amount of charge, CEC)
  → especially illite and similar minerals
- Concentration of competing cations

Understanding

- fairly good for the 'simple' components (montmorillonite, illite)
- limited regarding influence of weathering or alteration (e,g, micas), organic matter

Site-specific Evidence: Cs in Fukushima Soils

from *Ohno et al. 2012*



Typical Profile

Sorption/Extractions (Iwata et al. 2012)

- K_d for Cs sorbed on uncontaminated Fukushima soil from 0.1-10 mM solutions: ~ 5-200 L/kg
- K_d desorption: factor ~ 5-20 higher (200 h)
- KCl > NH_4Cl > $MgCl_2$ (0.1 M)

Evidence from Microscopy & Spectroscopy (Iwata et al. 2012, Qin et al. 2012)

- Fukushima soils contain montmorillonite, kaolinite, illite, chlorite, micas (XRD)
- Main Cs sinks (SEM-EDX)
- Cs present as inner- and outer-sphere complex (EXAFS)
  → dehydrated/hydrated Cs^+ located at planar sites and high-affinity sites (FES)

Cs Interaction with Argillaceous Substrates

Relevance

- Transport / retention of Cs in environment
- Extraction / decontamination measures

Different types of phyllosilicates (3 groups, e.g. Sposito 1981)

- expandable 2:1 (montmorillonite) or 1:1 (kaolinite) clays → reversible
- (largely) non-expandable 2:1 clays (illite, micaceous clays)
  - small fraction of sites with steric hindrance, high affinity for cations that are easily dehydrated (Cs^+, K^+, NH_4^+)
  - Cs reversibility strongly dependent on type/concentration of competing cation
- 2:1 expandable, high-charge clays (e.g. vermiculite, also illite in some cases)
  - depending on site occupancy (charge neutralization), structure may collapse
  - irreversible trapping of Cs

Cs Interaction with Argillaceous Substrates

Non-linear sorption in many cases (→ example PSI)

- direct result of presence of different exchange sites with
  - different concentrations
  - different affinity for Cs ions
- can be reproduced by ion exchange models

first step of uptake, may be folllowed by more complicated processes → "reversible " / "irreversible"

Reversible sorption: question of selectivity and ion concentration

(→ when Cs sorption complex is still communicating with external solution)

- Sorption of Cs in argillaceous substrates often dominated by illite
- Several site types for illite
  - planar sites (~ as on montmorillonite, high capacity/low affinity)
  - frayed edge sites (FES, high affinity/low capacity)
  - type-II sites (high affinity/low capacity, evidence from NMR)
- Selectivity of high-affinity sites (steric restrictions, size of hydrated ions)
  - high for Cs^+, K^+, NH_4^+ → "reversible sorption"
  - very low for Na^+ (may compete against Cs at very high conc.) → "reversible sorption" / "irreversible sorption "
  - none for Ca^{2+} etc. (inaccessible) → "irreversible sorption "
  - dilution → "irreversible sorption "

Cs Interaction with Argillaceous Substrates

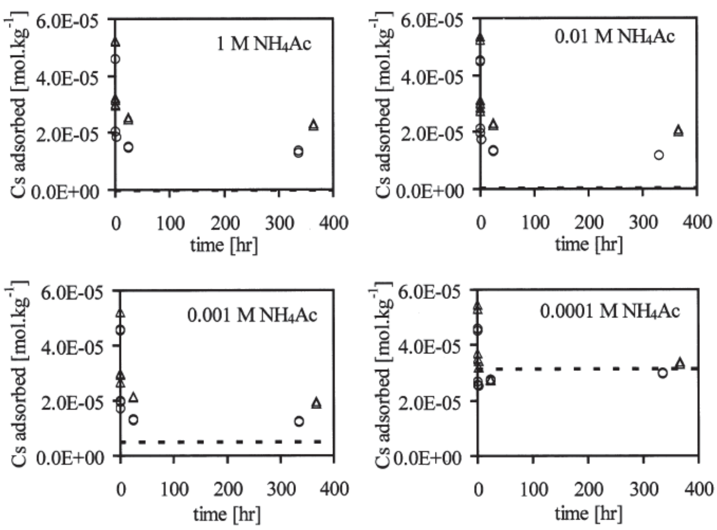
Kinetics (in case of reversible sorption)

- …of course, desorption often takes time…
- e.g. de Koning & Comans (2004), illite: 5 min adsorption, $t_{1/2}$ desorption ~ 8-10 weeks

True irreversibility in some situations

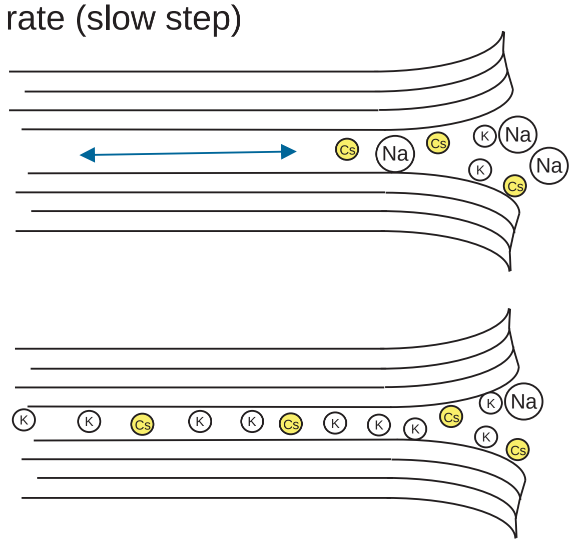
- de Koning & Comans (2004), illite
  - partial collapse of FES when illite with Cs sorbed is exposed to high concentration of extractant (NH_4Cl)
  - Cs follows reversible ion exchange
    - at $[NH_4^+]$ < 1E-04 M
    - when desorption is caused by competition for FES by competing sorbent (resin)

from de Koning & Comans (2004)

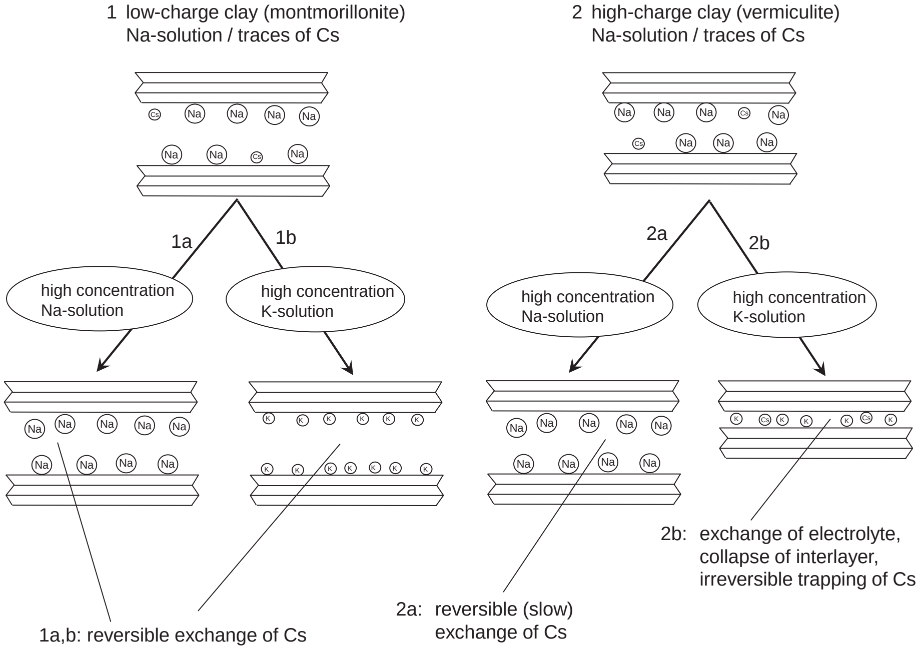


Cs Interaction with Argillaceous Substrates

- Liu et al (2003), micaceous Hanford sediment (NaOH-influenced)
  - Cs sorbed on FES-type sites and planar sites
  - Fast (ion exchange) → slow (diffusion) desorption steps
  - A significant part of Cs on (outer) FES seems to be rapidly exchangeable, slow process ascribed to recessed high-affinity sites
  - Significant effect of extractants on Cs desorption rate (slow step)
    - fast in high-Na solutions
    - much slower in K- and Rb-solutions (ascribed to interlayer/FES collapse)



Cs Sorption / Reversibility



- illustration of reversibility issues using vermiculite
- similar effects to be expected for frayed edges (illite, mica)
- based on findings of e.g.
  - Zachara et al. 2002
  - Liu et al 2003
  - de Koning & Comans 2004

Cs Sorption / Natural Organic Matter

Interaction with solid organic matter

- Cs binding to solid organic matter is weak, Cs easily exchangeable
- Of little relevance compared to clays (Dumat et al. 1997, Macguire et al. 1992)

Influence of dissolved organic matter

- Dissolved organic matter can sorb on clays and modify surface
- Organic sorption is most likely for edge surface, affecting exchange sites near edge
- Consistent with strongest effect observed for illite
  → decrease of K_d of about factor 5 at 50 mg OC/kg clay
  (Dumat & Satunton 1999, Bellenger & Staunton 2008)

Cs Sorption / Desorption - Simple Systems

E.g.: Illite (Poinssot et al. 1999, Bradbury & Baeyens 2000)

- Cs sorption on argillaceous rock as function of Cs concentration
- Ion exchange model for illite based on a number of experimental sorption data (literature & in-house) on pure illites

Model Approach

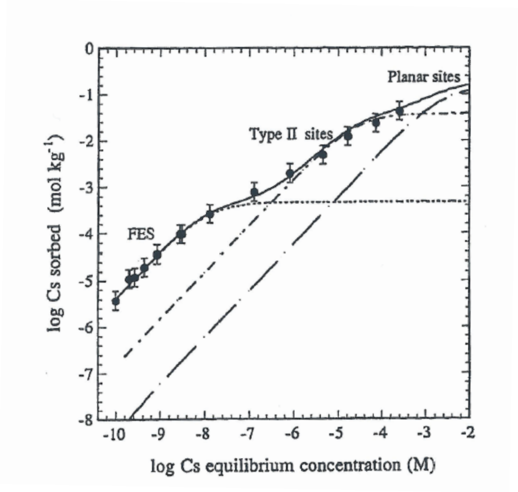
- Sorption in argillaceous rock dominated by illite
- 3 site types for Cs sorption on illite, fixed ratio (from model parameterization)
  - planar sites (~ as on montmorillonite, high capacity/low affinity)
  - frayed edge sites (FES, high affinity/low capacity)
  - type-II sites (high affinity/low capacity, evidence from NMR)
- Simple ion exchange with selectivity coefficients specific for illite
  → Cs sorption on FES reversible with respect to exchange against K^+ & NH_4^+ but nearly/completely irreversible with respect to Na^+/Ca^{2+}
- Cs mainly at FES & type-II sites when [Cs] < ~10^{-3} M

"reversible sorption"

"irreversible sorption "

Cs Sorption / Desorption - Simple Systems

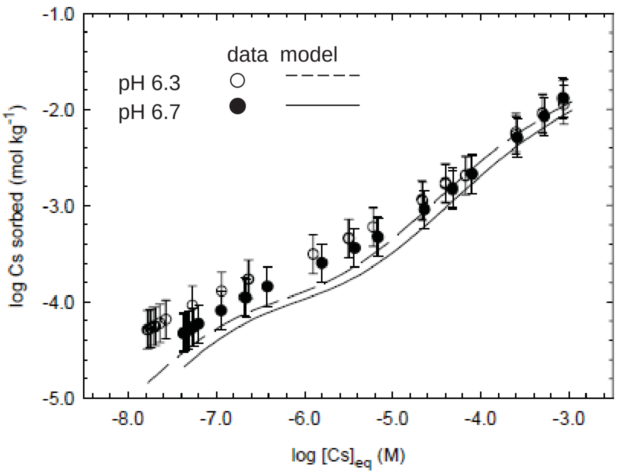
Reference Illite



Na-illite de Puy, 0.1 M $NaClO_4$,
from Bradbury and Bayens 2000)

Application Opalinus Clay

(illite smectite, mixed layer I/S
chlorite, kaolinite, quartz, carbonates)



from Lauber et al. 2000, in synthetic porewater

Cs Mobility and Fate - a few Examples

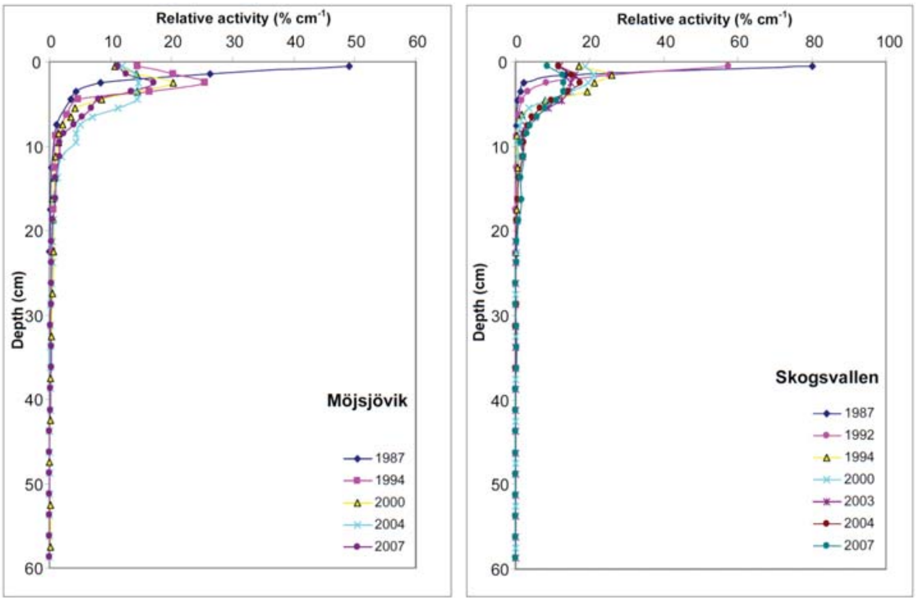
Chernobyl fallout - example from Sweden (Persson 2008)

- 21 years after the accident, most Cs still present in the upper 10 cm
- Comparisons with earlier studies suggest decreasing migration rates (0.2-0.5 cm/a at present) and a strong decrease in availability/plant uptake

→ Factor 10-20 decrease of migration near Fukushima after ~3 mt. (Shiozawa 2013)

- Transfer to plants highest in organic soils, lowest in clay soils
- Migration rate not clearly linked to soil property, but to hydrology (biology)

from Persson 2008



Cs Mobility and Fate - a few Examples

Long-term deposition - 80 y soil archive in France (Monna et al. 2009)

- Main mechanism of ^{137}Cs removal is radioactive decay, Cs migration is less relevant
- Cs migration was highest in plots treated with K-fertilizer, possibly due to blocking of exchange sites by K

Hanford contaminated sediments (e.g. Zachara et al. 2002)

- Sediments contain weathered micas, chlorite, vermiculite, smectite and are influenced by chemistry of liquid waste (Na-brine)
- Cs was sorbed on low- & high-affinity sites,
  - most high-affinity sites present on weathered mica (EMP)
  - sorption could be described with an ion exchange model similar to PSI-model
  - overall selectivity similar to illite
- At very high salt concentrations, Cs migration is most extensive. While Cs sorbs only to high affinity sites, Na^+ is competing efficiently under such conditions.

Approaches to Cs Transport Modeling in Soil/Subsurface

Physical/chemical models

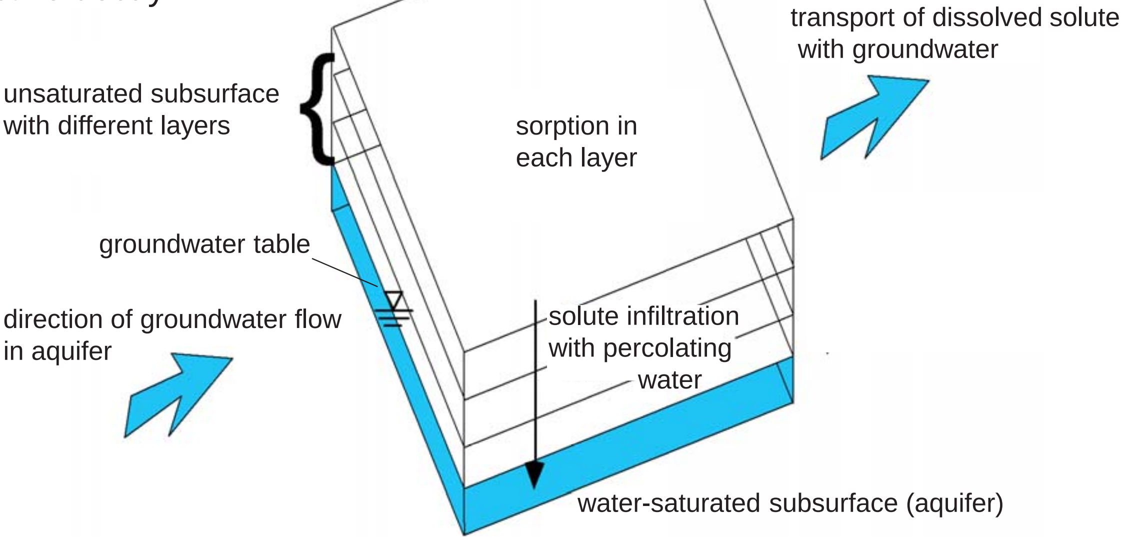
- Address the vertical (downward) transport in a soil column and/or subsequent transport in underlying strata (aquifer) through advective/dispersive flow.
- Retention often handled through fix (conditional) K_d values or retardation coefficients. Some models consider chemical reactions explicitly (reactive transport)

Transfer models

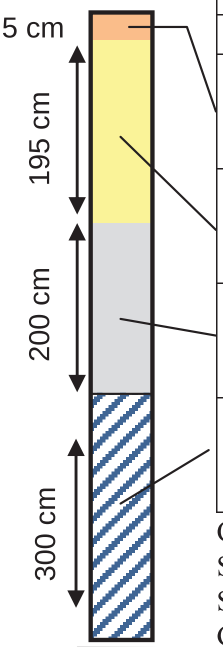
- Not aimed at describing physical/chemical processes
- Use of macroscopic transfer functions or rates to describe the movement of e.g. Cs from one environmental compartment to another.
- Transfer functions/rates often lump many processes together

Cs Mobility in Soils & Aquifers - a Simple Illustration (BMG report to JAEA)

- downward transport in soil by advection/dispersion
- horizontal advective/dispersive transport in aquifer
- fix K_d for each model compartment (no reactive transport)
- no radioactive decay



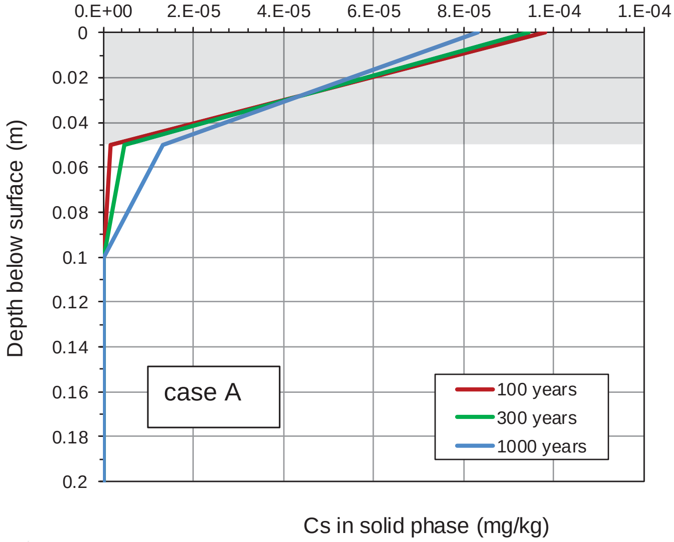
Cs Mobility in Soils & Aquifers - a Simple Illustration

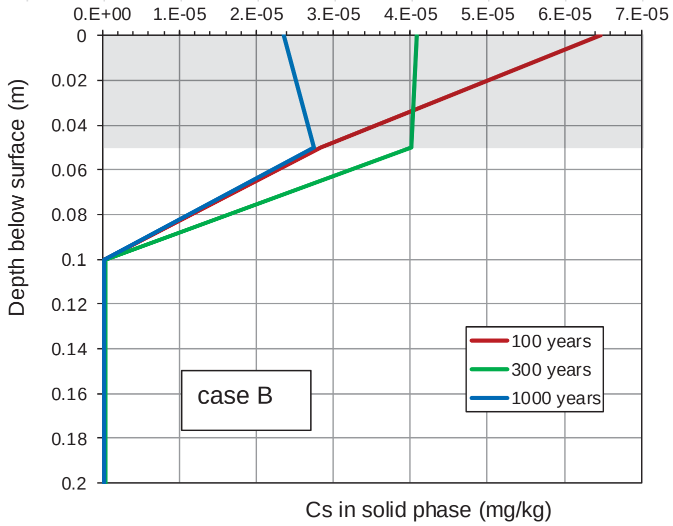


parameter	case A	case B	case C	case D
initial Cs mass in top layer(mg)	0.875	0.9	0.9	0.91
top layer (unsaturated) hydraulic conductivity (m/s) K_d Cs (m^3/kg)	• CL • 1E-09 • 5	• SM-ML • 5E-07 • 5	• SM-ML • 5E-07 • 0.1	• SW • 5E-04 • 0.1
2nd layer (unsaturated) hydraulic conductivity (m/s) K_d Cs (m^3/kg)	• SW • 5E-04 • 0.05	• SW • 5E-04 • 0.05	• SW • 5E-04 • 0.001	• SW • 5E-04 • 0.001
3rd layer (unsaturated) hydraulic conductivity (m/s) K_d Cs (m^3/kg)	• GW • 5E-03 • 0	• GW • 5E-03 • 0	• GW • 5E-03 • 0	• GW • 5E-03 • 0
aquifer (saturated) hydraulic conductivity (m/s) K_d Cs (m^3/kg)	• GW • 5E-03 • 0	• GW • 5E-03 • 0	• GW • 5E-03 • 0	• GW • 5E-03 • 0

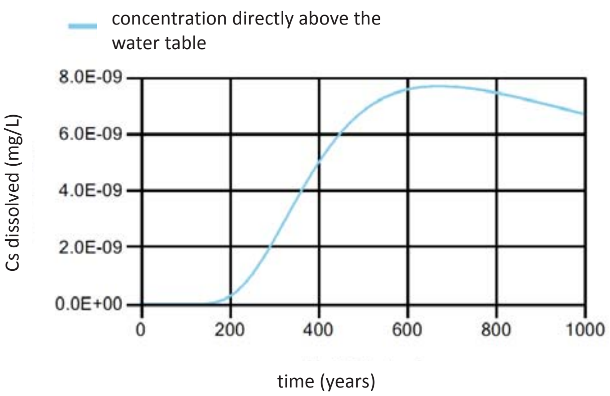
CL clayey soils (clays, gravelly or sandy clays)
SM-ML silty to clayey sand
SW well graded, fine to coarse sand
GW well graded, fine to coarse gravel

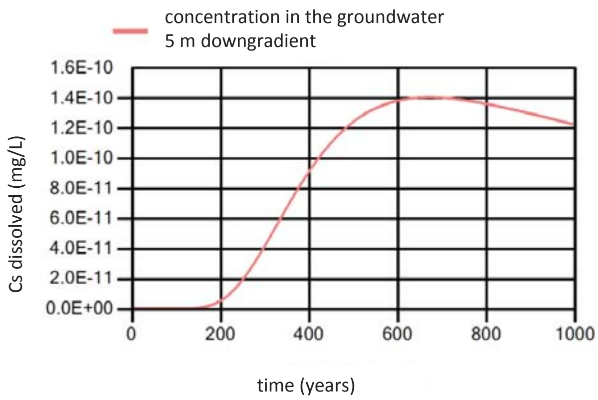
Cs Mobility in Soils & Aquifers - a Simple Illustration

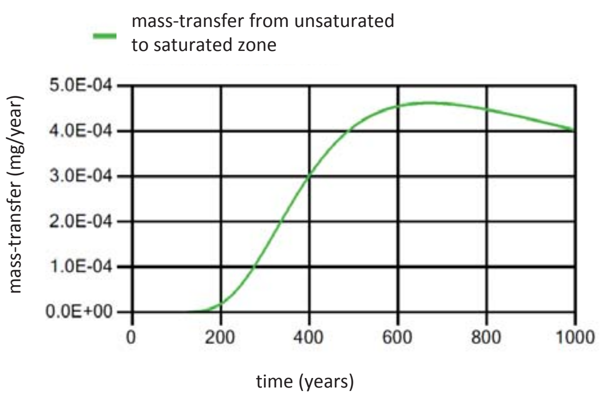


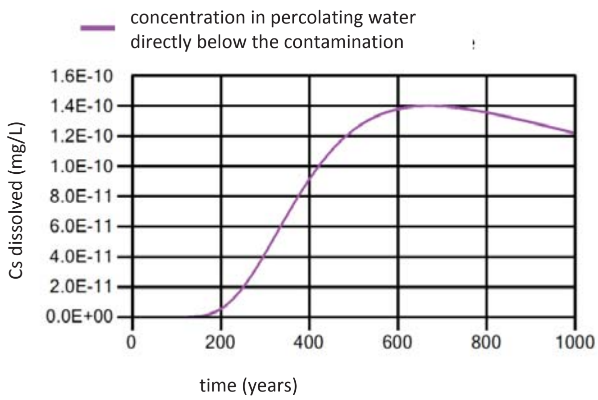


Cs Mobility in Soils & Aquifers - a Simple Illustration

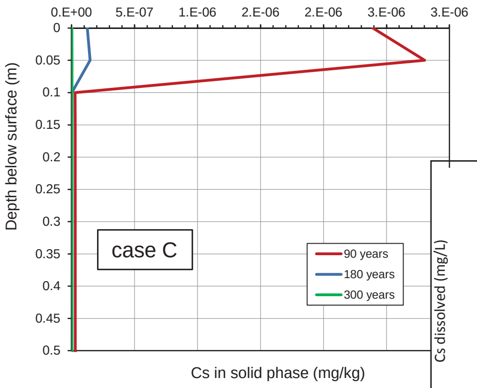


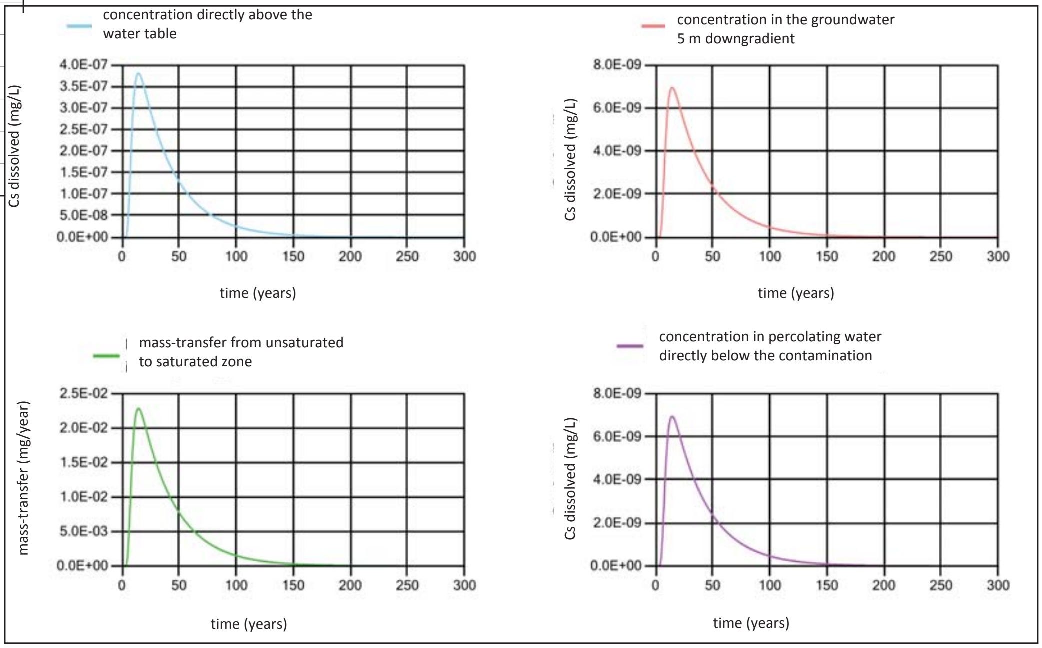






Cs Mobility in Soils & Aquifers - a Simple Illustration





Status / Potential relevance regarding Cs-contamination in Fukushima area

Cs mobility

- experience suggests that fixation of Cs in soil may become stronger with time
  → monitoring to confirm (careful extractions, plant uptake…)

- Cs is likely to be not very mobile and remain in top soil layer, and decay may be most efficient mechanism for 'removal'
  → monitoring (profiles)

- Sorption of Cs on clay substrates can be approximated as reversible may be modeled (directly or by estimating K_d) with ion exchange models, given that
  - high-affinity sites are included (→ reversibility with respect to few other ions)
  - sufficiently long timescales are being considered
  - low concentrations are concerned (→ no change of mineralogy)

  → could be refined/demonstrated with Fukushima soils or mineral separates
  → reversibility/kinetic aspects need to be tested/verified with site-specific samples
  → especially weathered micas may need more efforts than 'normal' illite

Status / Potential relevance regarding Cs-contamination in Fukushima area

Cs mobility

- Retention/mobility of Cs as a function of geochemical conditions can be reasonably well estimated/modeled
  → system understanding should be tested / demonstrated

- risk may be related to immobilized Cs and direct (soil /dust ingestion) or indirect (plants, milk…) intake, and less to transport of (dissolved) Cs to important aquifers
  → transport of dissolved Cs to important water resources could be estimated
  → monitoring of critical pathways

this is different from e.g. surface runoff

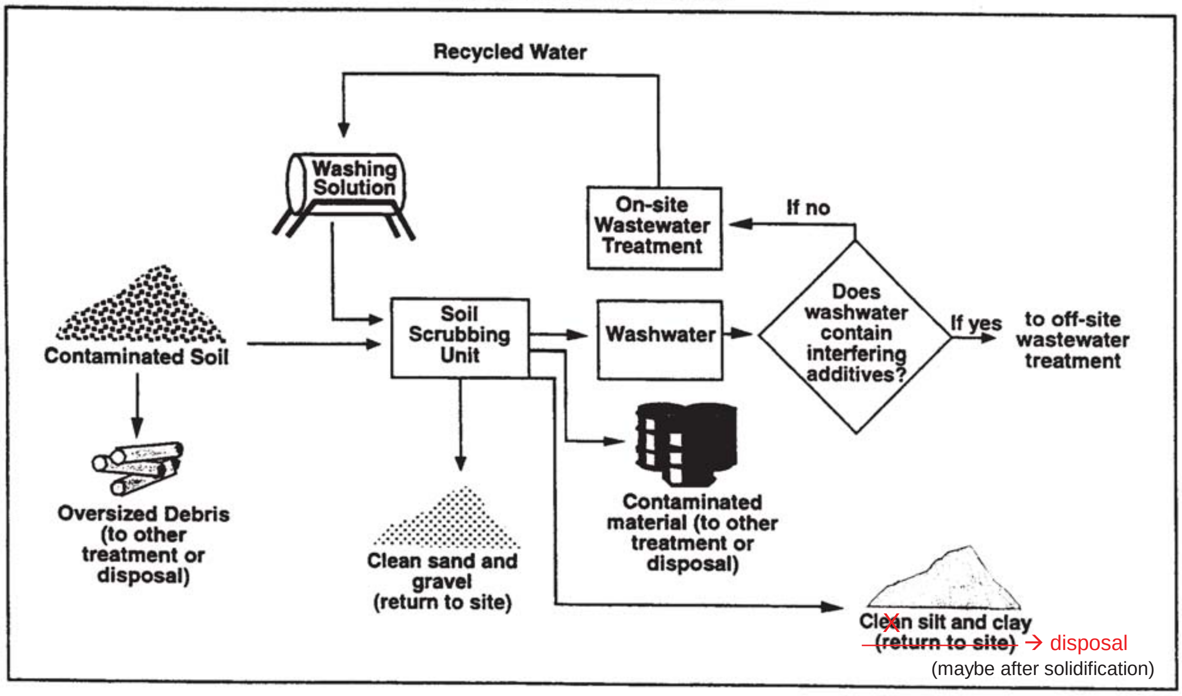
→ Cleanup

- Extraction of Cs is difficult (high K, NH4 … concentration can be counterproductive)
- As Cs is nearly exclusively bound to clays, wet/dry mechanical separation of fine fraction of soils (often few percent) could be efficient for removing Cs and reducing the volume of excavated soil
- Size fractionation (soil washing) fairly established process
  (needs to be optimized for each soil type)

Status / Potential relevance regarding Cs-contamination in Fukushima area

Cleanup

The Soil Washing Process (USEPA 1996)



Status / Potential relevance regarding Cs-contamination in Fukushima area

Cleanup

Status / Potential relevance regarding Cs-contamination in Fukushima area

→ Agricultural practices

- K- or NH_4-amendments most likely to have an effect (+/- depending on conc.…)

and a very general remark at the end (not restricted to Cs behavior…)

→ Communication (again)

- strong fear of radiation (and subsequent PTSD) is a real health concern (a conclusion of an UNSCEAR assessment of Chernobyl)
- careful, correct, continuous …as few contradictions as manageable