NMBU
Norwegian University of Life Sciences

Norwegian Institute of Public Health

NIVA
Norwegian Institute for Water Research

CERAD

CENTRE FOR ENVIRONMENTAL RADIOACTIVITY

Norwegian Meteorological Institute

Statens strålevern
Norwegian Radiation Protection Authority

Comet Field Course, Kiev, September, 2016

Senter for fremragende forskning

Radionuclide speciation, mobility and bioavailability, influencing environmental behavior

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We are exposed to a series of radionuclides in mixtures with other stressors (metals, organics, etc)

Natural sources:
Cosmic and terrestrial derived:

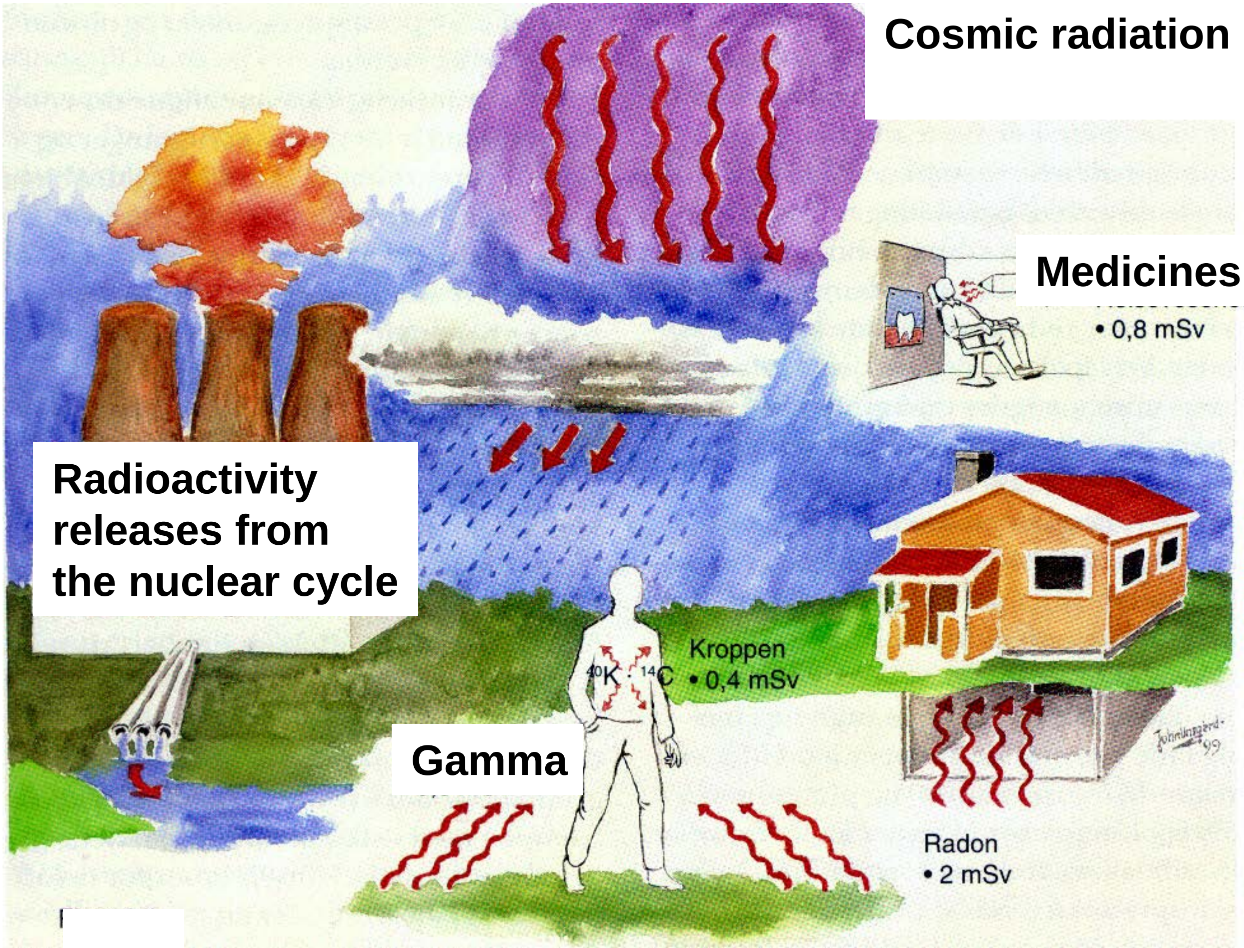
- U-series

Anthropogenic sources:

Man made produced contaminants

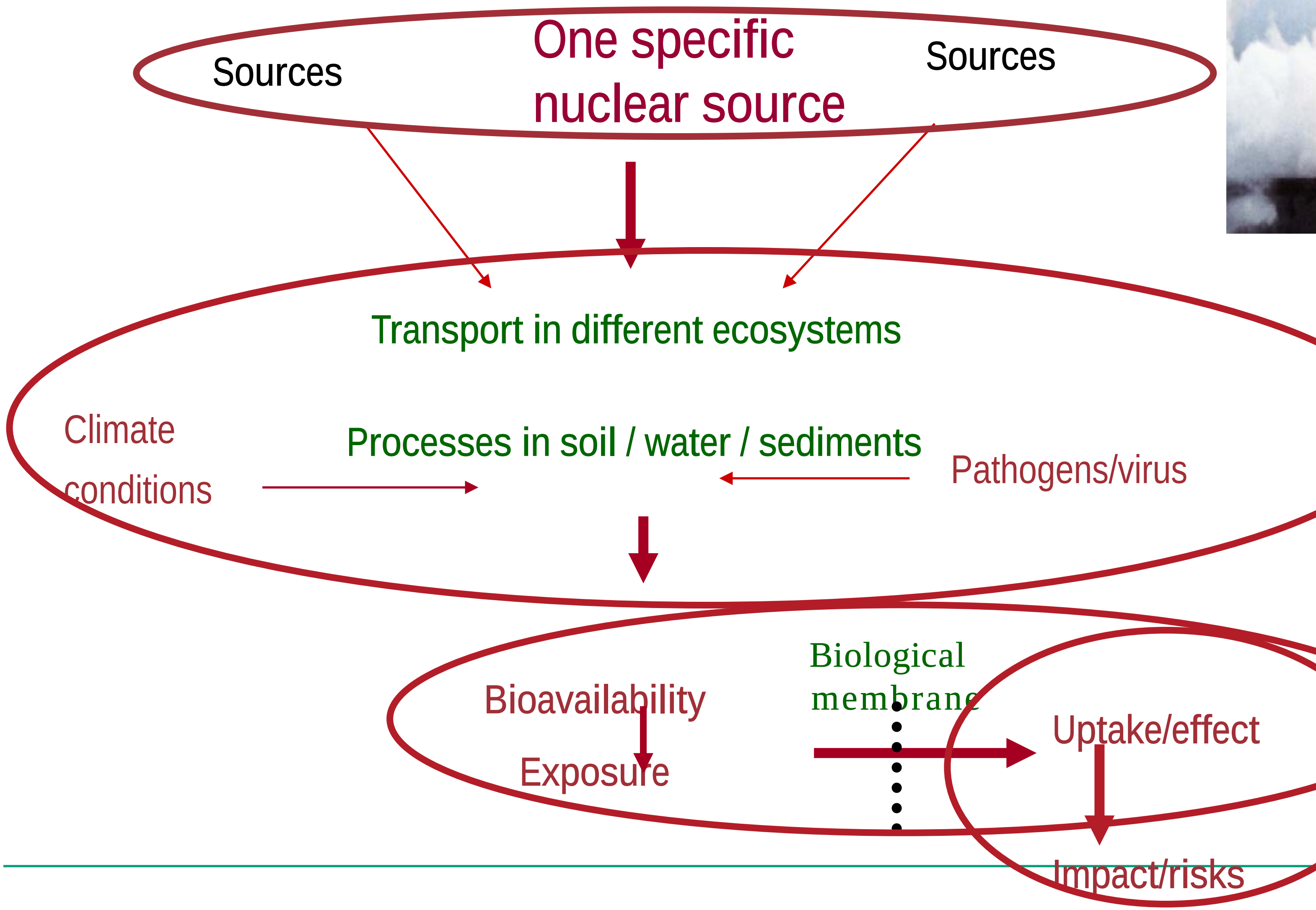
- plutonium

Releases of radionuclides followed by dry and wet depositions, ecosystem transfer



Inhalation, skin deposition, intake of food, water: organics, metals, radionuclides

Challenges: to link releases of radionuclide species from one source via ecosystem transfer to dose, effects, impact and risk assessment under various climate conditions

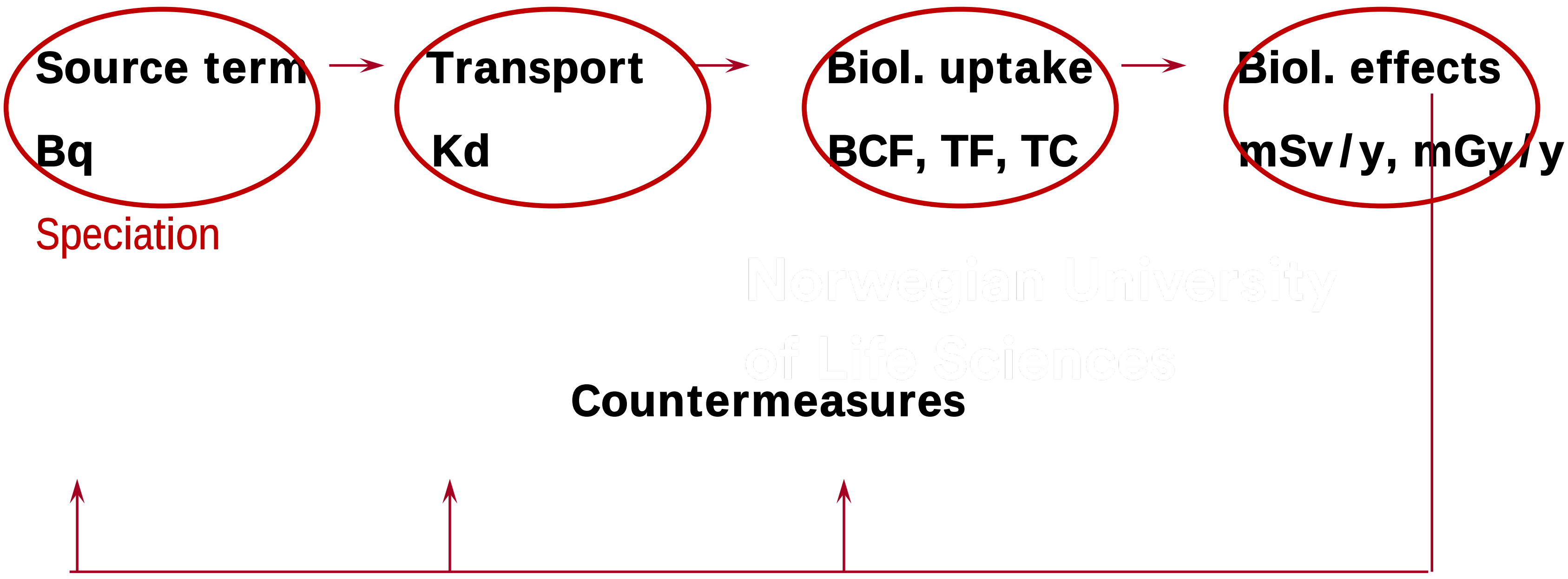


Complex system – many stressors/variable antioxidant status

Take home message

- Radionuclides can be present in different physico-chemical forms influencing ecosystem transfer/mobility, biological uptake and effects
- Transfer (Kd and TF or BCF) depends on speciation, ecosystems and biological species, and will apply to a time function f(t)
- Radionuclide species depend on sources and release conditions and transformation processes occurring in the environment
- Hazards can be underestimated if radionuclide speciation – the presence of particles – is ignored
- Advances speciation/fractionation techniques are needed to distinguish between radionuclides species.

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



Short and long term dose, impact and risk assessments

Focus: The source term/deposition and radionuclide speciation influence the ecosystem transfer, and effect estimates

Nuclear sources have contributed to major releases of radioactivity – Red: NMBU expeditions

- Nuclear weapon tests (Kazakhstan)
- Conventional detonation of weapons (Greenland, Spain)
- Nuclear reactor explosions and fires (Ukraine, UK)
- Accidents with reactor driven vehicles: satellites, submarine accidents (Norway)
- Effluents from nuclear installations (UK, France, USA, Russia, Canada)
- Leaching from dumped nuclear material (Kara Sea)
- Use of DU ammunition

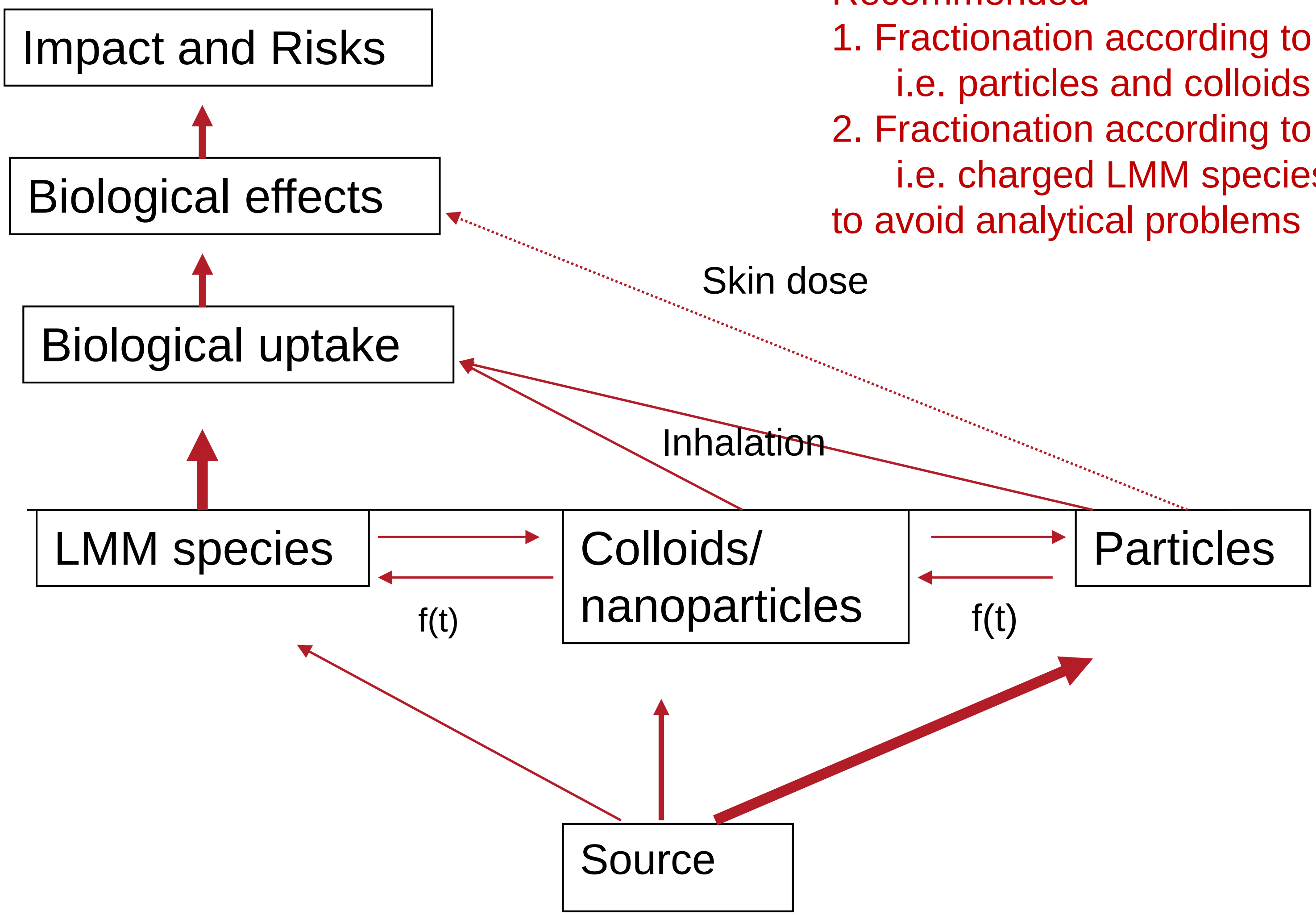
NORM/TeNORM

- Uranium mining and tailing (Central Asia)
- Alum/black shales (Norway)
- Non- nuclear industry: oil and gas, mining, etc

The speciation of radionuclides influences ecosystem transfer, biological uptake and effects

Recommended
1. Fractionation according to size
   i.e. particles and colloids
2. Fractionation according to charge
   i.e. charged LMM species

to avoid analytical problems



Bulk activity concentrations: sum of species, provide no info on processes affecting radionuclide species

Models and data needed

Model compartment	Information needed
Environmental impact, risks	Risk factors Dose conversion factors
Biological effect	Biological endpoints Critical organs Critical load
Bioaccumulation Biological uptake	Uptake/depuration Bioavailability
Mobility	Interactions *f(t)* Transformation*f(t)* Weathering *f(t)*
Source term	Speciation Isotopes, activity ratios, activity concentrations

Physico-chemical forms = speciation

Radionuclides, trace elements, trace metals, heavy metals, can be

- present in different physico-chemical forms:

ions, molecules, complexes, colloids, particles

- influencing the transport and mobility, bioavailability and biological uptake, distribution within an organism, accumulation and thereby the effect

Definitions: radionuclide species

Radionuclide species:

are defined according to their physico-chemical properties; molecular mass, charge properties, oxidation state – valence, structure, complexing ability, e.g. ions, molecules, complexes, colloids, particles

Speciation of radionuclides:

is defined as the distribution of radionuclide species in a system

Speciation analysis:

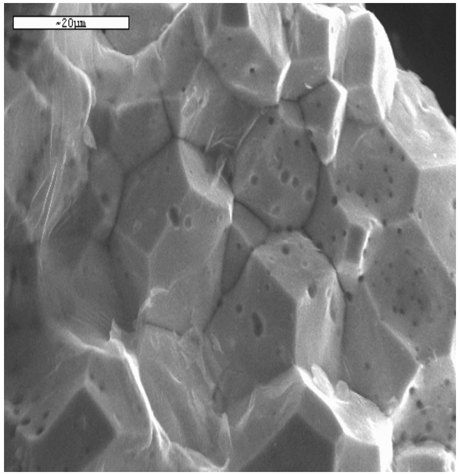
Application of analytical techniques to identify and quantify one or more individual radionuclide species in a sample (i.e. application of *in situ, at site, on line, at lab.* fractionation techniques prior to measurements).

According to/slightly modified IUPAC 2000 (Salbu, JER, 2009)

Definitions

- Radioactive particles

  in the environment are defined as localised aggregates of radioactive atoms that give rise to inhomogeneous distribution of radionuclides significantly different from that of the matrix background (IAEA, 2011).



Definition: Particles (IAEA, 2011)

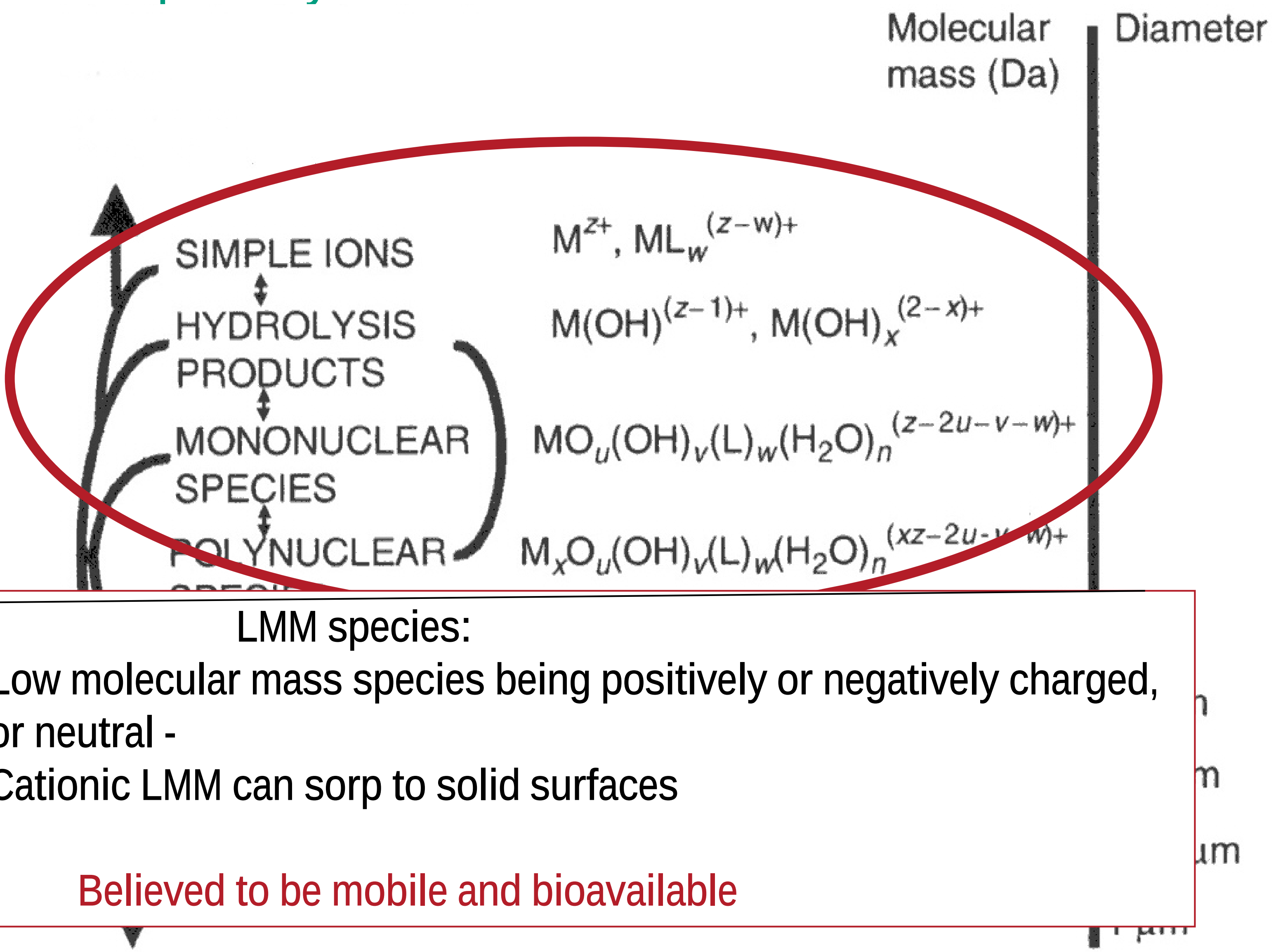
In water/sediment/soil/biota

- Fragments – larger than 2 mm
- Particle size range: 0.45 µm – 2mm
- Colloidal (nanoparticle) size range: 1 nm - 0.45 µm
- Low molecular mass (LMM) species: less than 1 nm

In air:

- Particles (submicrons in aerosols to fragments) are classified according to their aerodynamic diameters.
- Particles less than 10 µm are considered respiratory.

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



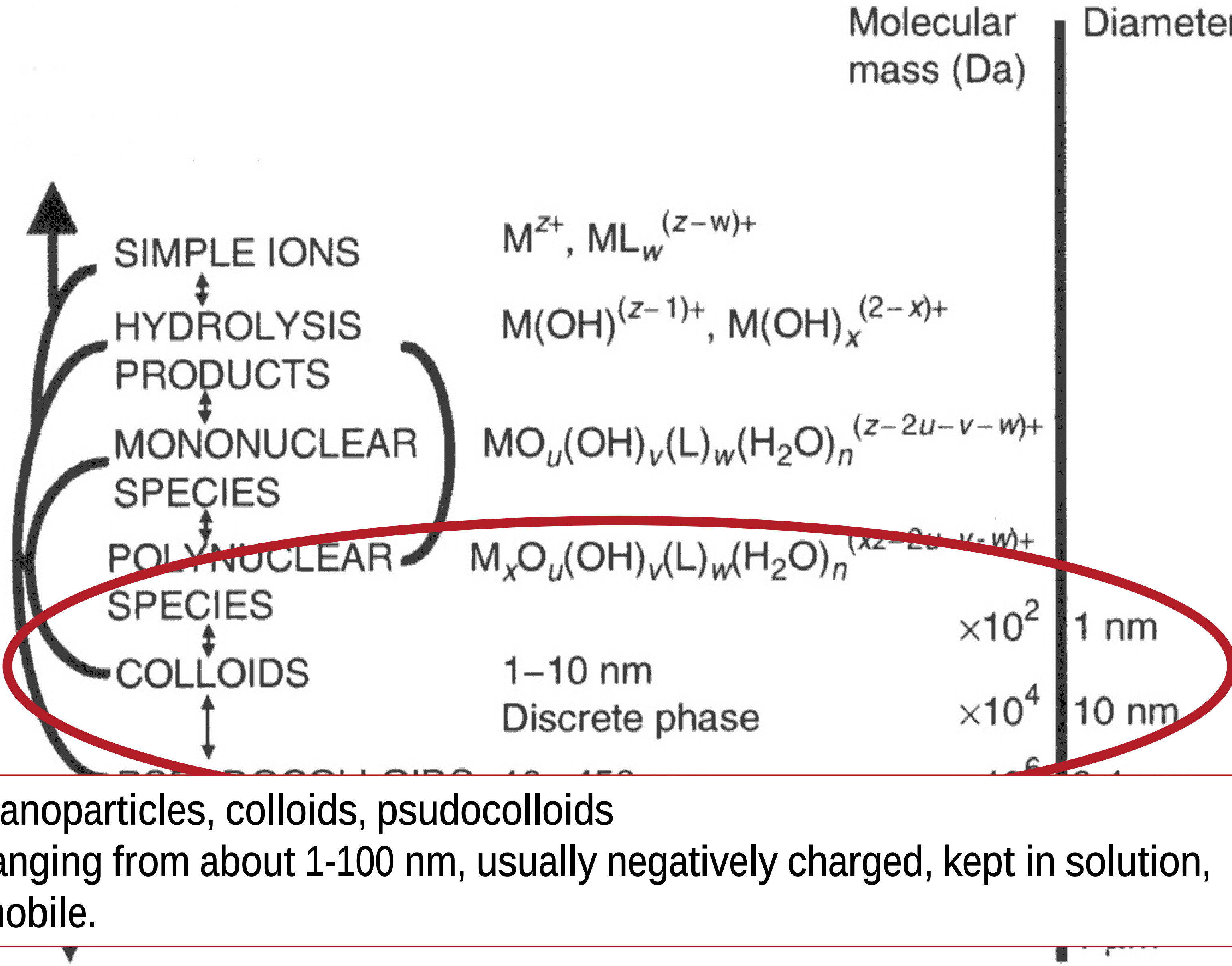
LMM species:

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

Cationic LMM can sorp to solid surfaces

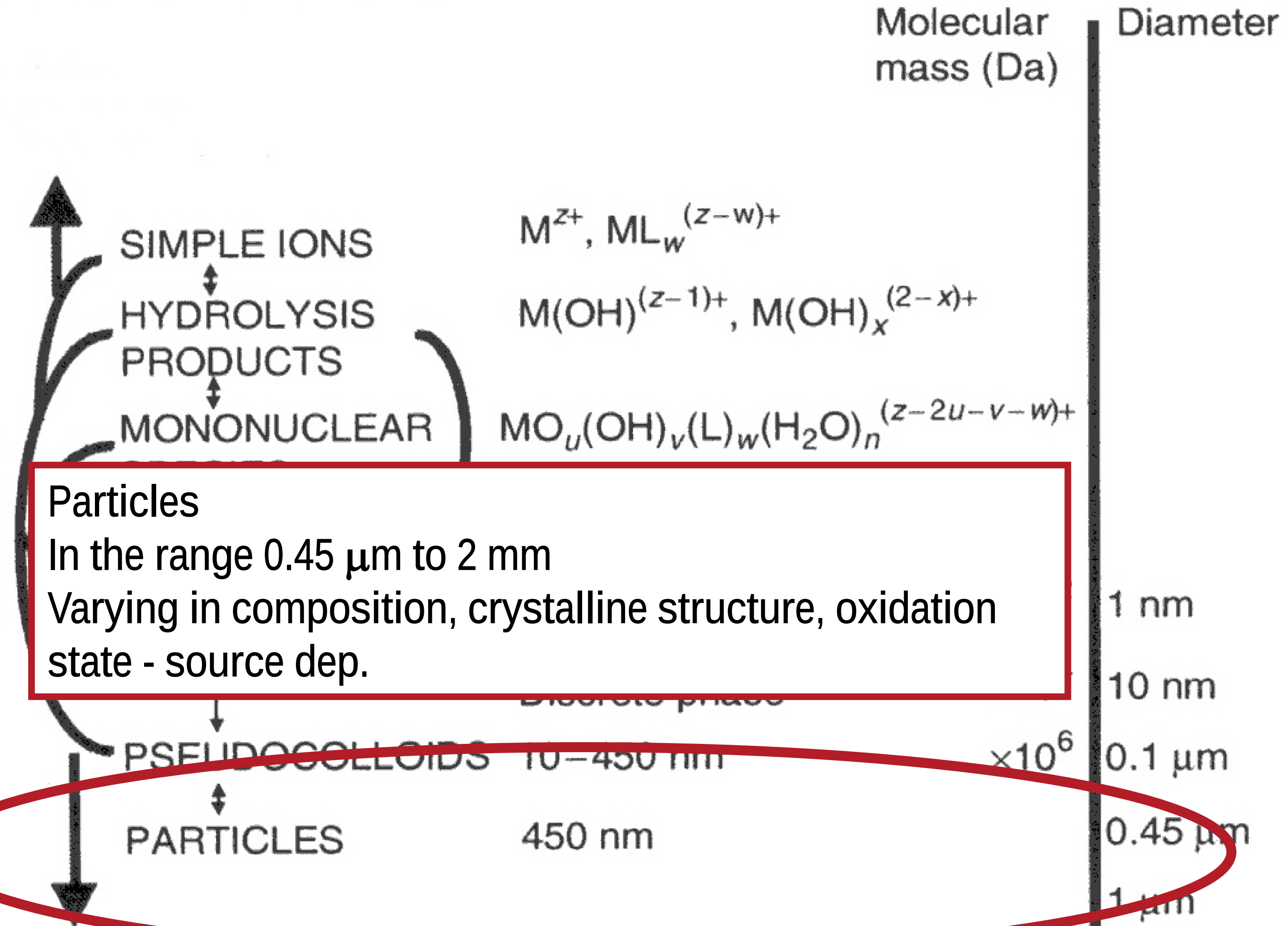
Believed to be mobile and bioavailable

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



Nanoparticles, colloids, psudocolloids
ranging from about 1-100 nm, usually negatively charged, kept in solution, mobile.

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



Particles
In the range 0.45 µm to 2 mm
Varying in composition, crystalline structure, oxidation state - source dep.

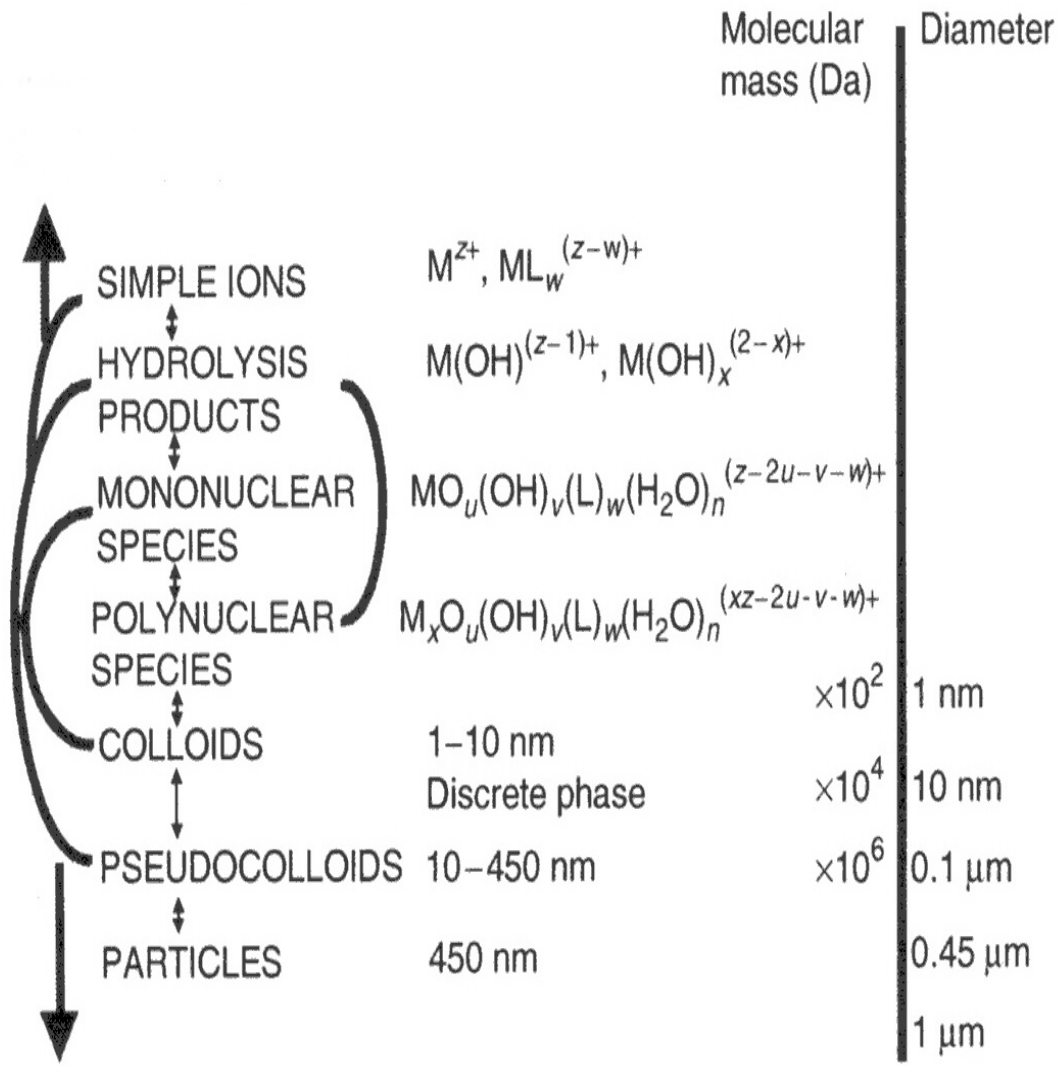
The system is dynamic, and transformation processes will influence the size distribution of radionuclide species f (t)

Molecular mass growth mechanisms:

- hydrolysis
- complexation
- polymerisation
- colloid formation
- aggregation

Mobilization mechanisms:

- desorption
- dissolution
- dispersion



Microchemical processes

- LMM species:
  - Hydrolysis
  - Polymerisation
  - Complexation
  - Co-precipitation
  - sorption
- Colloids:
  - Stable colloids- Brownian movement – behave concervatively in water
  - Unstable – forming aggregate – can be removed due to sedimentation
- Particles:
  - Weathering rates depend on composition, size, crystallographic structure, porosity, oxidation state
  - Weathering rates depend on soil pH and oxidation (microbial activity)

Source term – mobility – uptake – effect – risk
Dynamic processes f(t)

Input Source term:

Radionuclides, activity concentrations, isotope ratios, speciation

Speciation: depends on source and release conditions

Mobility:

Interactions *f(t)*, transformation*f(t)*, particle weathering *f(t)*

Depends on speciation

Mobility in soil/sediment

Kd = Bq/kg d.w. / soil/Bq/L water f(t)

Retention in soils/sediments depends on speciation

Analytical strategy for the determination of radionuclide species

Total elements

Sampling

sampling constant

Storage

effects f(t)

Preconcentration

chemical yield

Storage

effects f(t)

Analysis

methods of analysis

Speciation

In situ fractionation

sampling constant technique

Preconcentration

chemical yield

Storage

effects f(t)

Analysis

methods of analysis

Interpretation of data

Radionuclide speciation:
Combination of Size and Charge Fractionation Techniques, Solid State Speciation Techniques, and sensitive methods (ICP-MS, AMS)

Size fractionation	Charge fractionation	Solid state speciation
Filtration		…opy techniques
Tangentia… flow / hollo… ultra filtra…		…iation X-ray …nniques …-XANES,
Continous… centrifuga…		…pectroscopy …AMMA)
In situ dia… volumes)		… loss …spectroscopy (EELS)
Ultra cent…		Raman spectroscopy
Density centrifugation		Nuclear magnetic resonance spectroscopy
Dialysis / diffusion		
Gel chrom.		

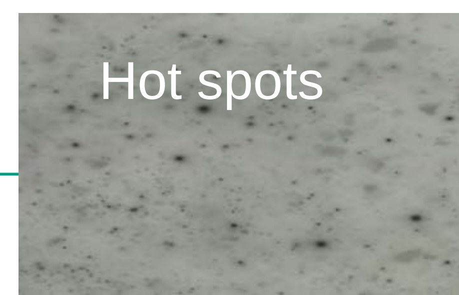
Low activity concentrations – no direct specie-specific techniques are available

Techniques must be combined to provide specie characteristics

Advanced techniques within other disciplines increasingly needed


In situ fractionation


N_2 tent for anoxic systems


Hot spots

Speciation of radionuclides in water

Diameter		1 nm	10 nm	0.1 µm	0.45 µm	1 µm	10 µm
Molecular mass		x 10^2	x 10^4	x 10^6		x 10^8	

Category	simple compounds	hydrolyzates/colloids	polymers / pseudocolloids	suspended particles
Cases	inorganic, organic ions, complexes, molecules etc.	nanoparticles polyhydroxo complexes polysilicates fulvic acids fatty acids	metal hydroxides clay minerals humic acids proteins	inorganic mineral particles organic particles microorganisms
	LMM	Colloids		Particles

Methods,

Determination of total activity concentration of radionuclides in acidified samples.

Dissolved radionuclides, determination of total in 0.45 µm filtered sampled and acidified

LMM species

Size fractionation techniques

- Diffusion rate measurement
- Ultrafiltration ultracentrifug. dialysis
- Filtration
- Sedimen-tation

Charge fractionation techniques

Ion chromatography – undefined fractions
Complexation – undefined fractions

Size and charge distribution pattern

T ... on

Recommended

1. Fractionation according to size
   i.e. particles and colloids
2. Fractionation according to charge
   i.e. charged LMM species

To avoid analytical problems

Diameter ... um 1 µm

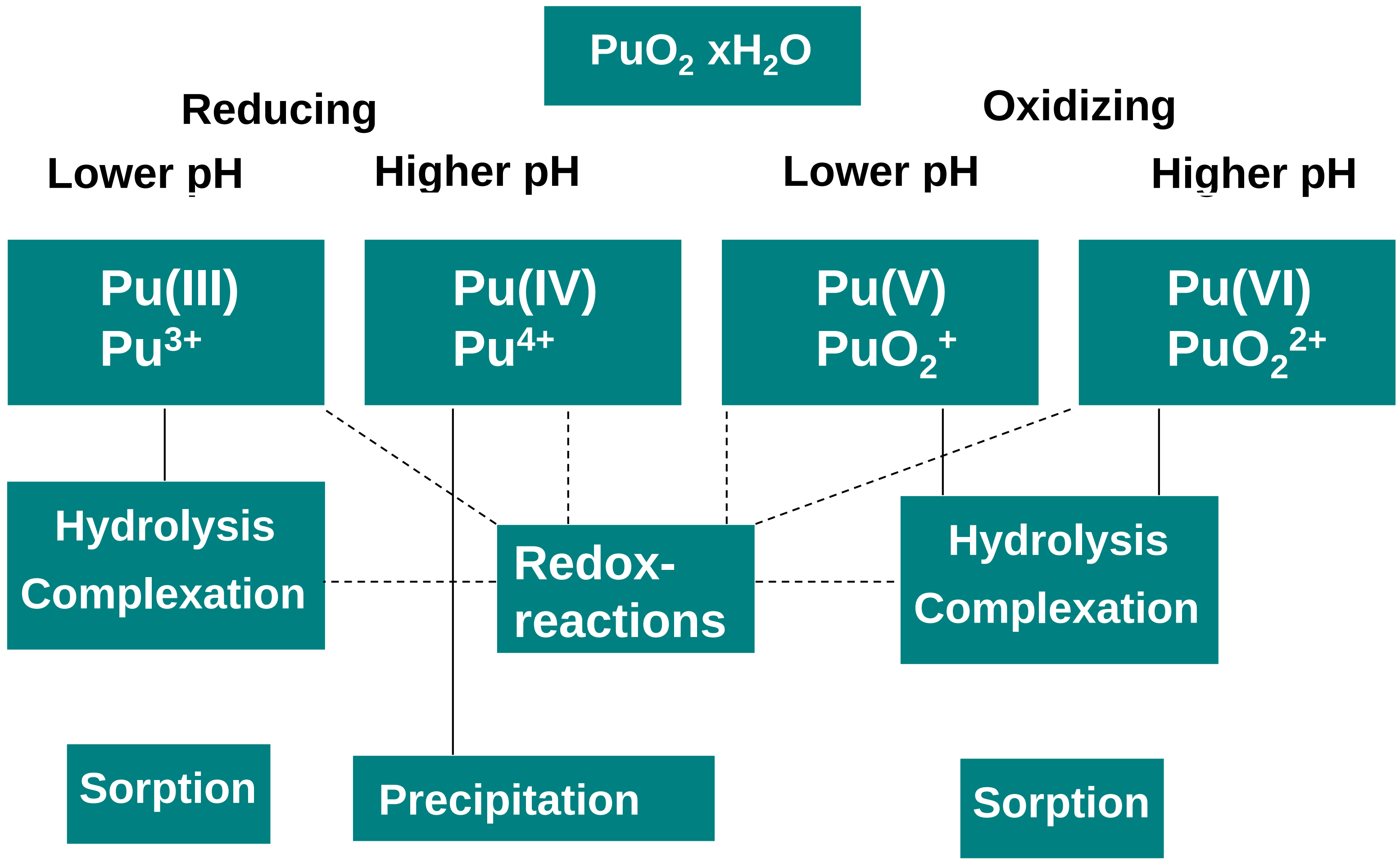
Species Lo m ... Particles

Mobile and bioavailable species

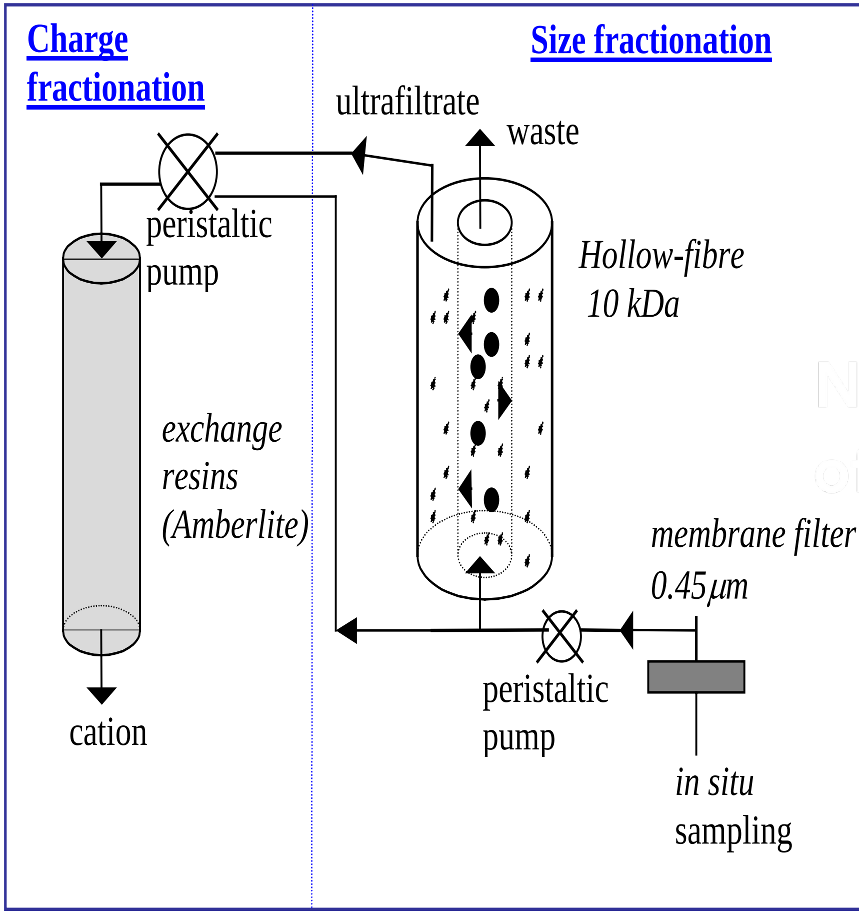
Inert species

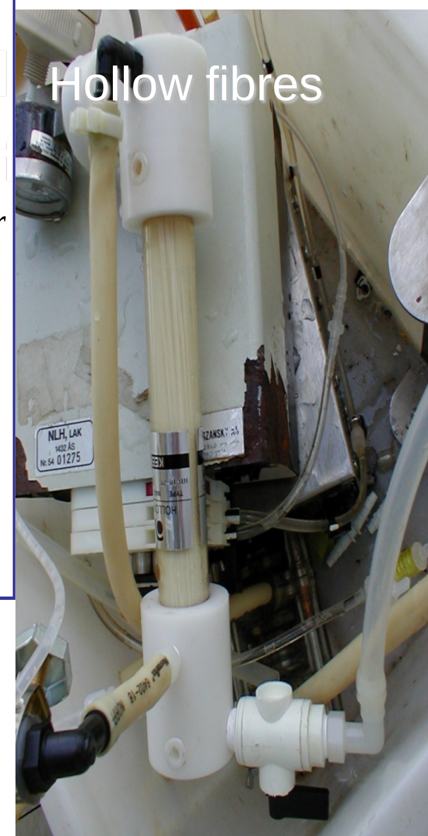
LMM positively/ negatively charge or neutral species

Pu in the environment



Size and charged interfaced system





Fractionation of radionuclides in rivers under high flow conditions

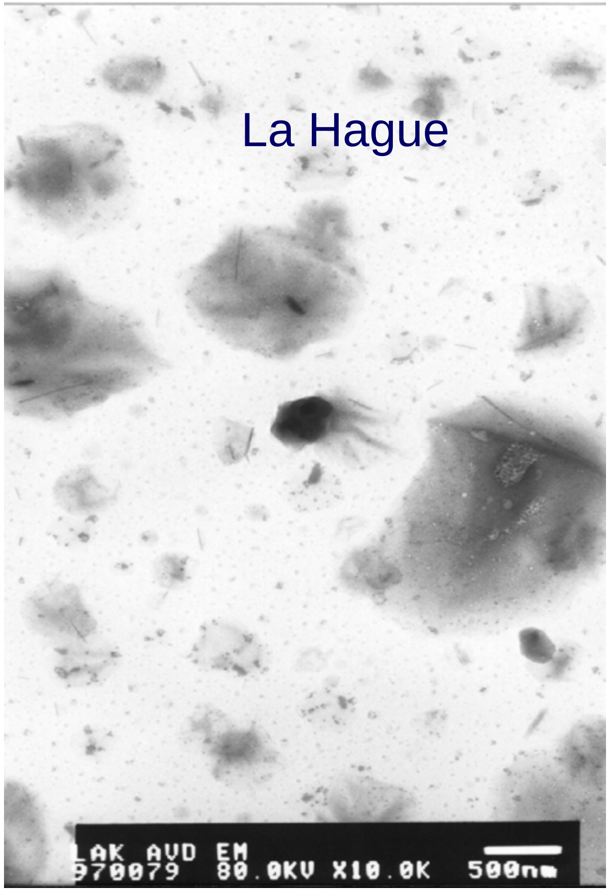
For identification of radionuclide species in the environment – during events - we need *in situ* fractionation techniques – avoid storage effects

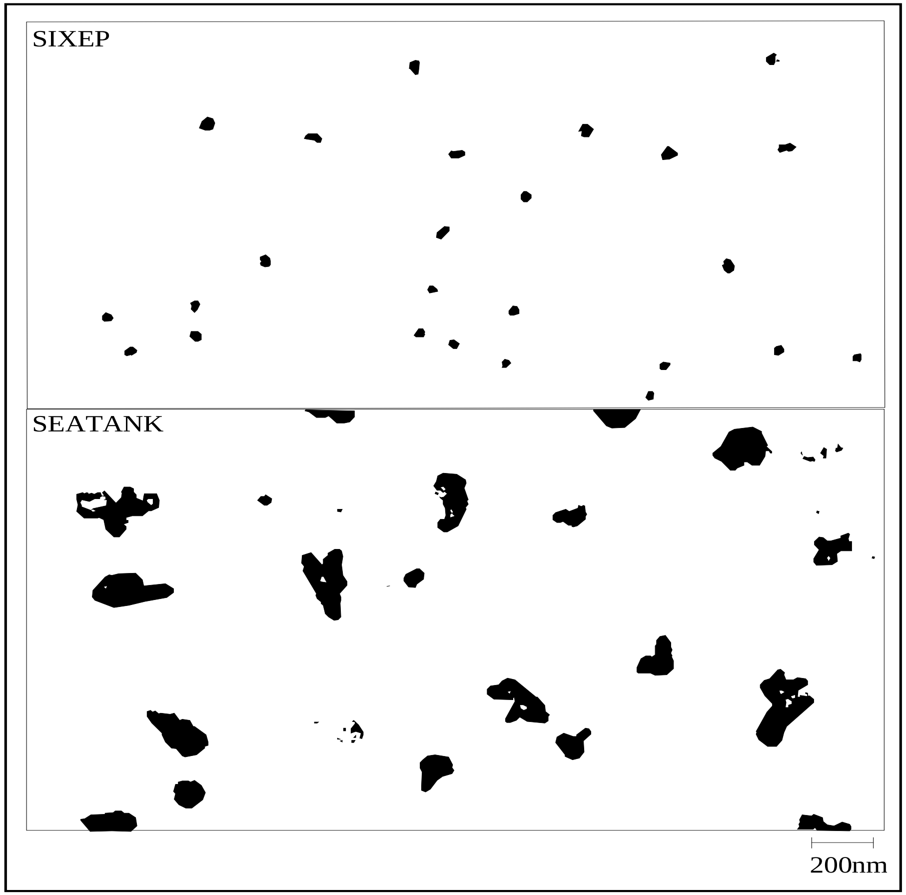
Fractionation in the field

Colloids in effluents from reprocessing plants

Transmission Electron microscopy (TEM) reflect the presence of colloids.

Effluents contain: ions, colloids, particles, Pu associated with colloids



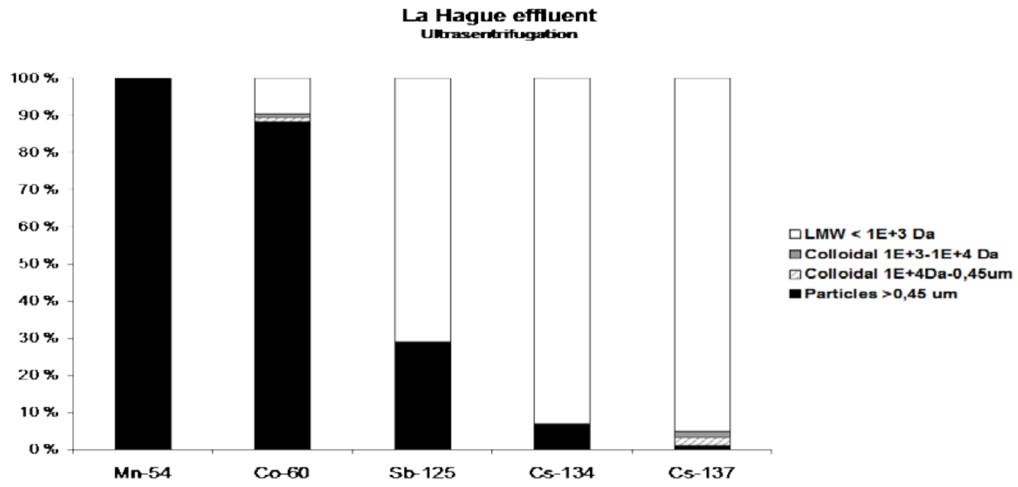


Sellafield

Cs-isotopes in marine waters

Large volumes pumped into a filtration device (1 or 0.5 µm) and sorbents to retain Cs^{+} ions

Water: Fractionation of radionuclide species

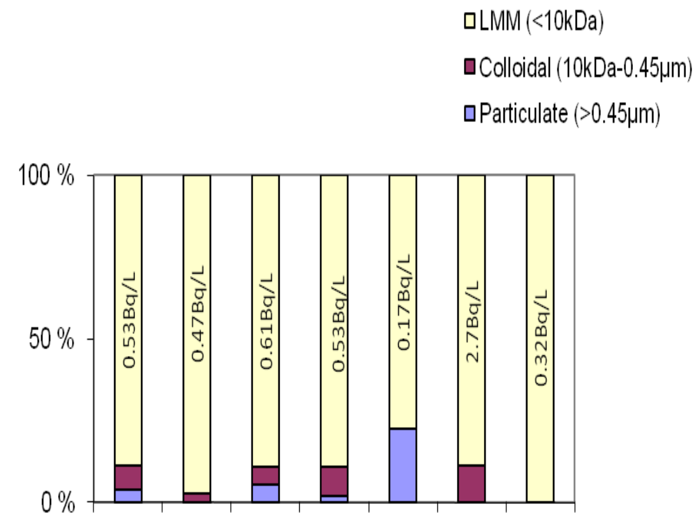


Case: Effluents from Sellafield and La Hague:

Particles: Mn-26, Co-60
Colloids: 30 % Sb-125
LMM: Cs-134, Cs-137

Anoxic lake water:
Fossile Lake Rørholtfjorden, Norway
Anoxic 15 m under 135 fresh water layer
Pu-isotopes: 50 % colloids in fresh water
Only LMM Pu species in anoxic water

Case: U mining site in Kyrgyzstan



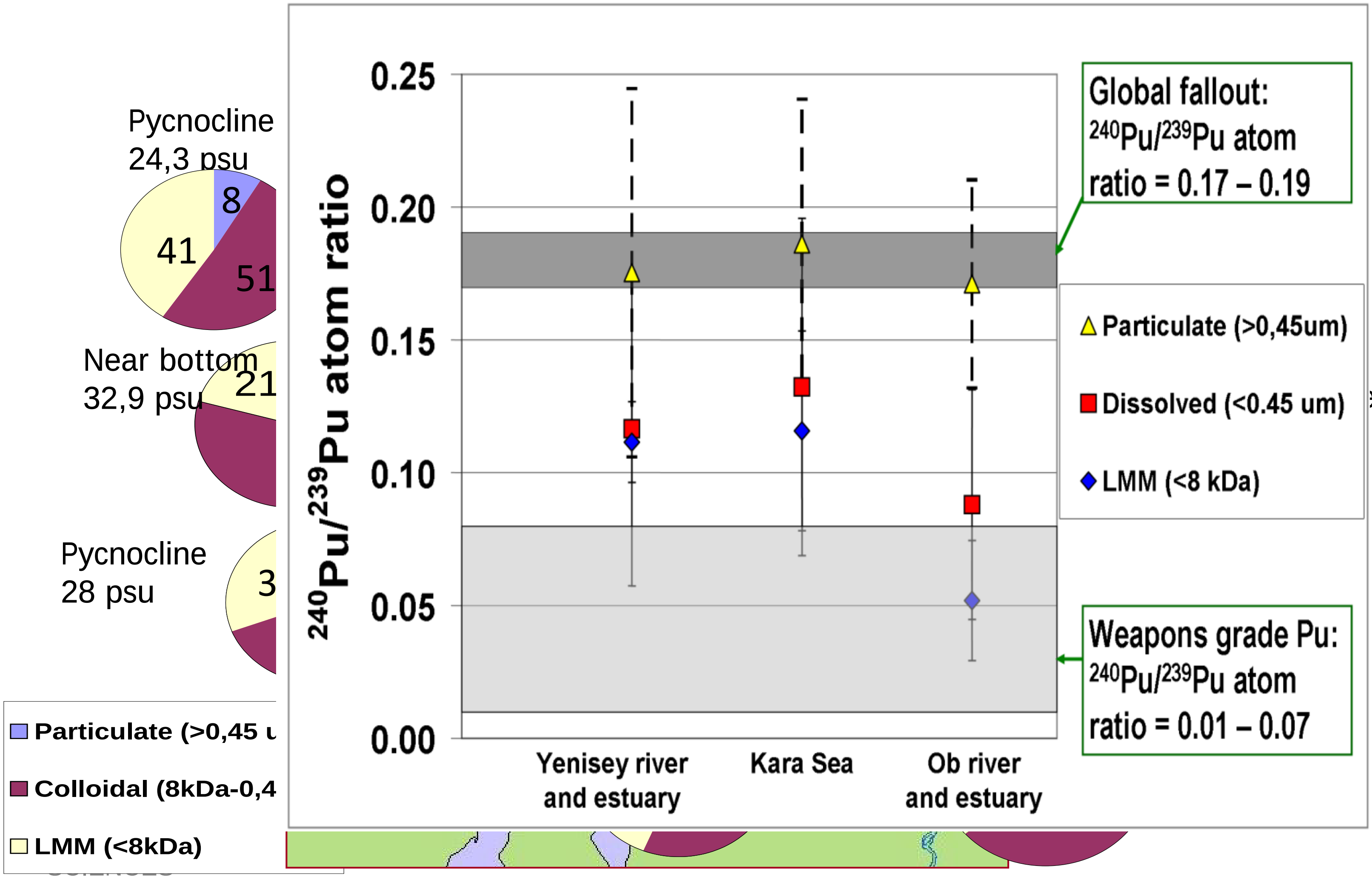
Sampling – anoxic systems
Case: anoxic deep layer (130.145 m) in Lake Rørholtfjorden

Precipitation of Fe and co-precipitationon of radionuclides/trace elements on contact with air

Pumping water into a N_2 tent

Hollow fiber fractionation within the tent

Case: Pu species in Jenisey River – total and ultrafiltered water + AMS:
Weapon grade Pu signal in the colloidal all the way into Kara Sea
Total sample = fallout (Lind et al. 2006)



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)

METHODS - DESTRUCTIVE TECHNIQUES

TOTAL CONCENTRATION by radiometric methods and mass spectrometry (ICP-MS, AMS, SIMS etc)

- Full dissolution/acid leaching
- Radiochemical separations

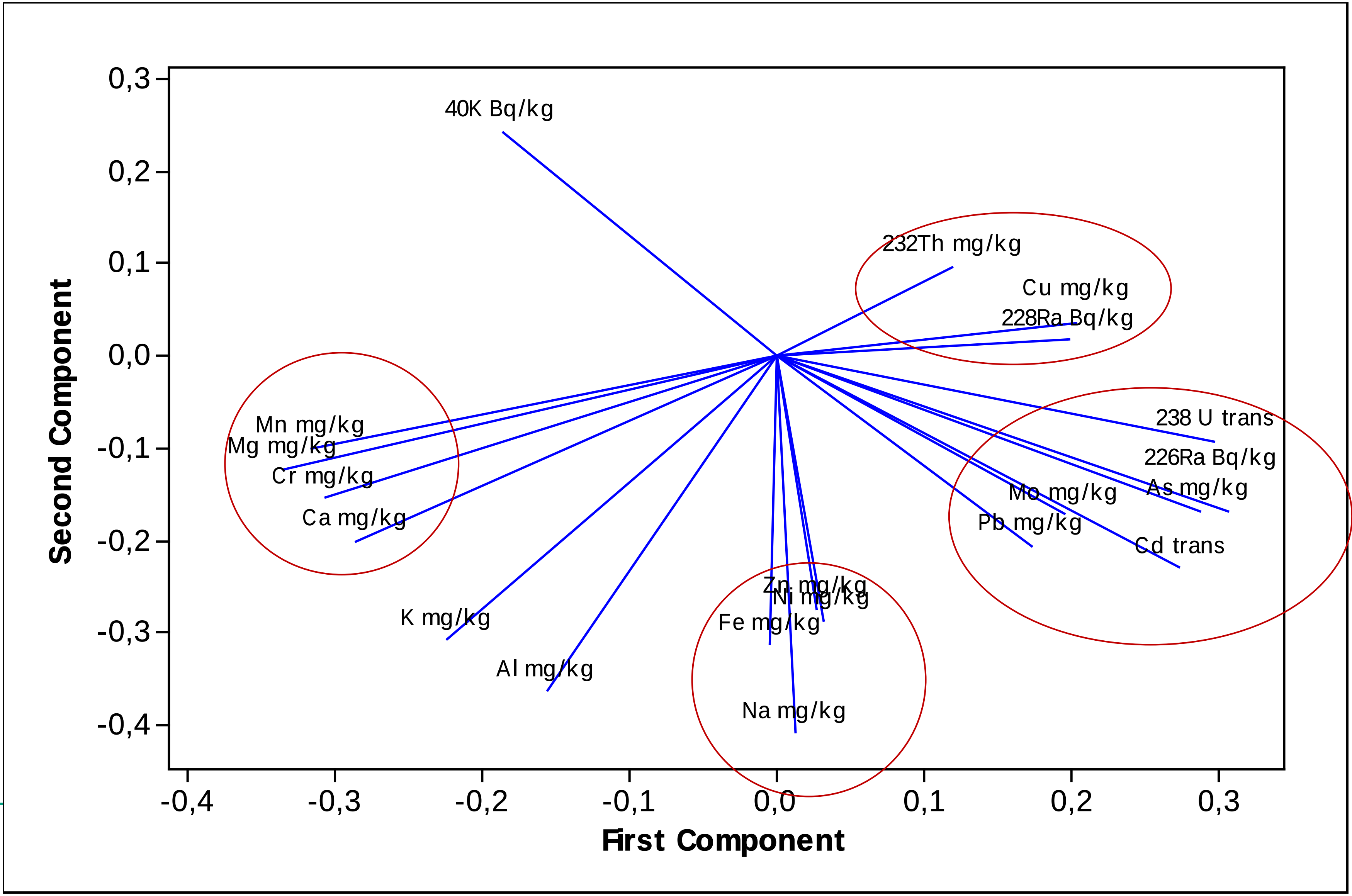
LEACHING EXPERIMENTS to estimate potential mobility and bioavailability

- Sequential extractions, increasing displacement/dissolution power
- Solubility in biologically relevant fluids (e.g. stomach juice)

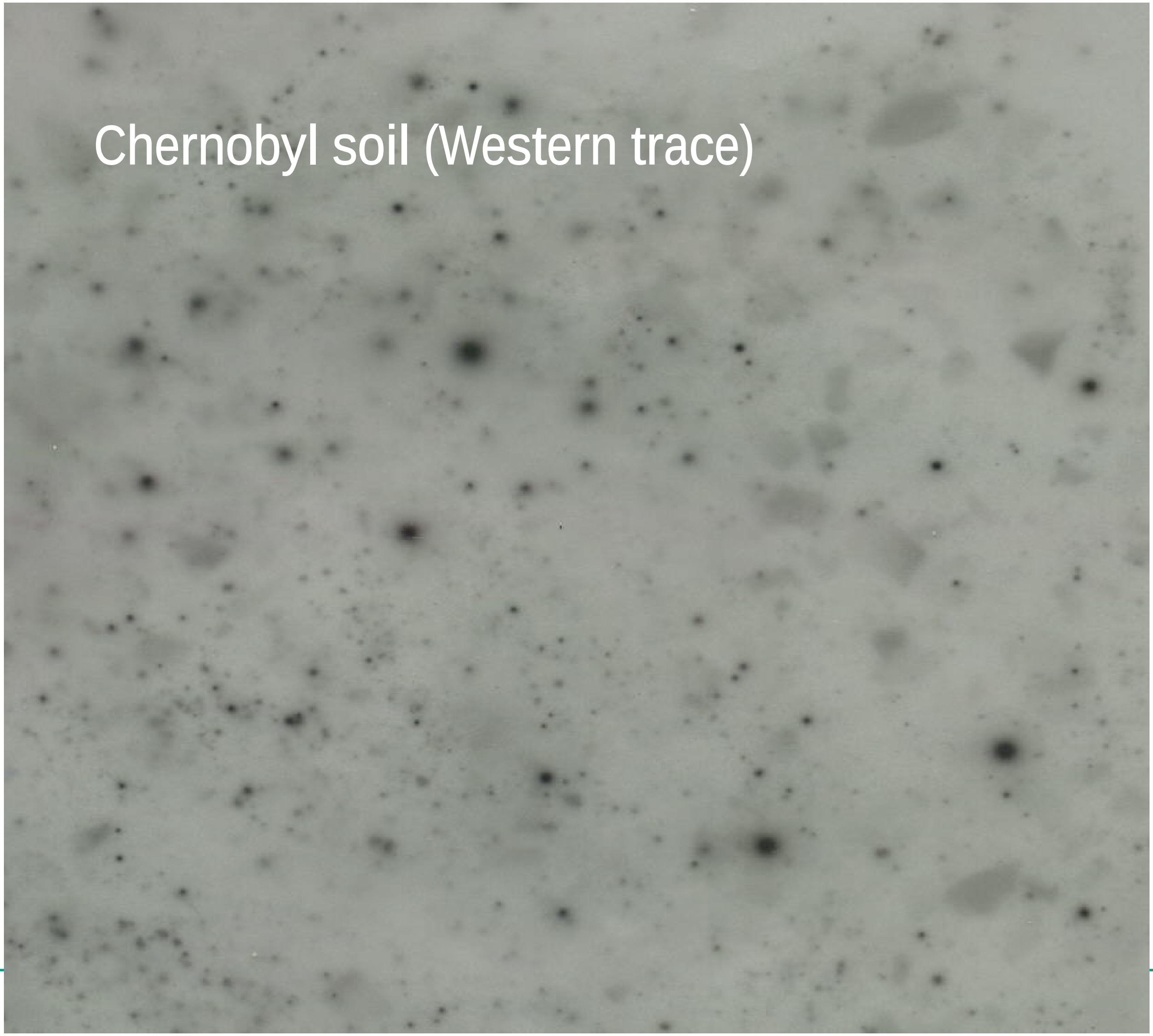
SOURCE IDENTIFICATION by radiometric methods and mass spectrometry

- Determination of isotopic ratios which can be used as fingerprints for different sources (U, Pu)

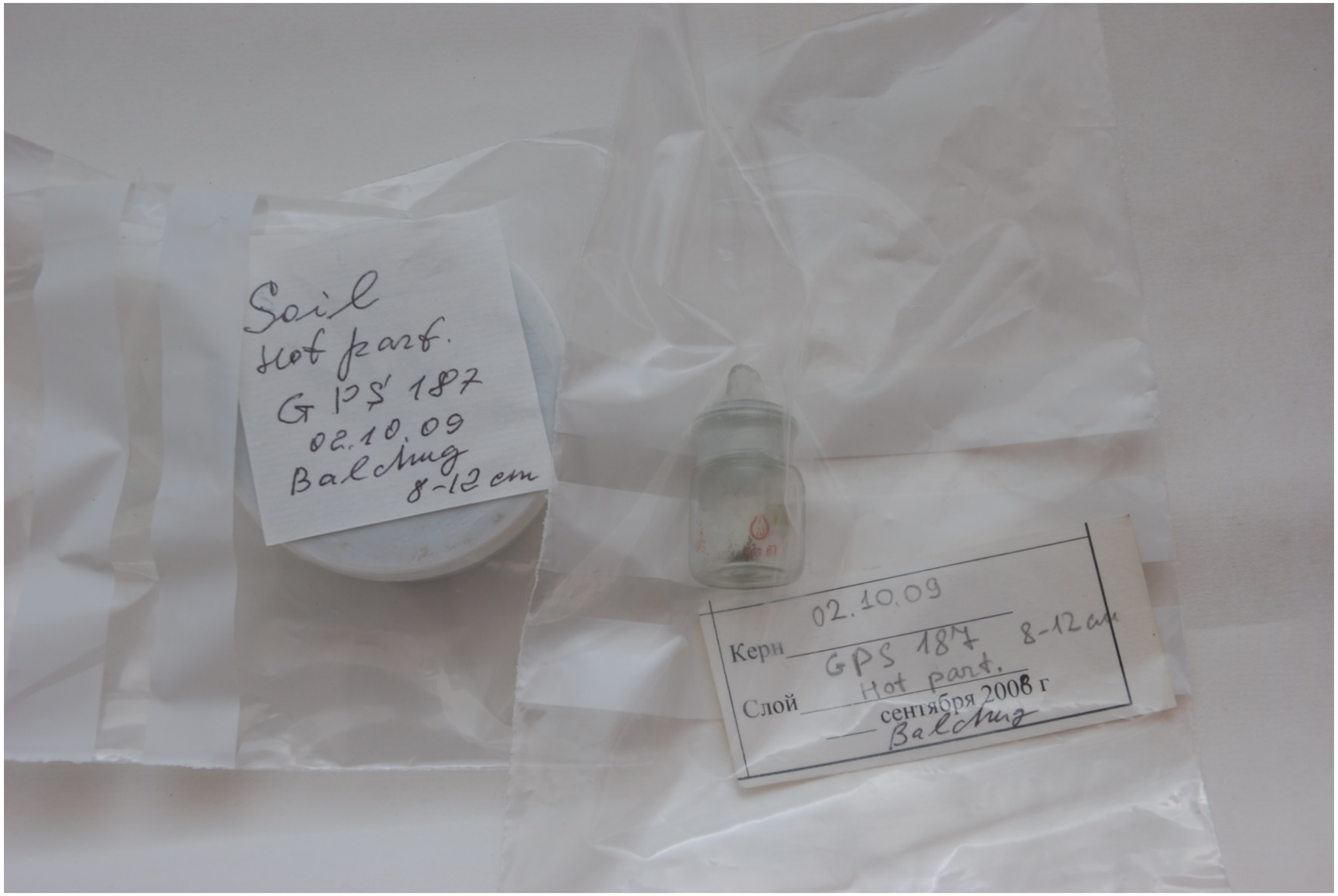
Principal component analysis (RDA) of soil components, where the 3 first components could explain 80 % of the variance.



Autoradiography of contaminated soil



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



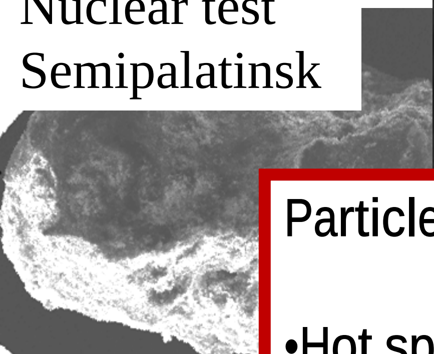
Bulk (minus particle): ~100 g
~40 counts per second
(NaI detector)

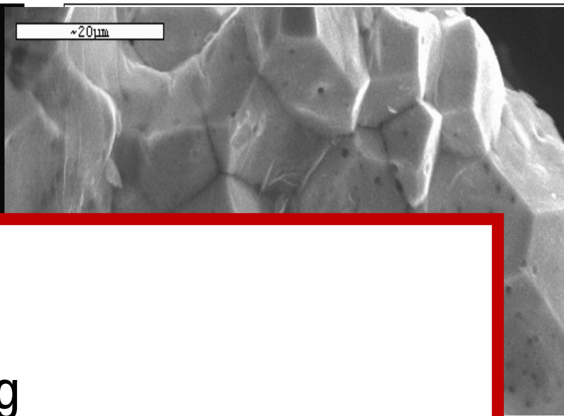
→ **Sample splitting**

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

Senter for fremragende forskning

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

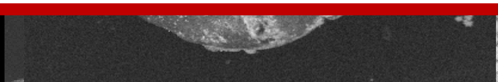


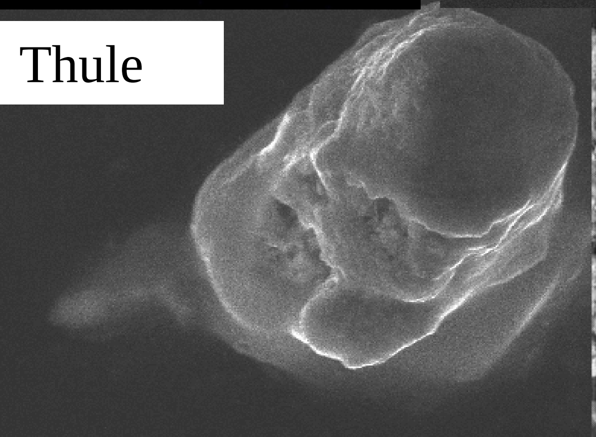


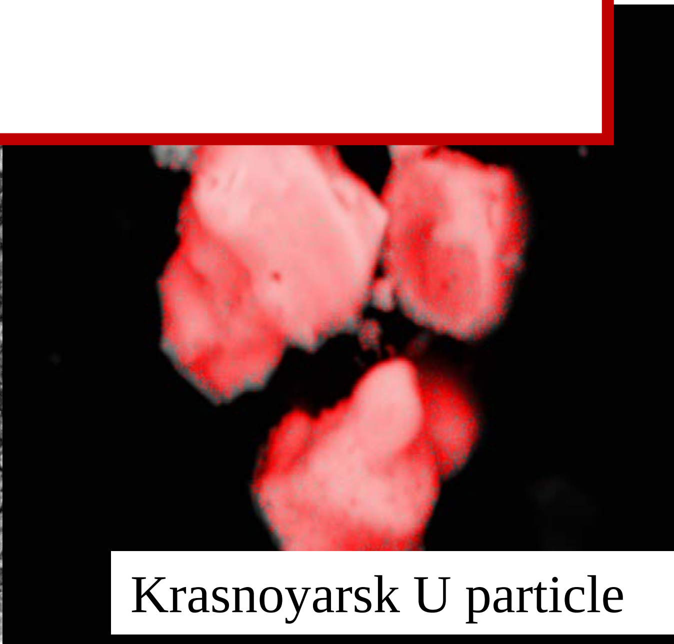
Particle deposition:

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

Adds significantly to the overall uncertainties







Advanced techniques available for particle characterization – state-of-the-art

- Hot spots/heterogeneities: digital autoradiography and sample splitting - gamma measurements
- Particle size, surface structure and elemental composition: ESEM with XRMA, TEM with XRMA
- Subsurface/volume elemental composition: SR-based 2D µ-XRF (fluorescens)
- Oxidation state determination: SR-based 2D µ-XANES (micro X-ray absorption near edge structure spectrometry
- Crystallographic structure: SR-based µ-XRD (micro X-ray diffraction)
- 3D elemental distribution: Confocal µ-XRF, TOF-SIMS
- 3D structure distribution: Tomographic µ-XRD

- Source identification: Isotope or atom ratios by MS techniques (ICP-MS, AMS)
- Weathering and mobilisation potential: Leaching experiments

Sorption mechanisms – important for mobility

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

Inert electrolyte

↓

Ionexchange pH

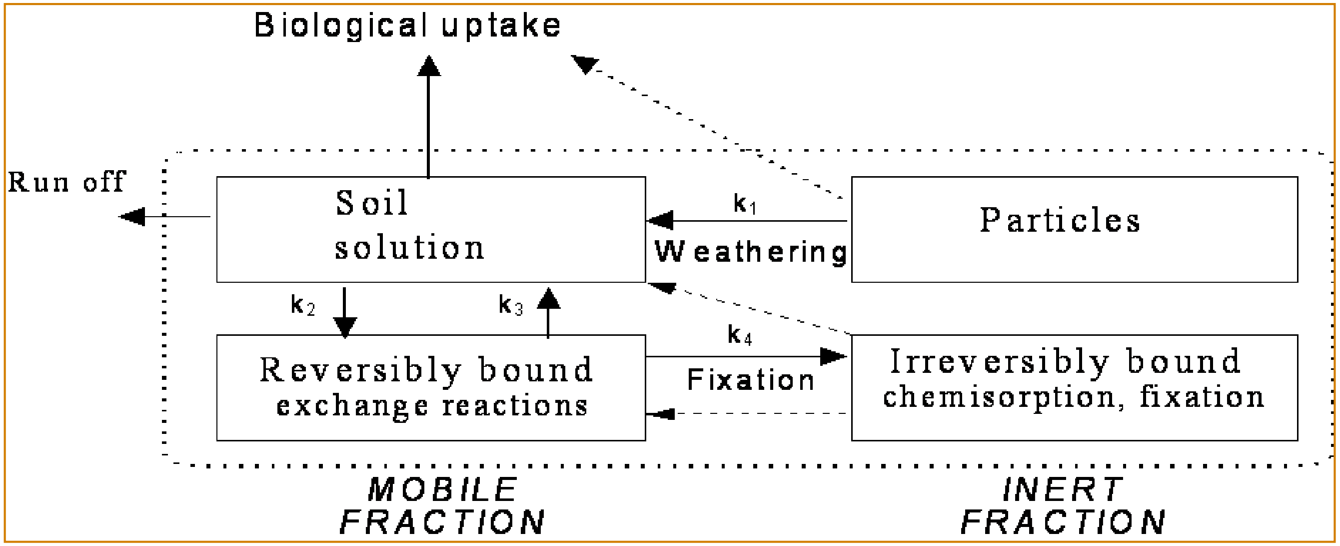
↓

red/ox

Strategy: sequential extractions

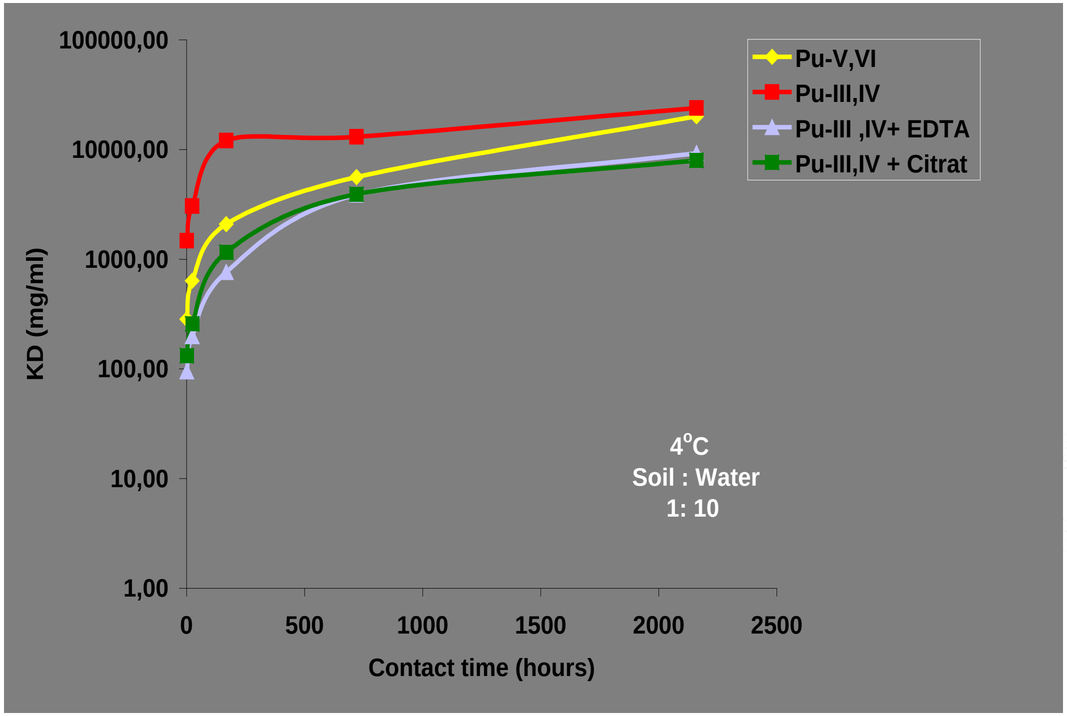
Increased dissolution power of agent

RADIOACTIVE PARTICLES→ point sources of potential short- and long-term radioecological and analytical impact



- Transformation prosesses f(t)
  - Weathering rates and remobilisation
  - Underestimation of transfer factors for ecosystems and environmental effects in particle contaminated areas (change in speciation, Kd and CF)

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

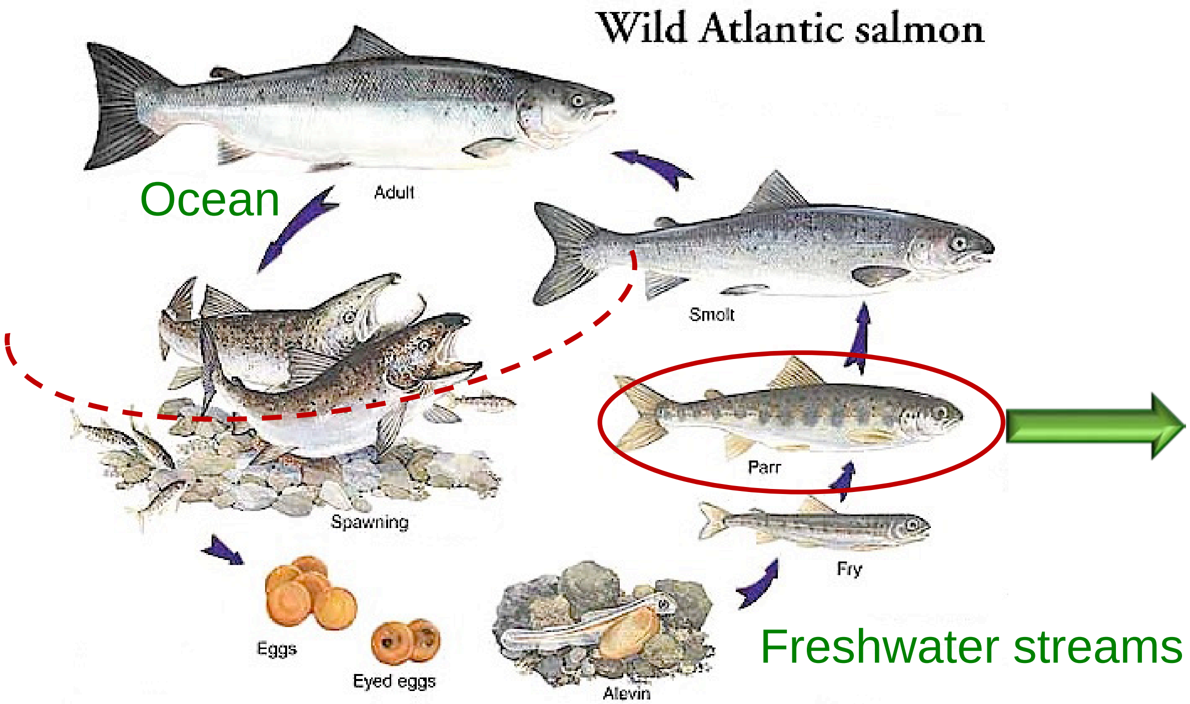


Speation:
Kd f(t) varies
1-2 orders of magnitude

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*

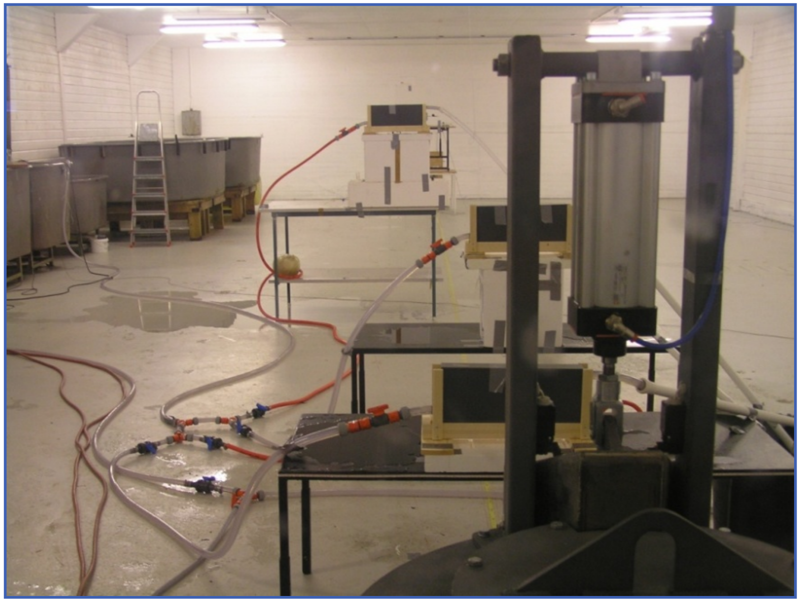
Case: Uptake in aquatic organisms – different life history stages of Atlantic salmon (*Salmo salar*)



Juvenile
Freshwater stage

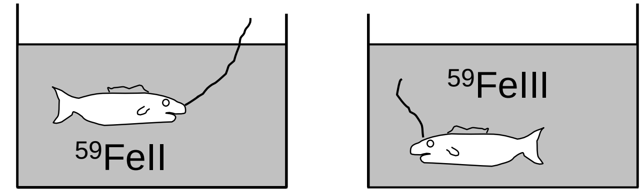
Sensitive life history stages: uptake, distribution, accumulation, depuration
Single and multiple stressors: additive, synergistic and antagonistic effects
Uptake mechanisms: gill deposition – transfer to blood

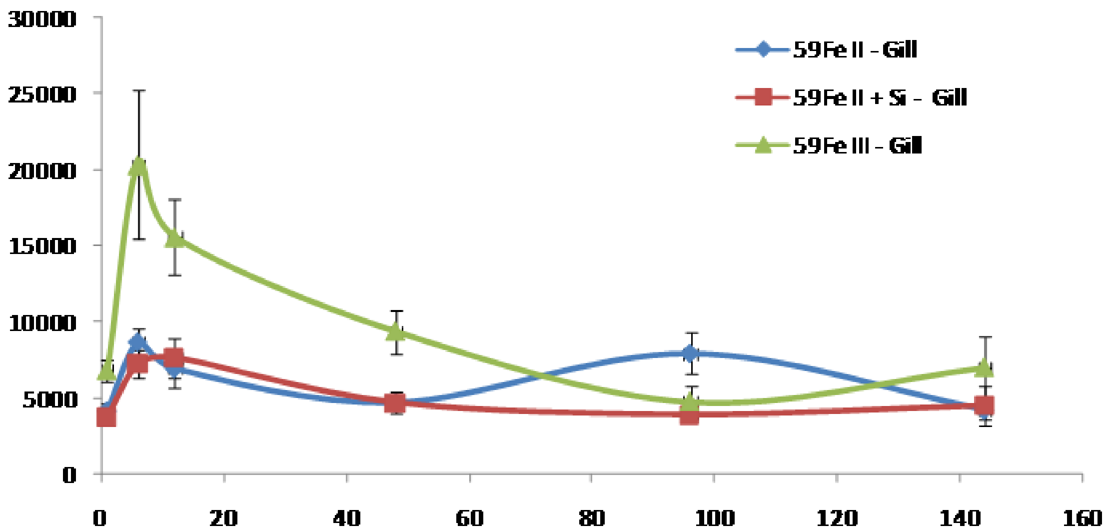
Experimental set up

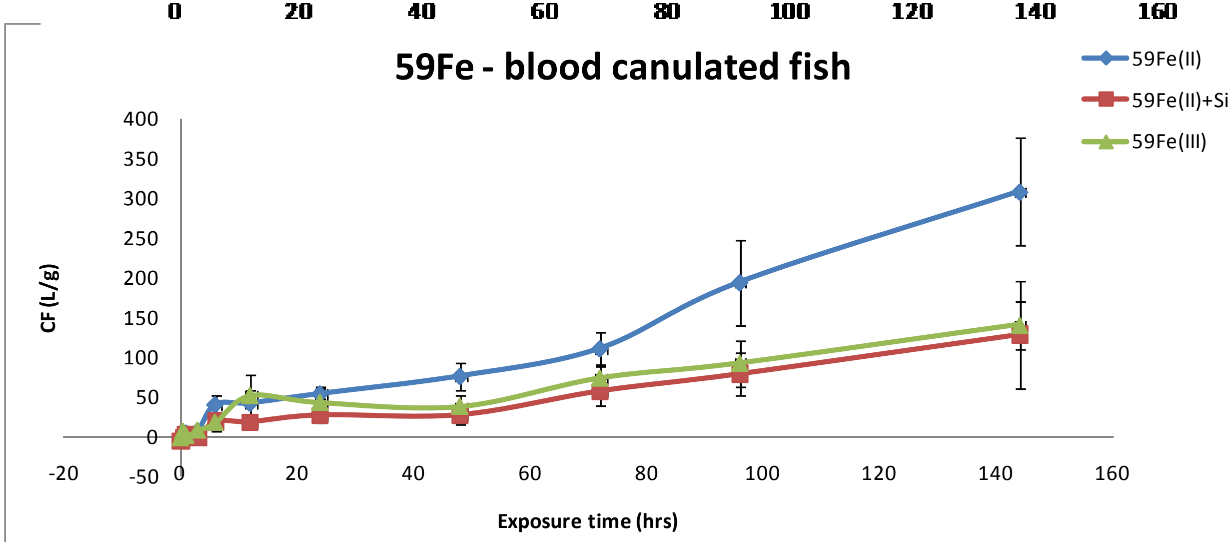


Photos: B.O.Rosseland

Accumulation and uptake of FeII and FeIII



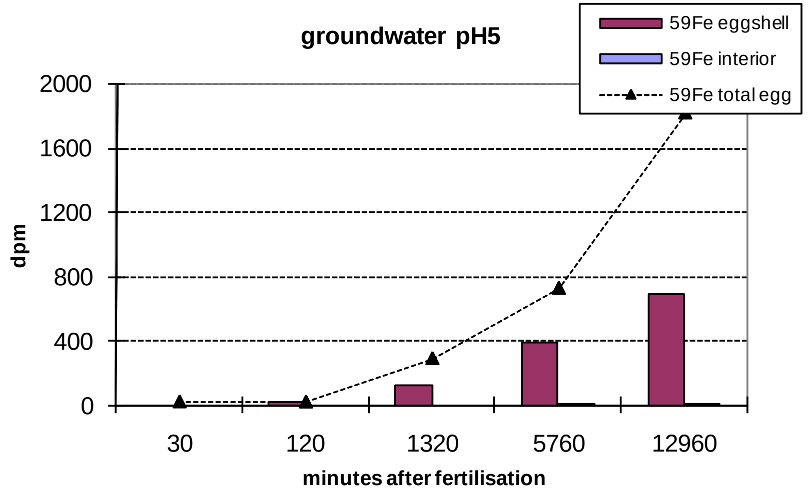


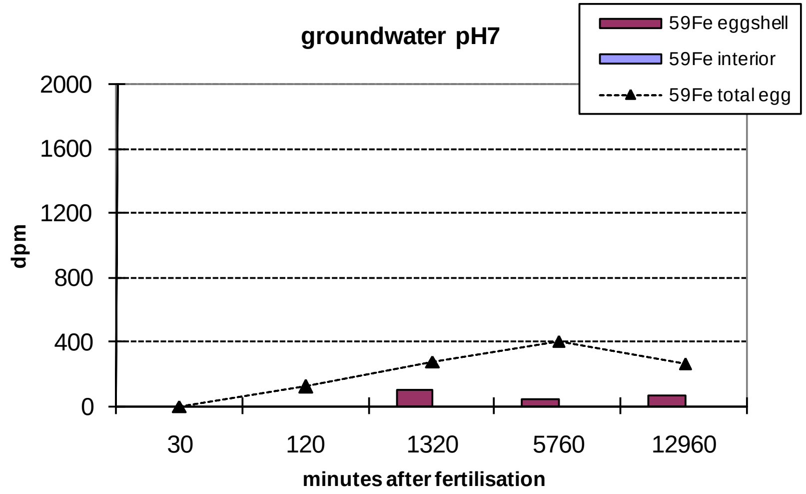


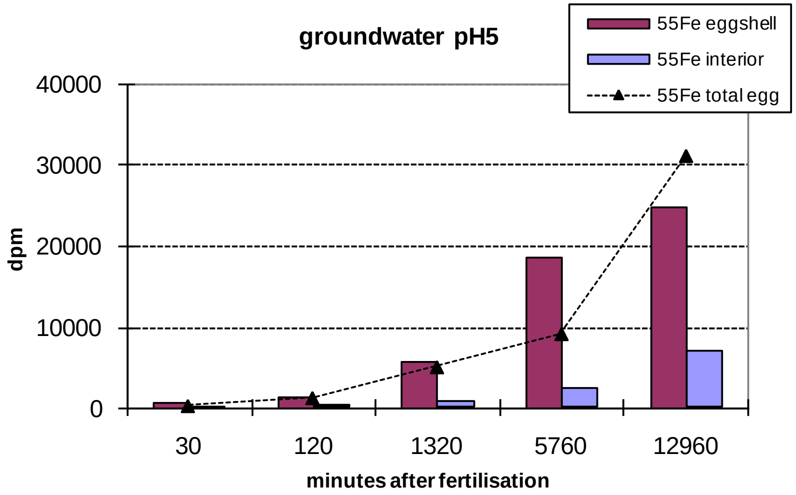
Aluminium in water and influence towards fish

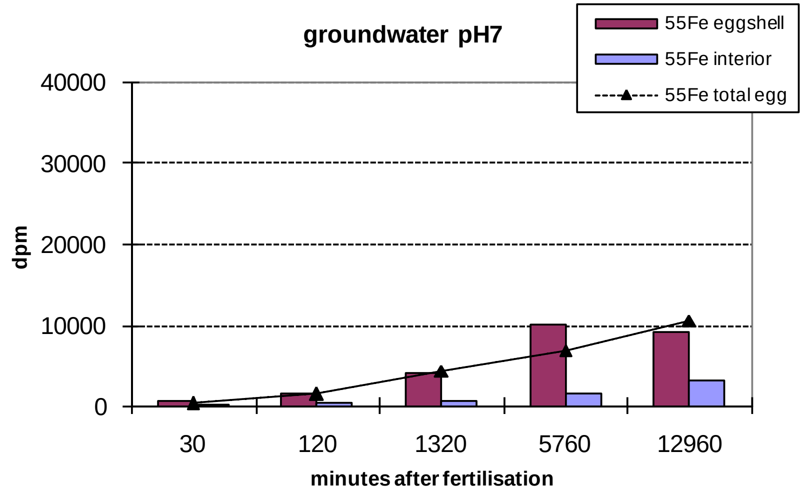
- Higher accumulation of FeIII on gills than for FeII ions, while FeII ions are transported more rapid from water into blood than FeIII ions.

Uptake of $^{59}Fe(II)$ and $^{55}Fe(III)$ in salmon eggs (30 min – 9 days after fertilization)



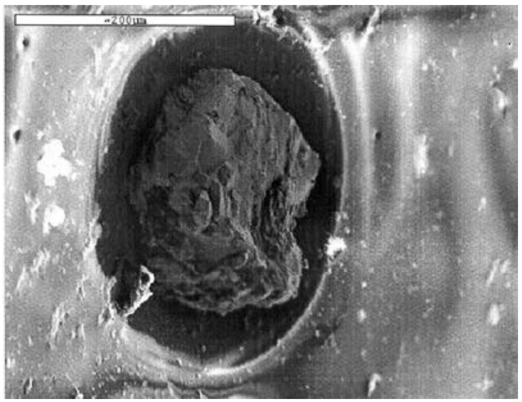






Source: spent U fuel particles
Impact: Retention of µm-nm particles

Radioactive particles retained in grazing goats,
Incorporated in GI tissues

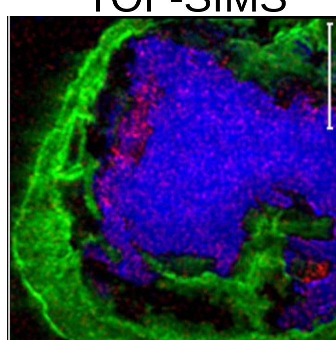


Dounrey particles given to Blue Mussels as food, retained in the gut and deposited in tissues

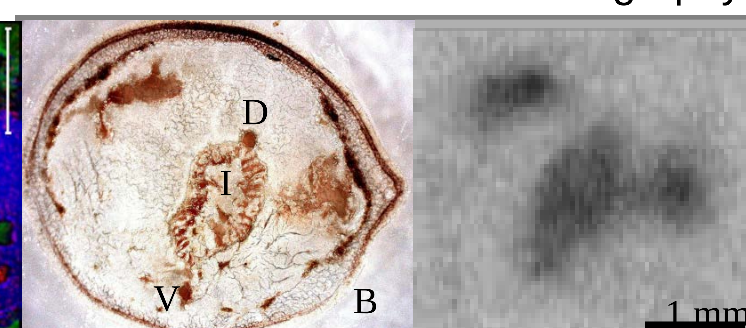
Severe skin dose about 30 mGy/hr, unevenly distributed
Microdosimetry challenge

^{60}Co NPs uptake in reproductive organs of earthwurms
Coutris et al, 2012

TOF-SIMS

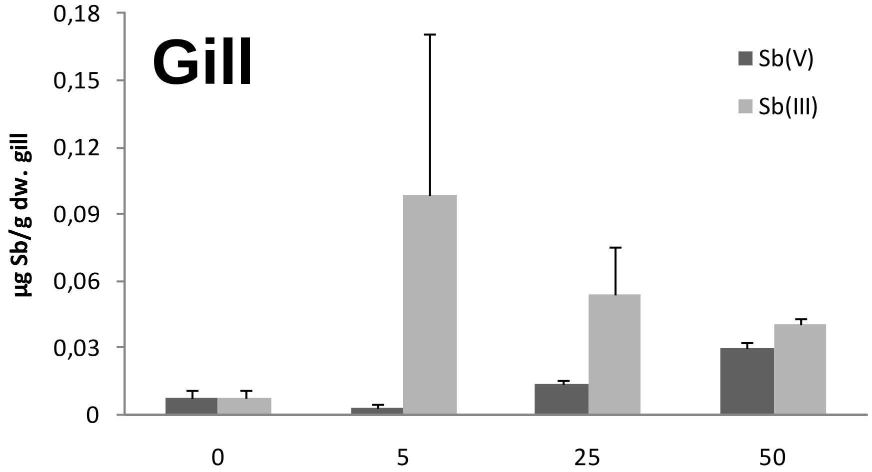


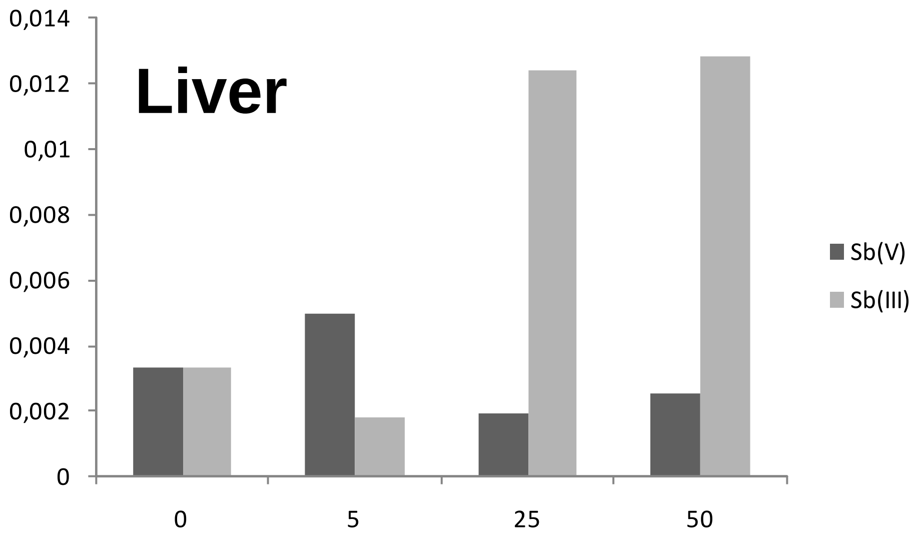
Autoradiography

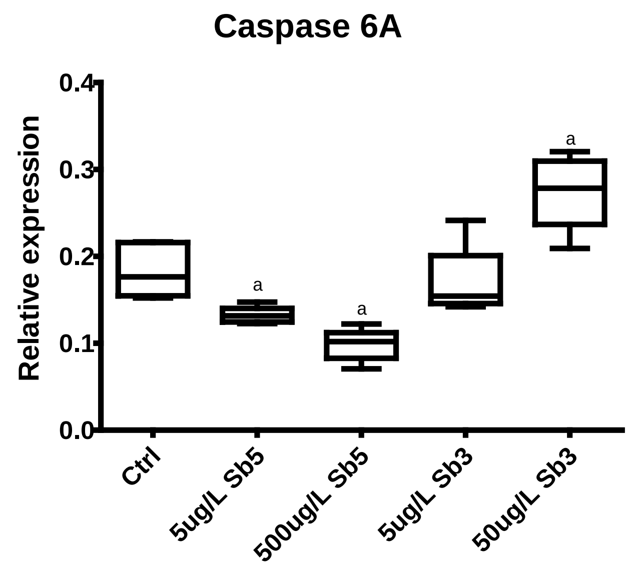


Sb(III) and Sb(V) –difference in uptake and effect (Heier et al, 2012)

- Salmon exposed to Sb(III) and Sb(V) (72 hours)







Why speciation?

Radionuclide speciation is essential for:

- source term estimates
- mobility and bioavailability
- ecosystem transfer processes
- impact and risk assessments
- remedial actions
- improvement of process-oriented models

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

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

Reducing the overall uncertainties:

- Source characteristics - Implementing particle distributions, speciation
- Implementing interactions/processes and kinetics
- Implementing proper endpoint determination
- Implement at site factual information/field experiments

Short and long term dose, impact and risk assessments

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

Conclusion

- Radionuclides can be present in different physico-chemical forms influencing ecosystem transfer, biological uptake and effects
- Transfer (Kd and TF or BCF) depends on speciation, ecosystem and biological species, and will apply to a time function f(t)
- Radionuclide species depend on sources and release conditions and transformation processes occurring in the environment
- Hazards can be underestimated if radionuclide speciation – presence of particles – is ignored
- Advances speciation/fractionation techniques are needed to distinguish between radionuclides species.


Senter for
fremragende
forskning
Questions???