Norwegian University
of Life Sciences

Norwegian Institute of Public Health

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CERAD

CENTRE FOR ENVIRONMENTAL RADIOACTIVITY

Norwegian
Meteorological
Institute

Statens strålevern
Norwegian Radiation Protection Authority

Comet Field Course, Kiev, September, 2016

Senter for fremragende forskning

Sequential extraction to estimate mobility

Norwegian University
of Life Sciences

Brit Salbu
NMBU/CERAD CoE

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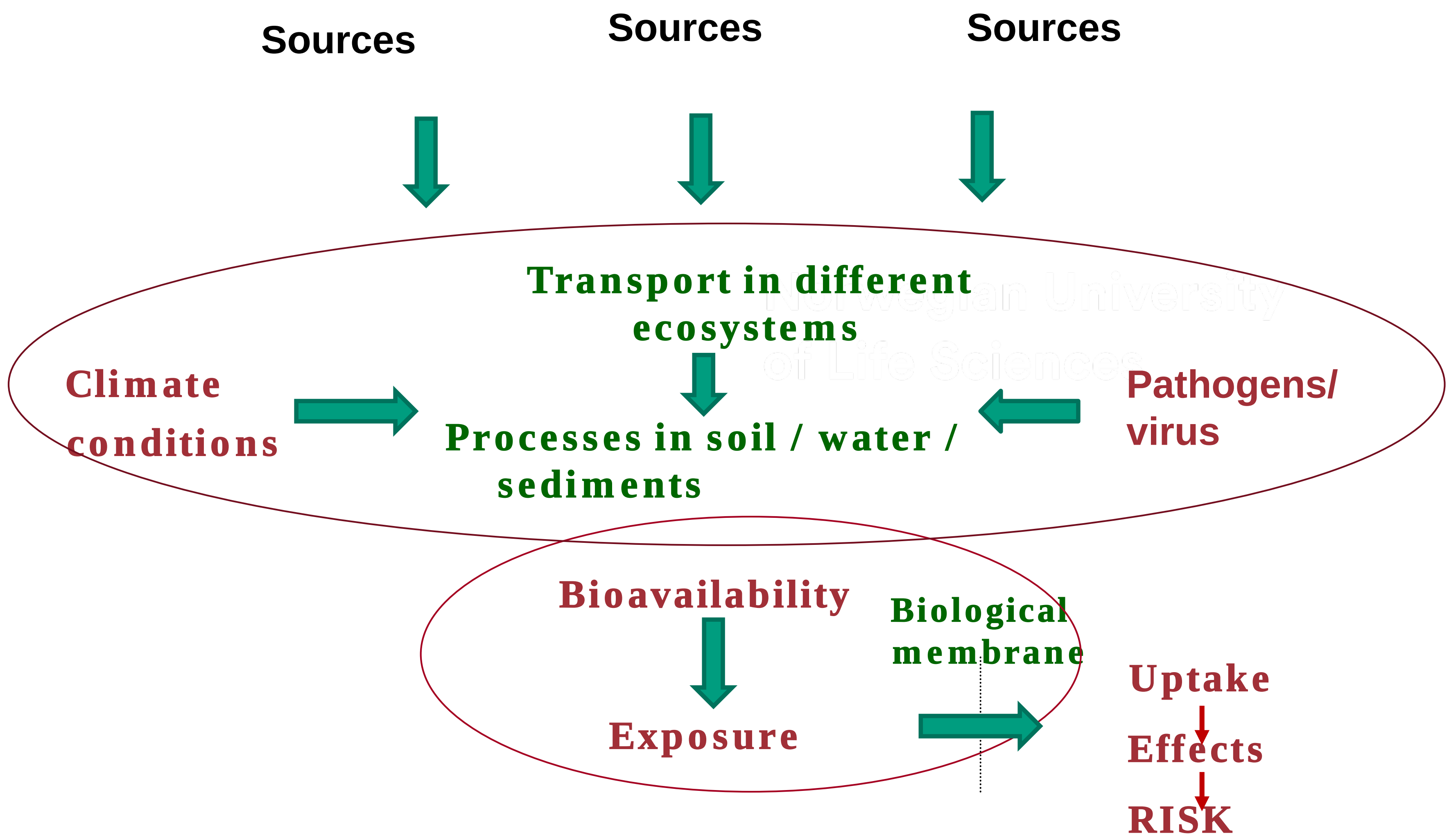
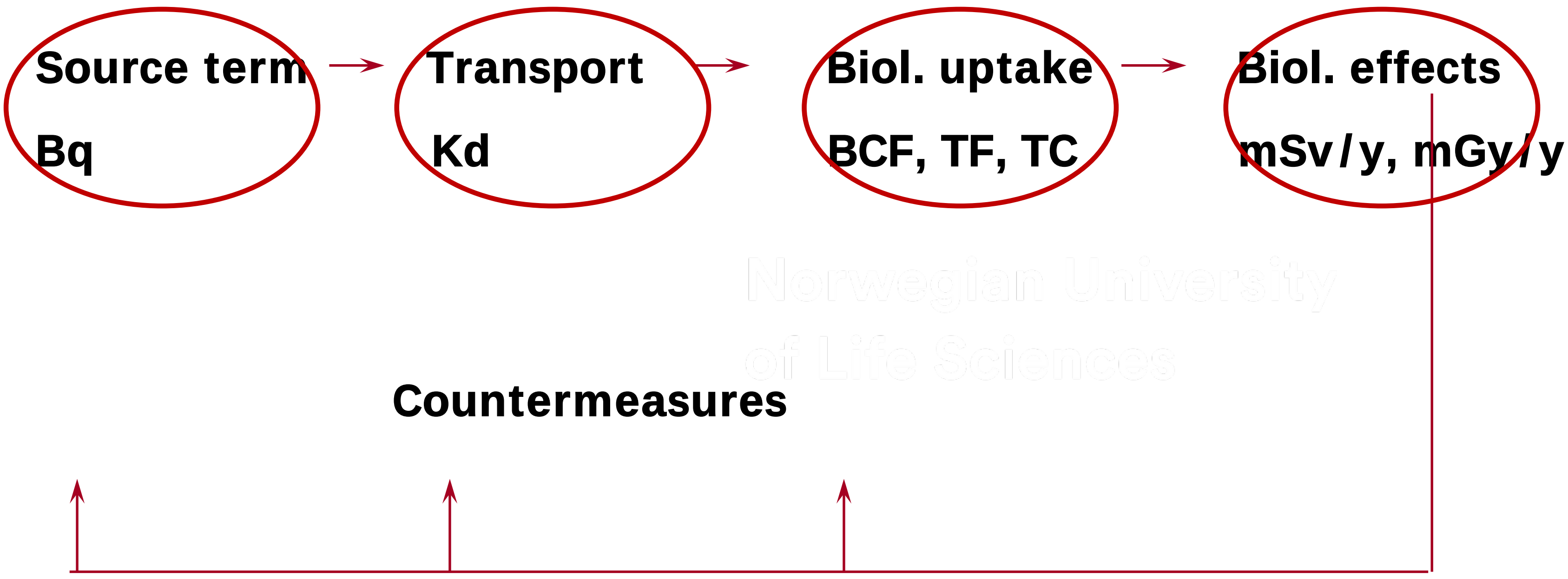
brit.salbu@nmbu.no

Radionuclides released from sources – ecosystem transfer – effects - risk



Source term - ecosystem transport – uptake - effects



Short and long term dose, impact and risk assessments

Focus: Factors contributing to uncertainties in the:
Source term/deposition, Ecosystem transfer, and effect estimates

Kd reflecting mobility

- Distribution coefficient, K_d, for the distribution of radionuclides in water and in soil/sediments
  - Kd = Bq per kg in soil/Bq per litre water

- Assumptions
  - Equilibrium conditions in the environment?
  - Assumed reversible processes – LMM species?

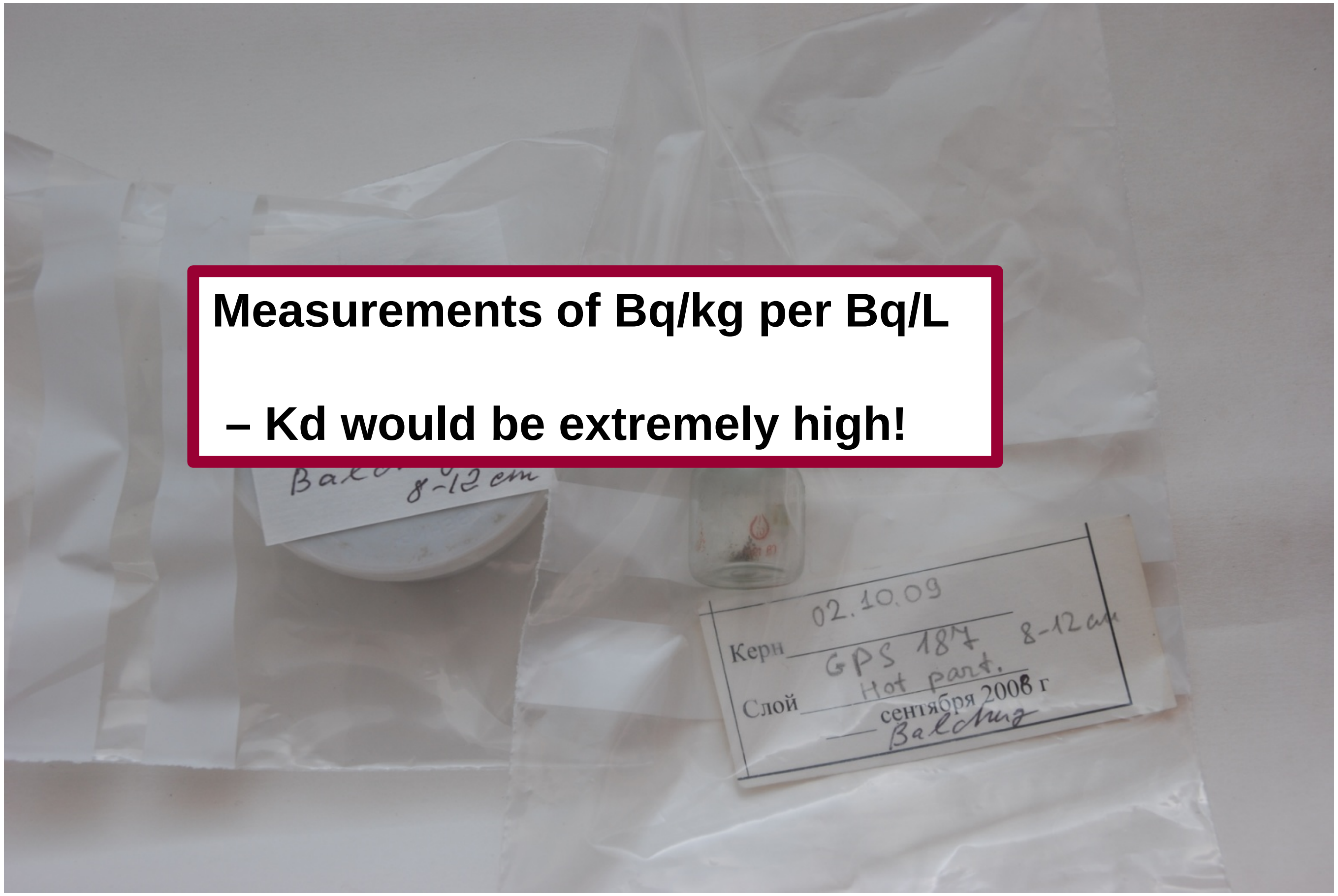
Concept

- What is Bq?
  - What is actually moving in the ecosystem?

- What does mobility mean?
  - What kind of interactions are we considering?
  - Retained in soil of sediment?
  - Able to remobilize?
  - Which species can do so?

Isolation of radioactive ^{137}Cs particles from soils
Sample splitting combined with γ-spectrometry

NMBU



Measurements of Bq/kg per Bq/L

– Kd would be extremely high!

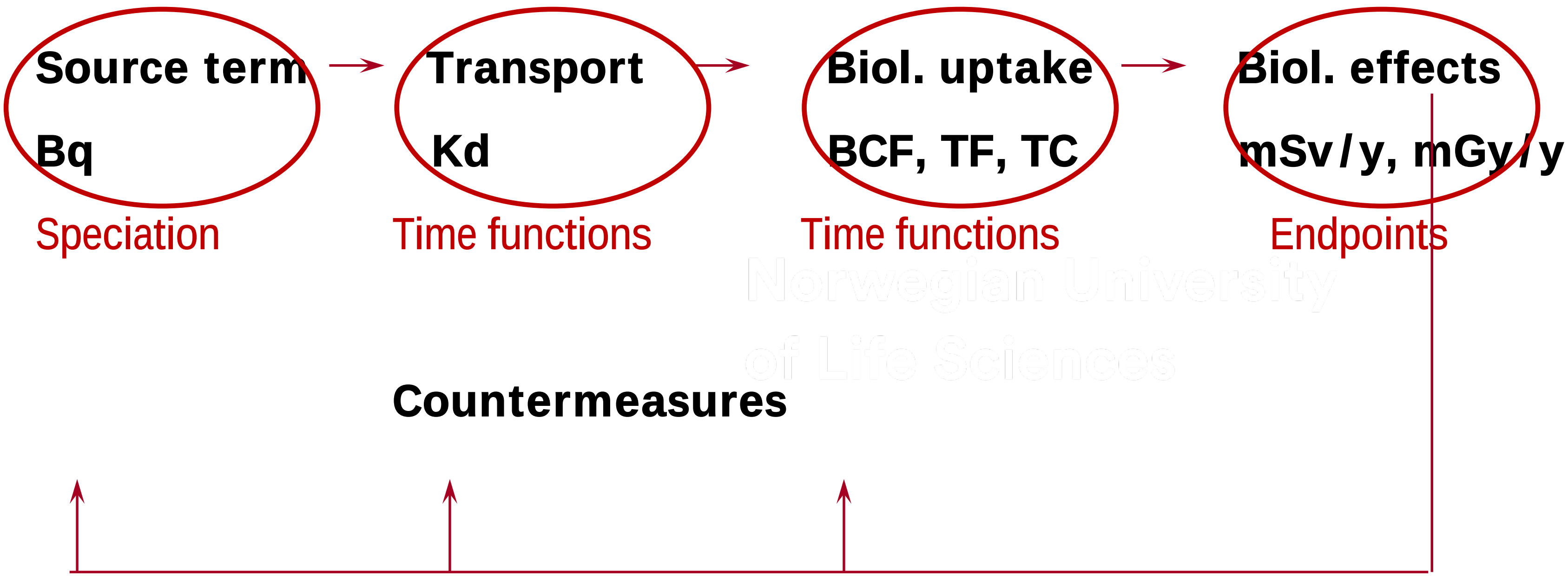
Bulk (minus particle): ~100 g
~40 counts per second
(NaI detector)

Sample splitting →

Isolated grains of soil incl. particle: mg
~60 000 cps -99,95%
436 000 Bq ^{137}Cs

Senter for fremragende forskning

Predicting power of models depends on the uncertainties: Source term - ecosystem transport – uptake - effects



Short and long term dose, impact and risk assessments

Focus: Factors contributing to uncertainties in the:
Source term/deposition, Ecosystem transfer, and effect estimates

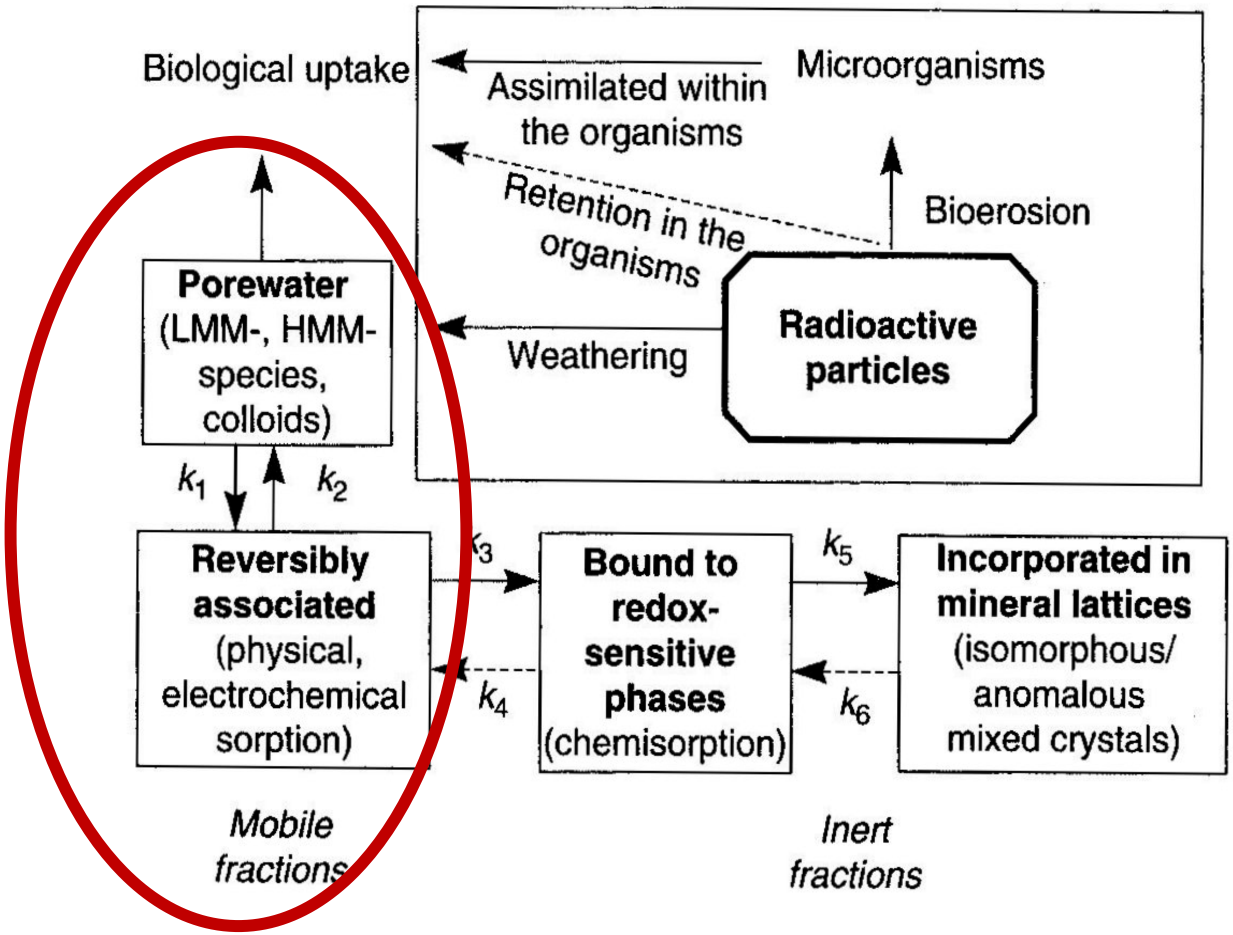
Transfer – traditions from the 1960ies

1. **Total activity concentration in soils or sediments** Bq/kg (dry weight or even wet weight??). No speciation, nor particle identification (acid rain and toxic Al)
2. **Total activity in water** Bq/L, without excluding particles, i.e. 0.45 micrometer filters used for dissolved trace elements
3. **Kd – transfer soil to water:** Total activity concentration in soils or sediments/ Total activity in water Bq/L, assumed that soil/water distribution coefficient is constant
4. **TF – transfer from soil to plant:** Total activity concentration plant/total activity concentration soil – assumed to be constant
5. **Transfer from plant to animal**. Total activity concentration in produce/total concentration fed/day x days

NB: Total activity concentrations applied (no speciation) and equilibrium conditions assumed (no dynamics)

Kd reflecting mobility

- Distribution coefficient, K_d, for the distribution of radionuclides in water and in soil/sediments
  - Kd = Bq per kg in soil/Bq per litre water
- Assumptions
  - Equilibrium conditions in the environment?
  - Assumed reversible processes – LMM species?
- Problems
  - Apparent Kd based on total activity concentrations may not reflect reversible species
  - Different species in the soils – particles and colloids retained
  - Apparent Kd will be overestimated, and can change with time due to particle weathering



- The term “mobile species” in soils and sediments refers to LMM species, e.g. ions or complexes soluble in soil water and species reversibly associated with solid surfaces.
- The term “inert species” includes radioactive colloids, pseudocolloids and particles deposited in soils or sediments, as well as radionuclides irreversibly bound to or incorporated into mineral lattices.

- The systems are dynamic; equilibrium may establish relatively rapidly between LMM forms in soil solutions and species reversibly associated with surfaces of solids, but slowly for species penetrating diffuse double layers of colloids and particles into mineral lattices.

Sequential extraction – estimating mobility

- To predict the persistence and potential mobility/ bioavailability of radionuclide/heavy metal contamination in soils and sediments.
- important for predictive models and environmental assessments

- Heavy metals/radionuclides associated with exchangeable phases, are assumed to be easily mobilized by ion exchange reactions and are therefore available for root uptake.
- Pollutants associated with oxidized phases, are assumed to be exchangeable.
- Pollutants associated with inert phases (e.g., chemisorption) remain in the soil for longer periods, but can be mobilized by decomposition processes (*e.g., weathering and microbial activity*).

METHODS - DESTRUCTIVE TECHNIQUES

- TOTAL CONCENTRATION by radiometric methods and mass spectrometry (ICP-MS, AMS, SIMS etc)
  - Full dissolution/acid leaching
  - Radiochemical separations
- LEACHING EXPERIMENTS to estimate potential mobility and bioavailability
  - Sequential extractions, increasing displacement/dissolution power
  - Solubility in biologically relevant fluids (e.g. stomach juice)
- SOURCE IDENTIFICATION by radiometric methods and mass spectrometry
  - Determination of isotopic ratios which can be used as fingerprints for different sources (U, Pu)

K_D variation f(t) - pseudo-equilibrium conditions

Processes	Model
Physical sorption	Multi layer model Freudlich
Electrostatic sorption Chemisorption	Monolayer model Langmuir
Exchange reactions	Heterogeneous systems

Sorption mechanisms – important for mobility

Physical sorption	**Consecutive layers reversible**
Electrochemical sorption	**Monolayer reversible**
Chemisorption	**Monolayer irreversible**

Inert electrolyte

↓

Ionexchange pH

↓

red/ox

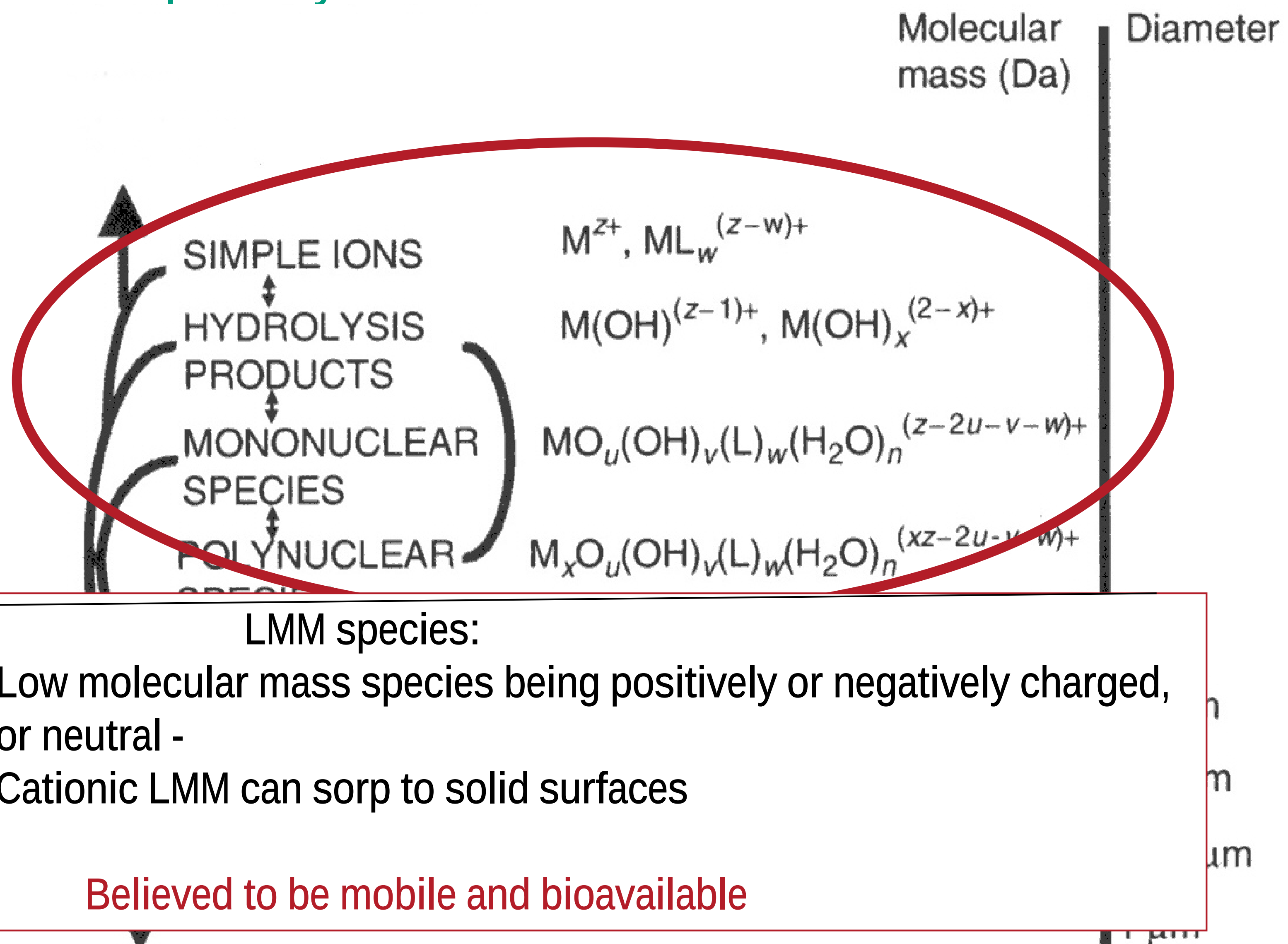
Strategy: sequential extractions

Increased dissolution power of agent

Sequential extraction
– processes, models, agents and reagents

Processes	Model	Agents	Reagents
Physical sorption	Consecutive layers, reversible reaction	Indifferent (inert) electrolyte	H2O NH4OAc, soil/ sediment pH
Electrostatic sorption	Monolayer, Reversible reactions	Ion-exchangeble species, increased acidity (pH)	pH<soil/sediment NH4OAc, pH5
Chemisorption	Monolayer, Irreversible reaction	Red/ox agents, increase in temperature	Weak reducing: NH2OH•HCl Weak oxidizing: H2O2, pH 2 Strong oxidizing: 7 M HNO3, 80°C

Size categories for different physico-chemical forms of radionuclides in aquatic systems



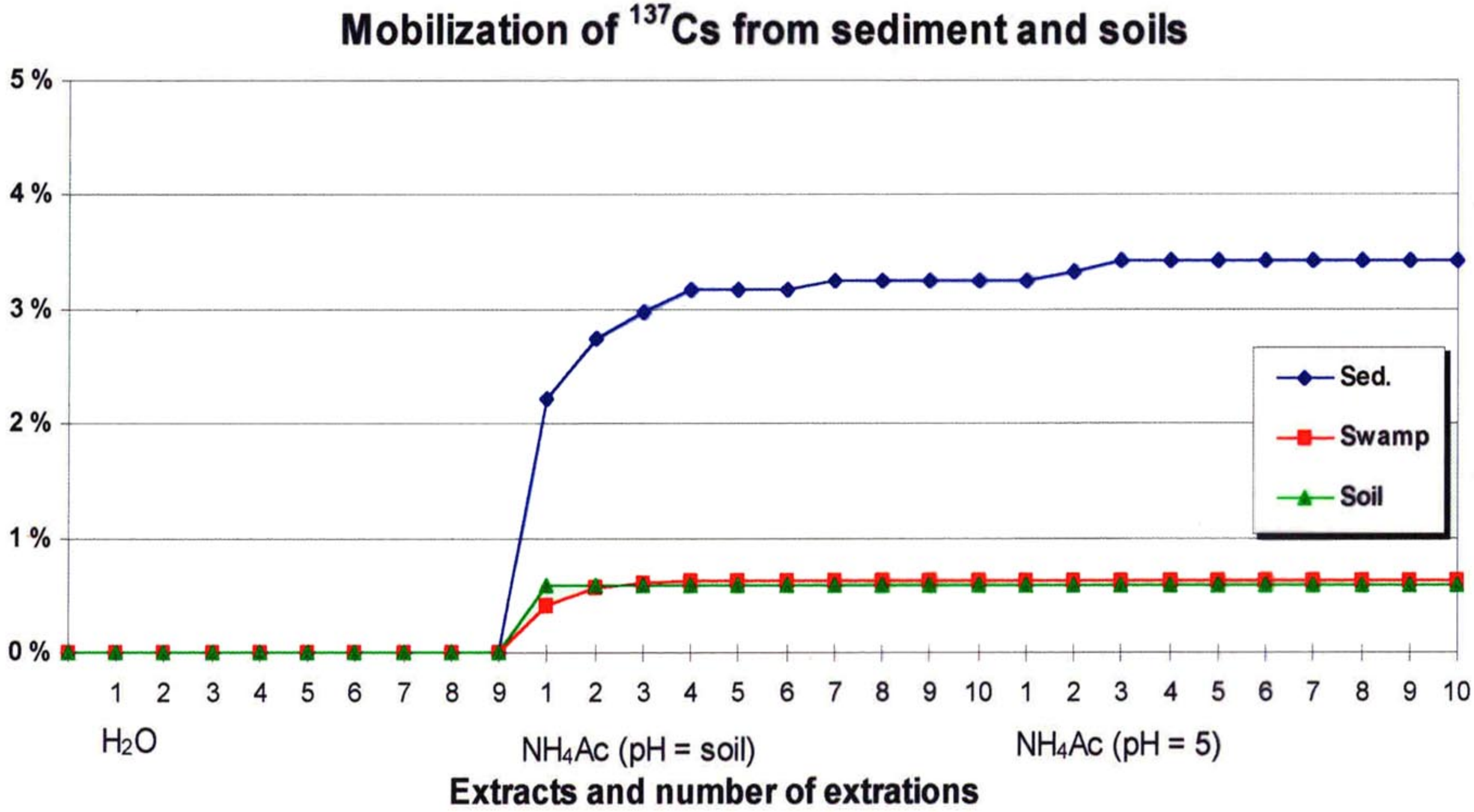
LMM species:

Low molecular mass species being positively or negatively charged, or neutral -

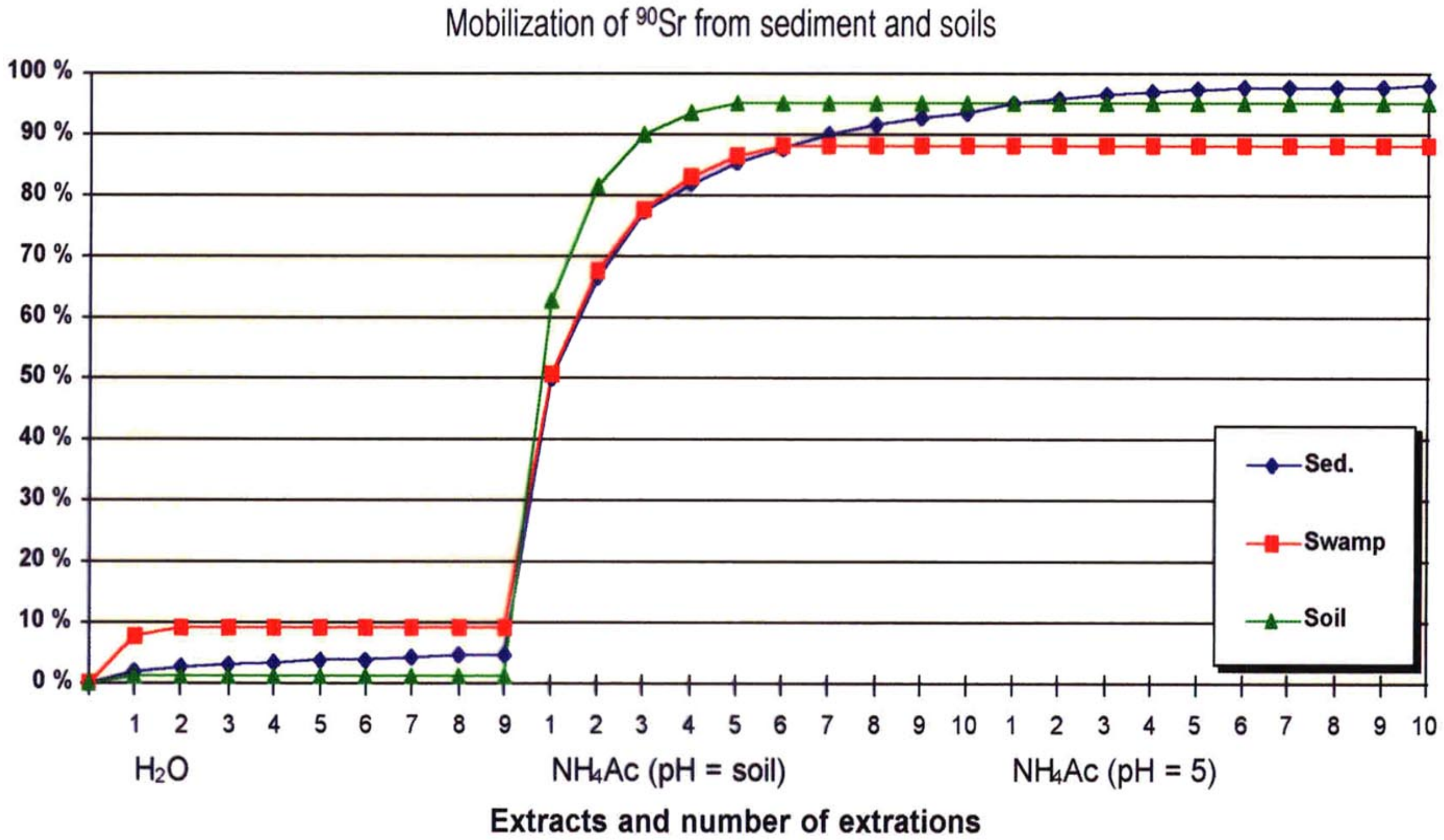
Cationic LMM can sorp to solid surfaces

Believed to be mobile and bioavailable

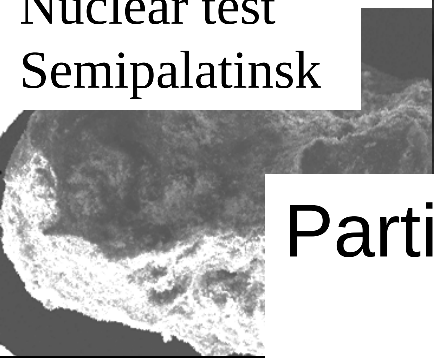
Release of ^{137}Cs following repeated extractions with water, NH_4Ac (soil pH), and NH_4Ac (pH 5)



Release of ^{90}Sr following repeated extractions with water, NH_4Ac (soil pH), and NH_4Ac (pH 5)

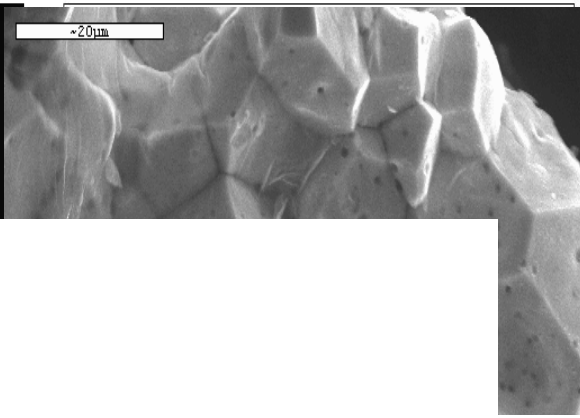


Radioactive particles released during "all" types of severe nuclear events. The source determines the composition, the release scenarios dictate particle properties


Nuclear test Semipalatinsk


Dounrey

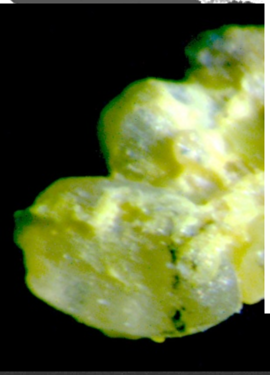

Sellafield

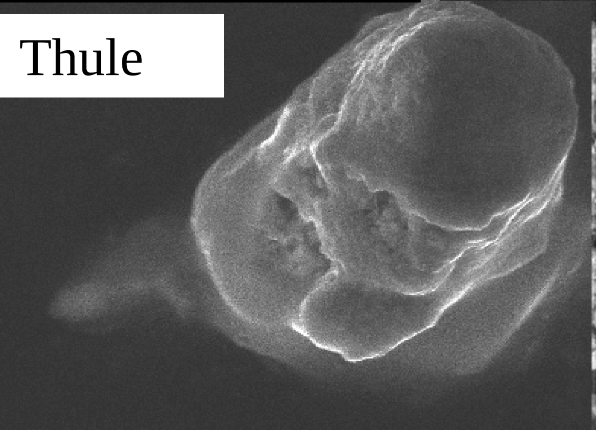


Particle deposition:

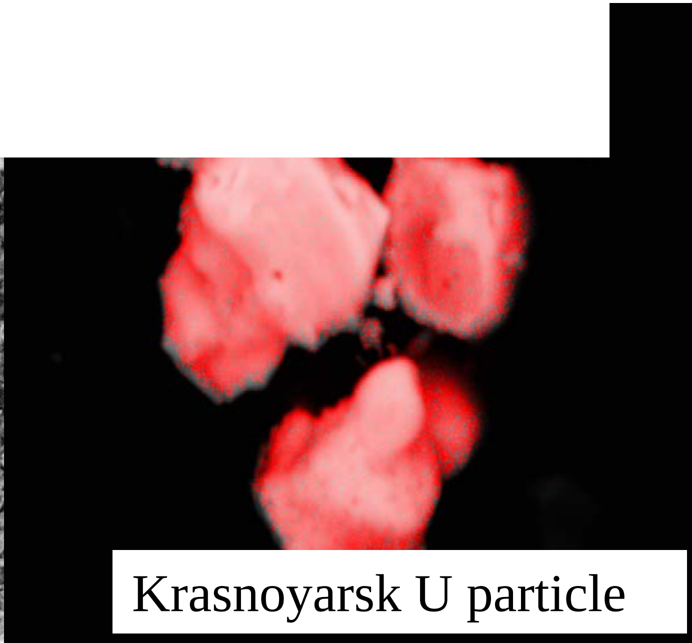
- Hot spots – problems with representative sampling
- Partial leaching – analytical errors - transuranics
- May underestimate the inventories

Adds significantly to the overall uncertainties



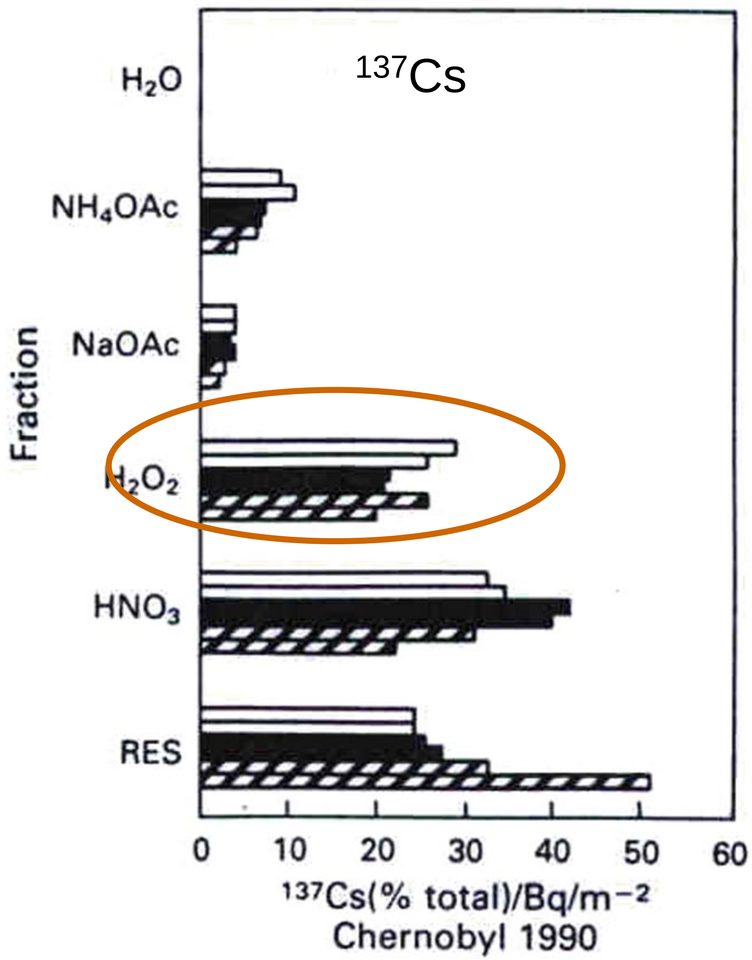

Thule

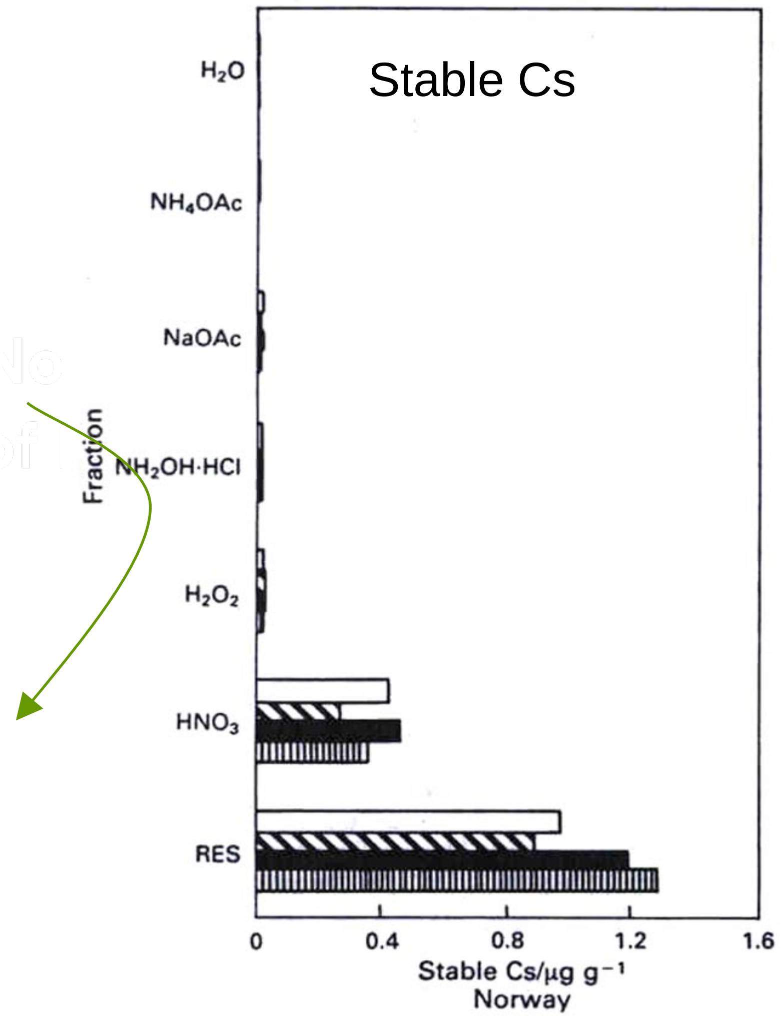

Corrosion product Waste in Kara Sea


Krasnoyarsk U particle

Source: Chernobyl soils containing particles
INFO: Sequential Extraction of Cs-137 and stable Cs

Weathering – predict decreased mobility and decreased doses

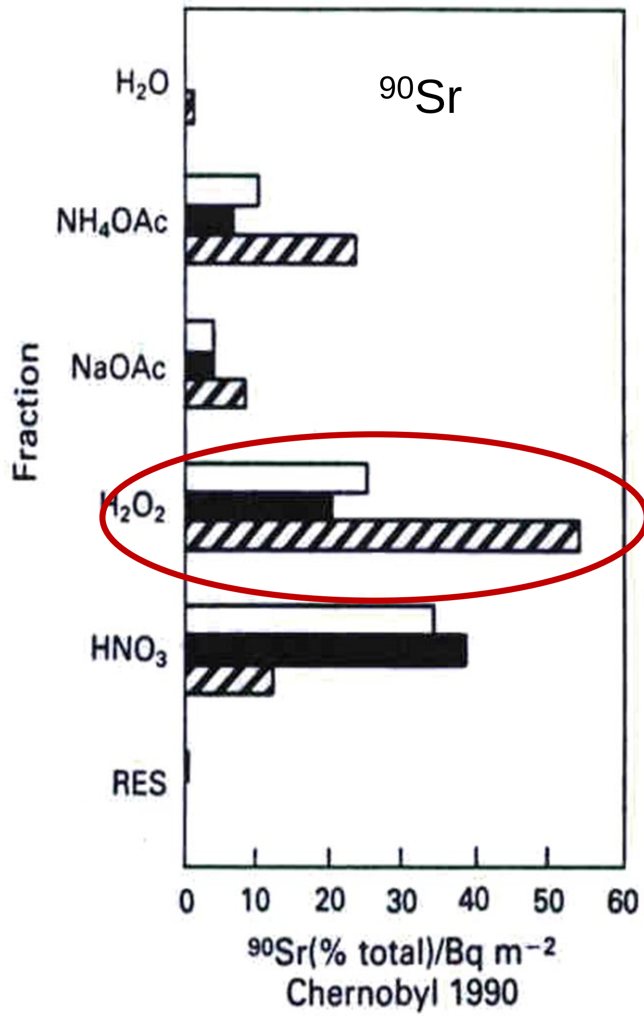


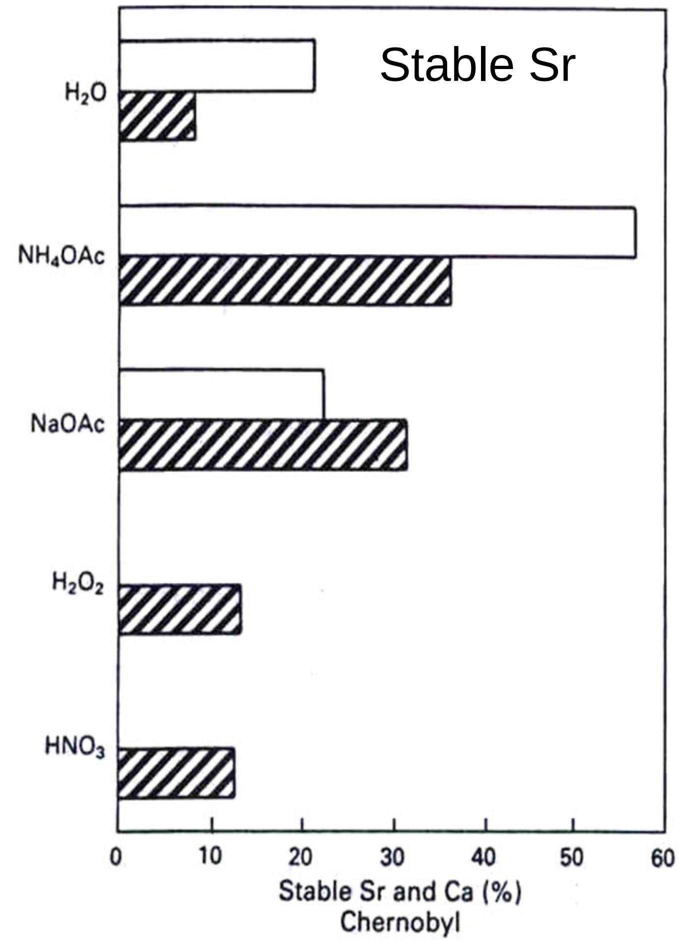


Oughton et al., *Analyst* 1992

Source: Chernobyl soils containing particles
INFO: Sequential Extraction of Sr-90 and stable Sr

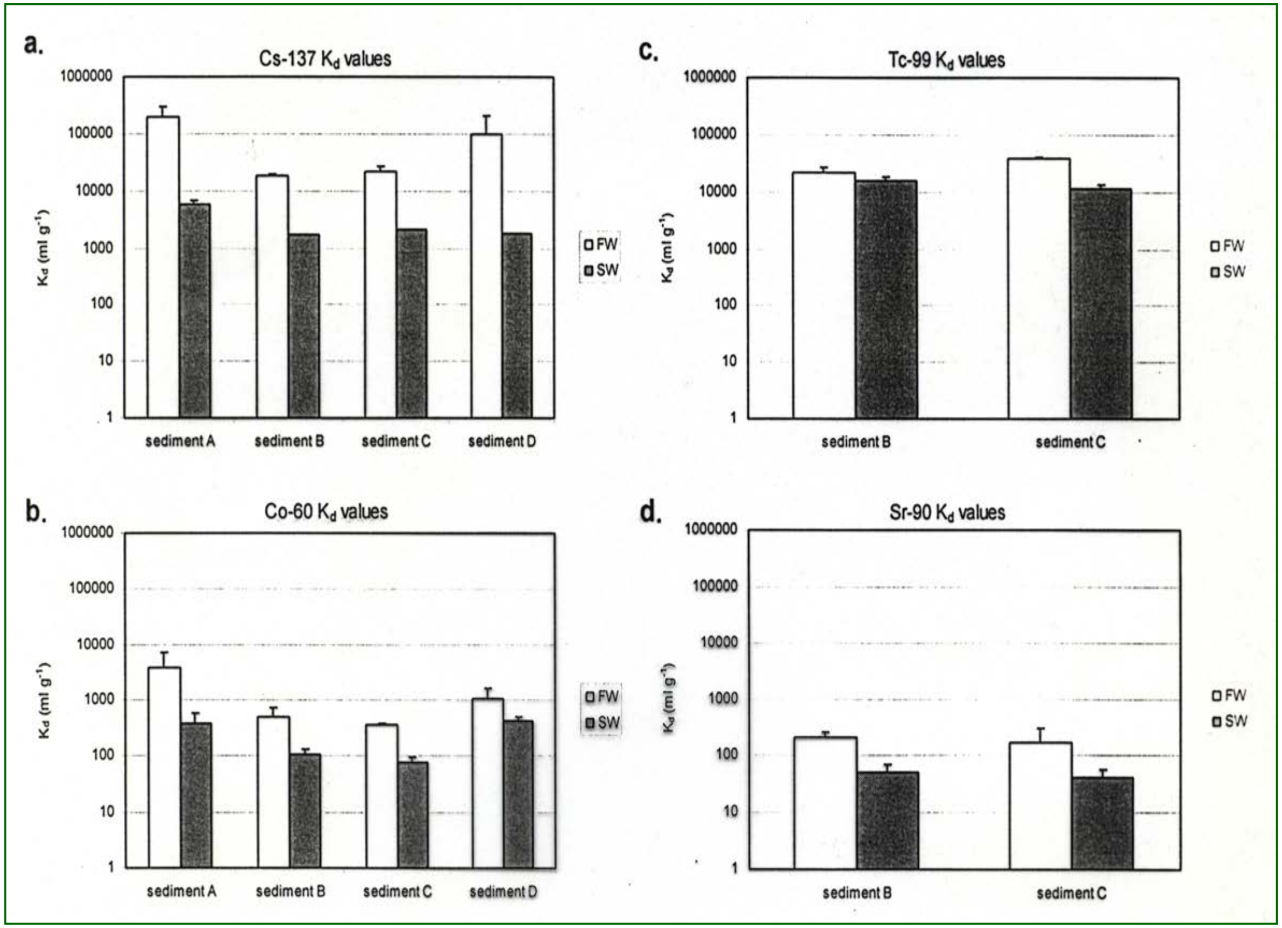
Weathering – predict increased mobility and increased doses





Oughton et al., *Analyst* 1992

Distribution coefficient (K_d) for radionuclides in Mayak reservoir 10 in contact with sea water

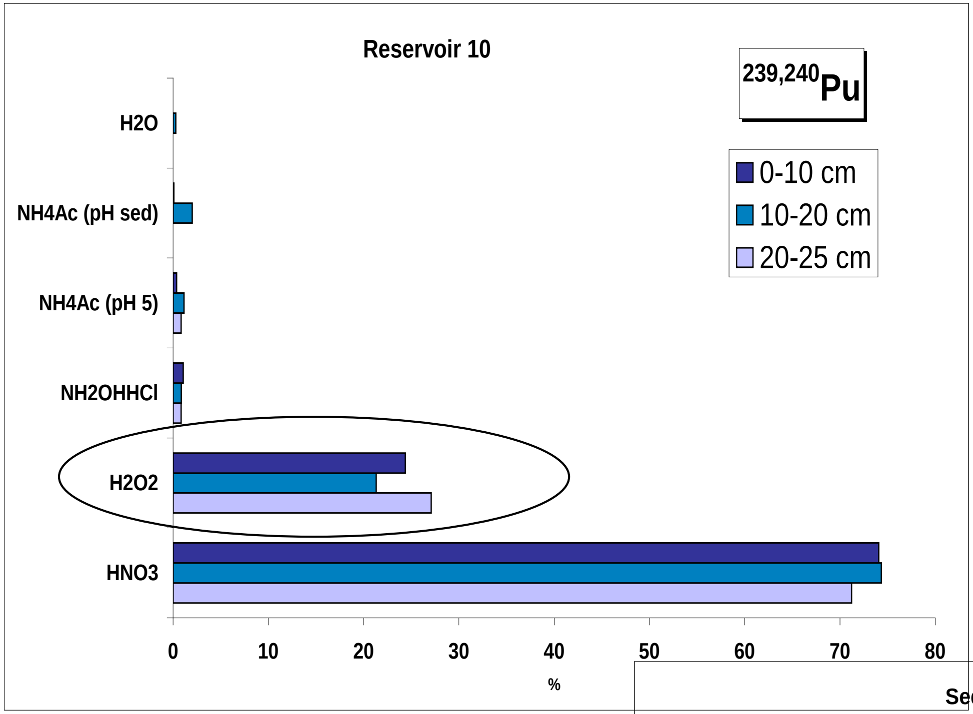


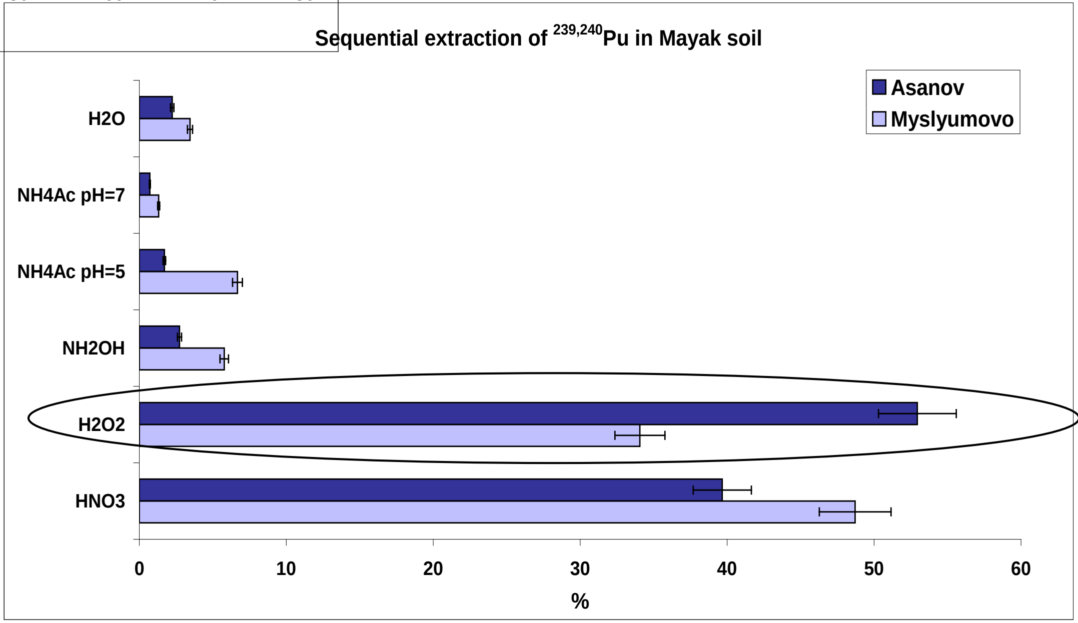
The distibution coefficient (K_d) decreased when Reservoir 10 sediments were transferred from a freshwater (FW 3) to a seawater (SW 1) environ-ment for

a) ^{137}Cs
b) ^{60}Co
c) ^{99}Tc and
d) ^{90}Sr

Remobilization in sea water

Pu speciation in Mayak samples
- different organic content



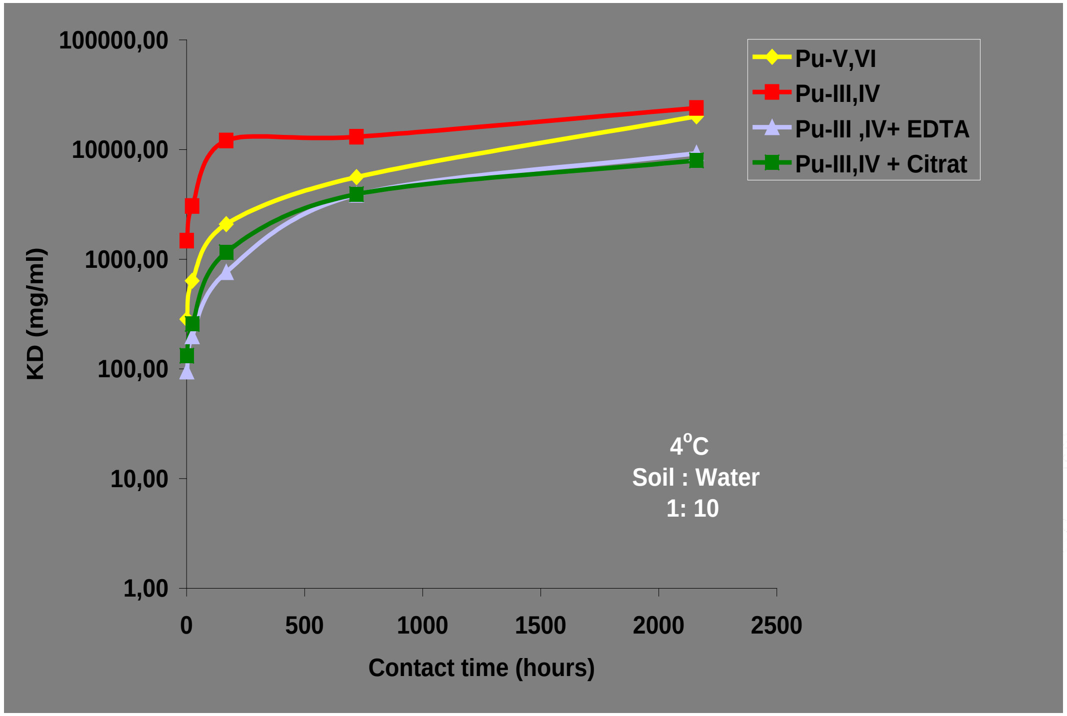


Skipperud, L., Oughton, DH., Salbu, B., Strand, P., Drozcho, E., and Mokrov, Y., (2004) "Plutonium contamination in soils and sediments at Mayak PA, Russia" *Health Physics*

Important to remember

- Reactions taking place in the laboratory during extraction are non-selective. They are likely to be influenced by the length of extraction time, separation technique, temperature and the mass:volume ratio used.
- Therefore, radionuclide and heavy metal concentrations measured in the extract solution are defined by the extractant and the experimental protocol.
- Fresh soil/sediment, not dried material
- Intrepretation
  - Interpret towards reagents used, not according to assumed phases

K_d for Pu species as f(t) in a soil-water systems

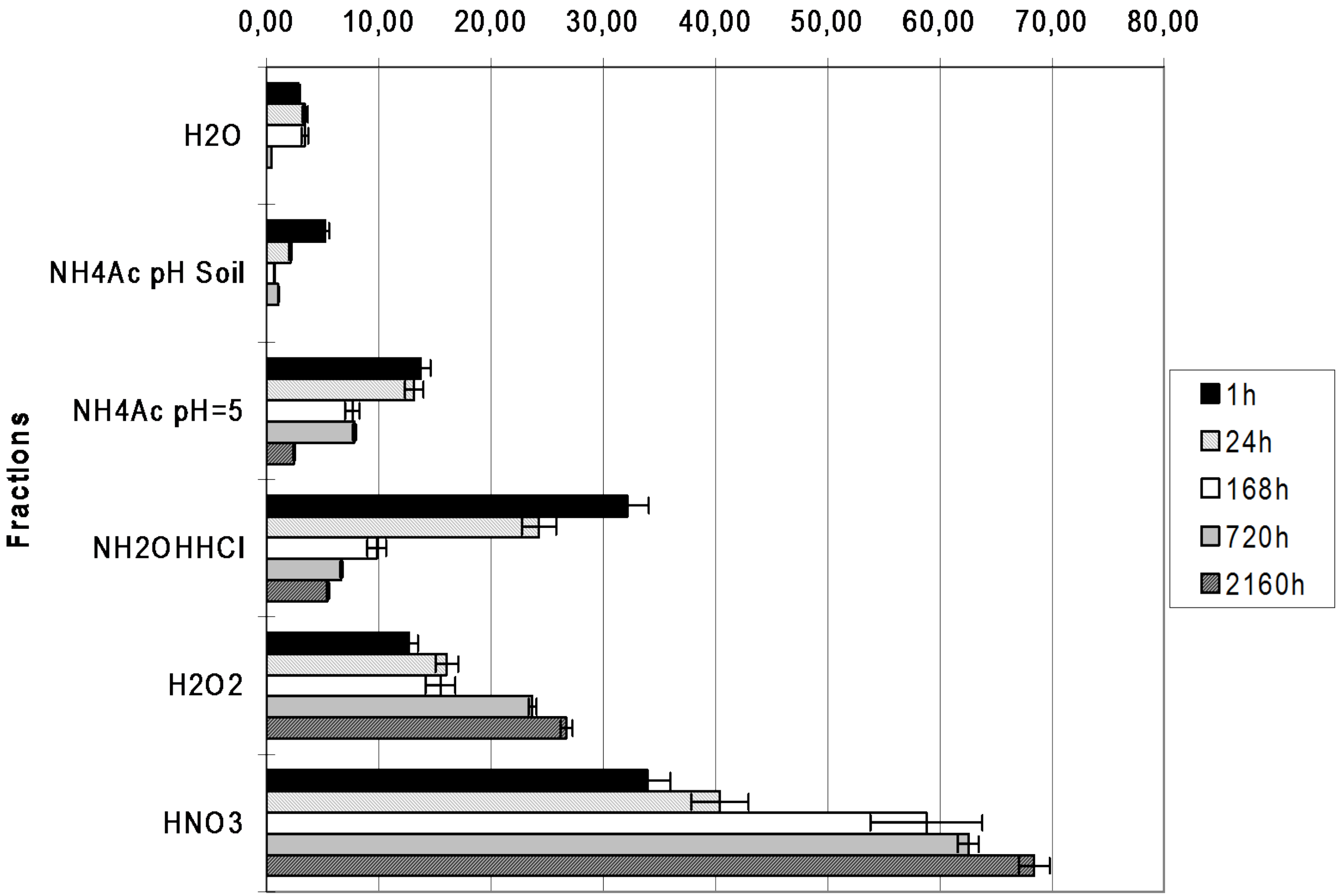


Speation:
Kd f(t) varies 1-2 orders of magnitude

Pu-species	T1/2 (d) Associated	T1/2 (d) Fixation
$Pu^{III,IV}$	0.4 ± 1 %	34 ± 7 %
$Pu^{V,VI}$	0.8 ± 10 %	40 ± 5 %
$Pu^{III,IV}$-organic	0.8 ± 1 %	39 ± 6 %

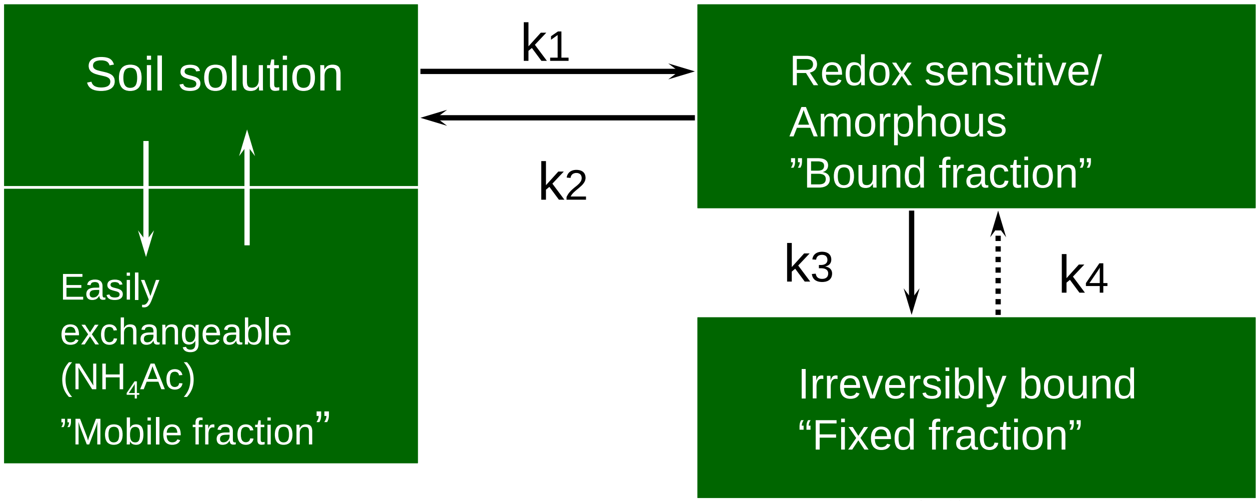
Skipperud, L., Oughton, D. H. and Salbu, B., (2000) *Science of the Total Environment*

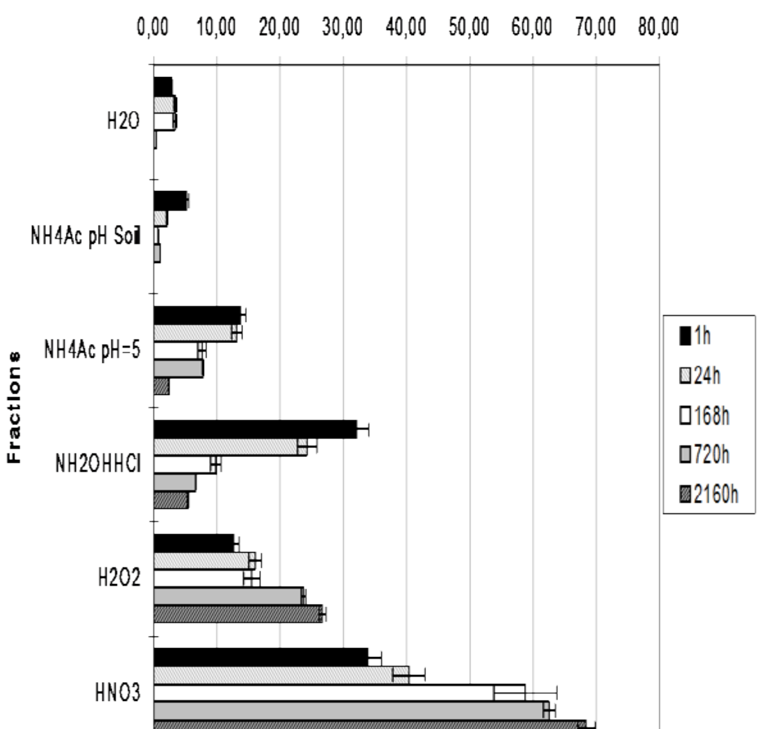
Distribution of Pu (%) in Soil-Water system as a function of contact time

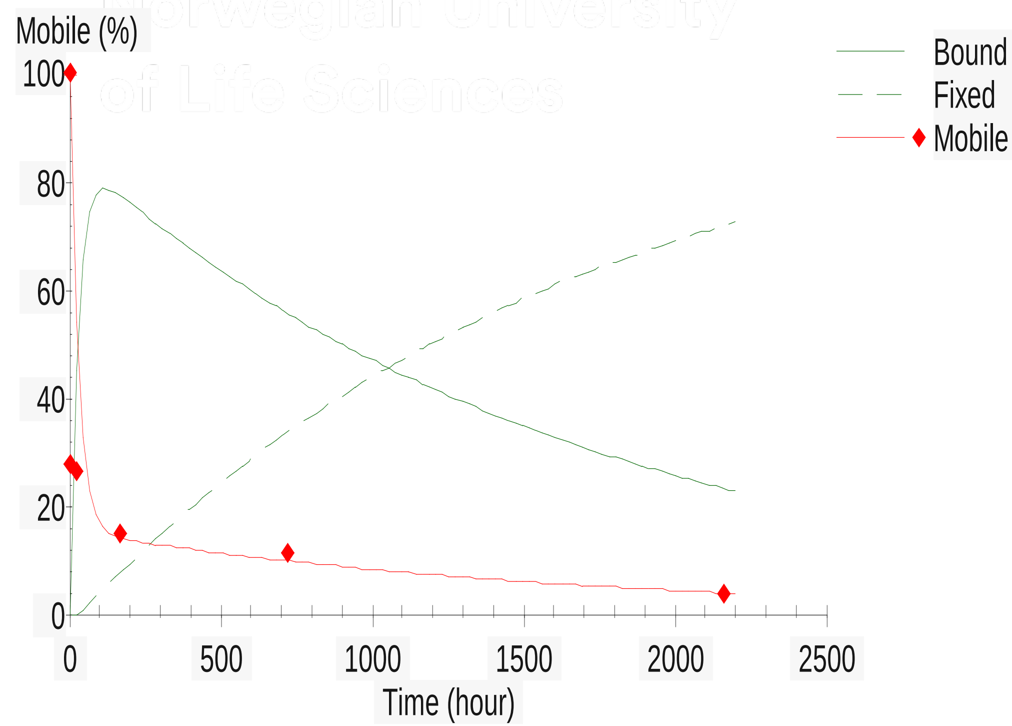


Skipperud, L., Oughton, D. H. and Salbu, B., (2000) "The impact of Pu speciation on the distribution coefficients in Mayak soil" *Science of the Total Environment*

Tracer experiments: Pu-species in soil/sediment – water systems

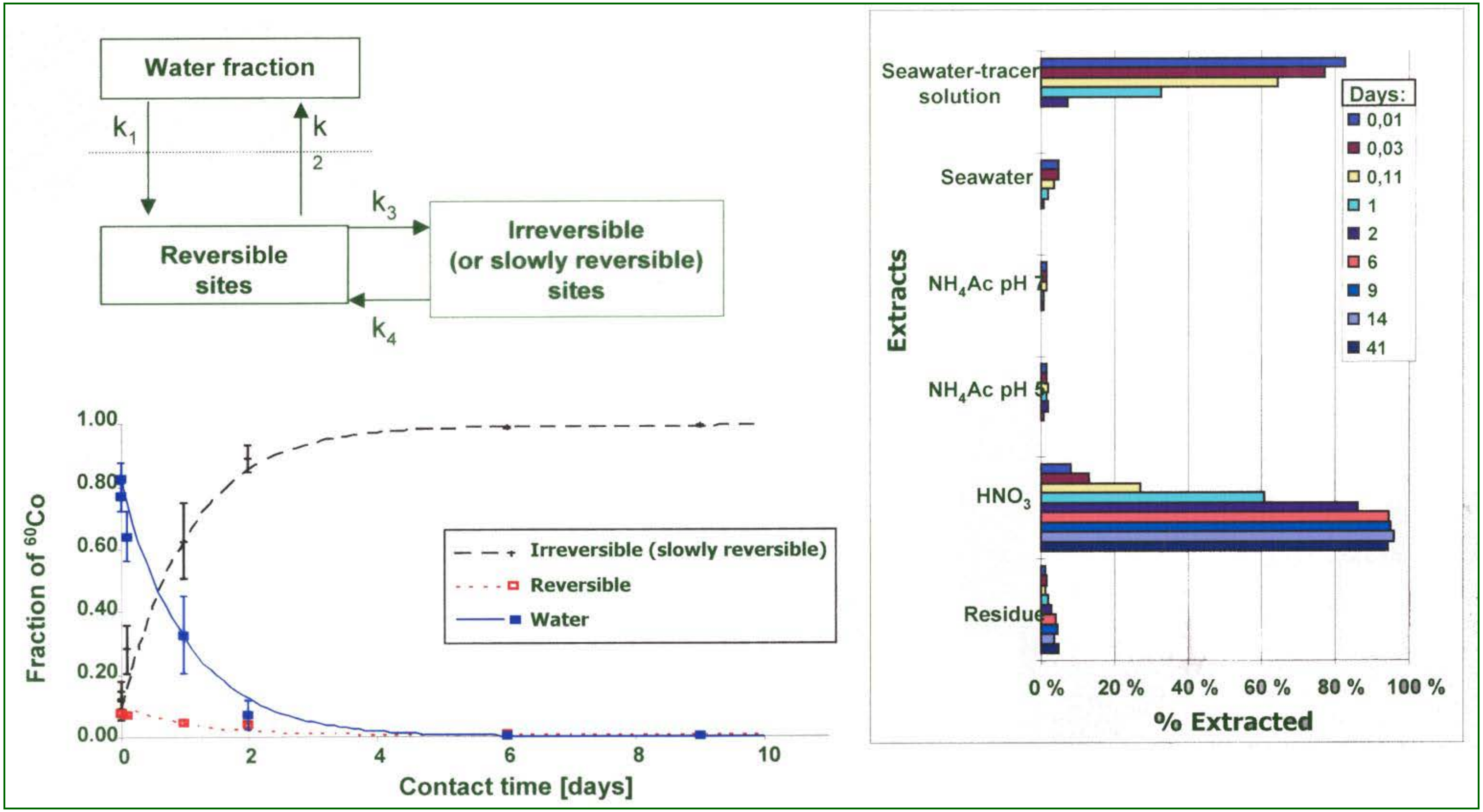






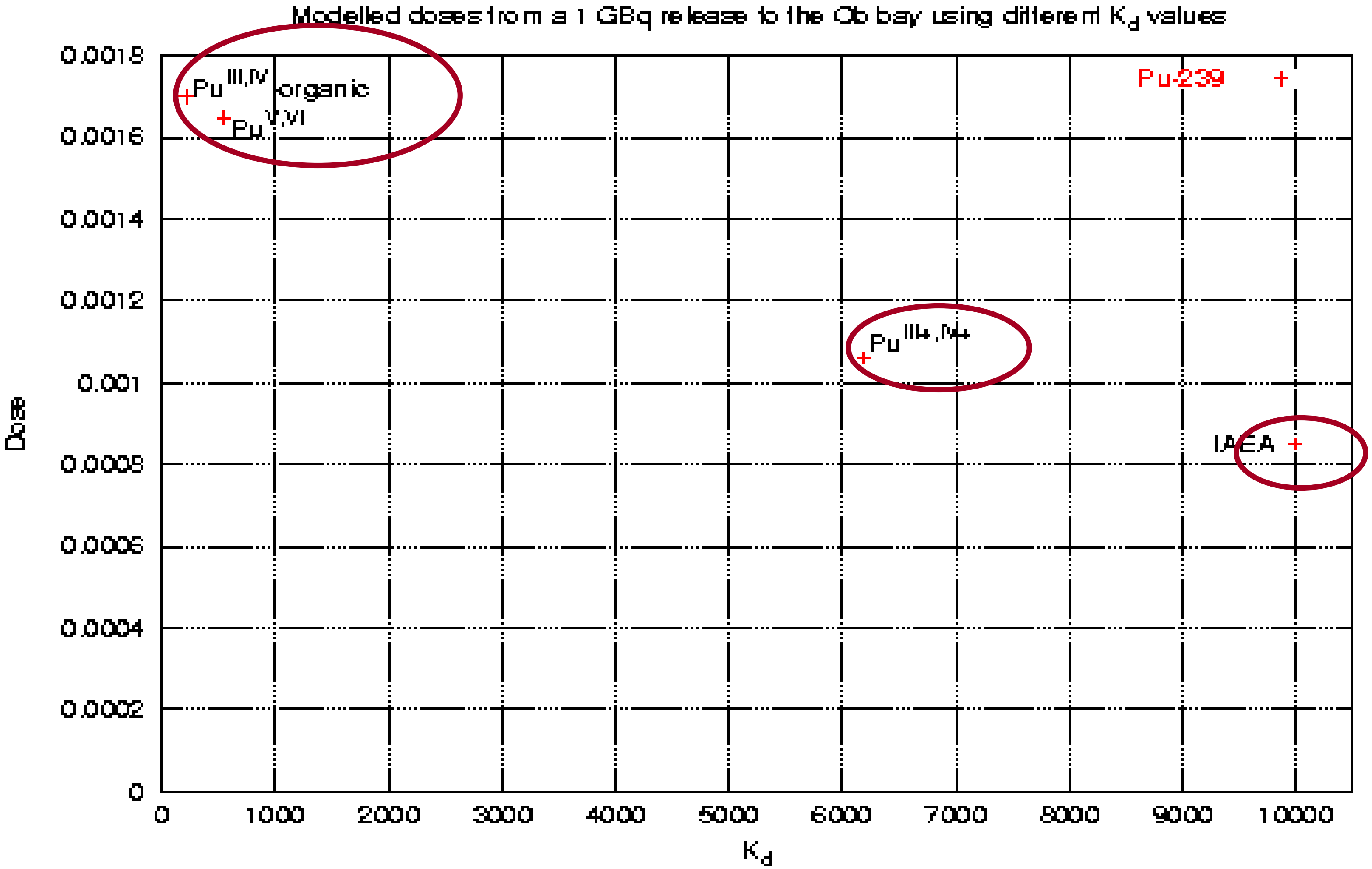
Solid-solution interaction kinetics using tracer additions, following the distribution of tracer f(t)

•



Information on kinetics

Modelling Doses to humans from release of 1 GBq Pu to the Ob Bay, using Kd f(speciation)



Pu^{III,IV}: High Kd

Pu^{V,VI} and Pu-organic: low Kd

Skipperud, L., Oughton, D. H., and Salbu, B., (2000) *Health Physics*

Higher doses than estimated using constant Kd for Pu

Kd

- Distribution coefficient, K_d, for the distribution of radionuclides in water and in soil/sediments at equilibrium conditions. Assumed reversible processes

- Kd = Bq per kg in soil/Bq per litre water

- Problems:
  - Equilibrium conditions?
  - Reversible processes?
  - Changes in speciation over time due to interactions?
  - Kinetics of interactions?

Uncertainties in ecosystem transfer:
Soil – water – vegetation – animal – man

Speciation: ions – complexes - colloids - particles

- Kd: soil – water distribution at equilibrium?
- Kd: sediment- water distribution: at equilibrium?
- CR - TC - TF - Tagg: uptake in plant – soil distribution at equilibrium?

Reindeer (NRPA):

Effective ecological half-times of ^{137}Cs has changed following the Chernobyl deposition in Norway.

- Initially: Effective ecological half-times of about 4 years.
- Mid 1990s: Slow decline, diminishing seasonal differences in concentrations.
- 2005-2010: About 27 years

Similar trends in concentrations in sheep, goats and cattle (NRPA).

Dynamic system - Kd and BCF/TC should rather be expressed as time functions f(t)

Kd reflecting mobility

- Distribution coefficient, K_d, for the distribution of radionuclides in water and in soil/sediments at equilibrium conditions. Assumed reversible processes

- Kd = Bq per kg in soil/Bq per litre water

- Alternative: Mobility factor:
  - Kd_{mob} = Bq per kg (mobile phases)/Bq per litre water
  - Include kinetics

Impact of mobile species and inert particles on ecosystem transfer and dynamics

Source term → **Transport processes** → **Biological uptake** → **Dose-assessment**

Impact of	Speciation	K_d	CF	mSV
Mobile species	**High load of mobile species**	**Low** **Increase *f(t)* when transformes into reactive species interacting with surfaces**	**High in fish** **Low in benthic** **Decrease *f(t)* in fish for reactive species** **Increase *f(t)* in benthic for reactive species**	**Underestimated short-term traditional dose-assessment** **Overestimated long-term traditional dose-assessment for reactive species**
Inert particles	**High load of inert species**	**Very high** **Decrease *f(t)* when transferred into mobile species (e.g. weathering and mobilization of ^{90}Sr)**	**Low in fish** **High in benthic** **Increase *f(t)* in fish for mobile species** **Decrease *f(t)* in benthic for mobile species**	**Overestimated short-term traditional dose-assessment** **Underestimated long-term traditional dose-assessment for mobile species**


Questions???