IRSN
INSTITUT
DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

Enhancing nuclear safety

Fate and behaviour of radium in water impacted by NORM

Importance of redox interfaces

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Introduction

Context and arising issues

- Mining operations increase the flux of contaminants to the surrounding environment

- Radium (Ra) : specific contaminant of NORM industries
  - Derives from uranium + coal mining activity, oil + gas production
  - Removal of Ra from wastewaters by co-precipitation into radiobarite
  - Barite is suspected to be dissolved under sulphate-reducing conditions

↗ Long-term effectiveness of Ra trapping ?

↗ Radium fate and behavior regarding the redox interfaces ?

↗ Groundwater – Surface water

↗ **Water – Sediment**

Studied zone

↗ Upper Silesia Coal Basin, Poland

- Underground coal mining activities
- Brines containing high concentration in Ba and Ra (up to 300 Bq L^{-1})
- Mixed with underground waters containing sulphate ions

➢ Much of the Ra isotopes trapped into radiobarite [$(Ba,Ra)SO_4$] in the bottom deposits of settling ponds [Chalupnik et al. JER 2001]

↗ Former settling pond

- ↗ In operation from 1977 to 2001
- ↗ Since 2001 it serves as storage reservoir
- ↗ Back to the « wild »

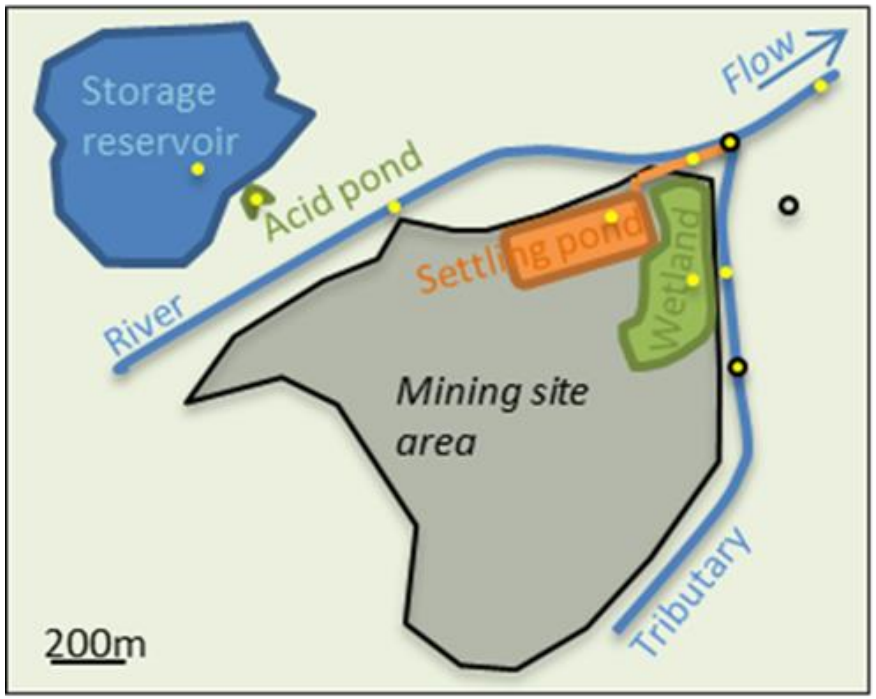
↗ Analogue of long-term situation of Ra-rich waste storage

Methods : empirical approach

- Collaboration IRSN and GIG (Central Mining Institute, Poland)
  - Samplings and analyses

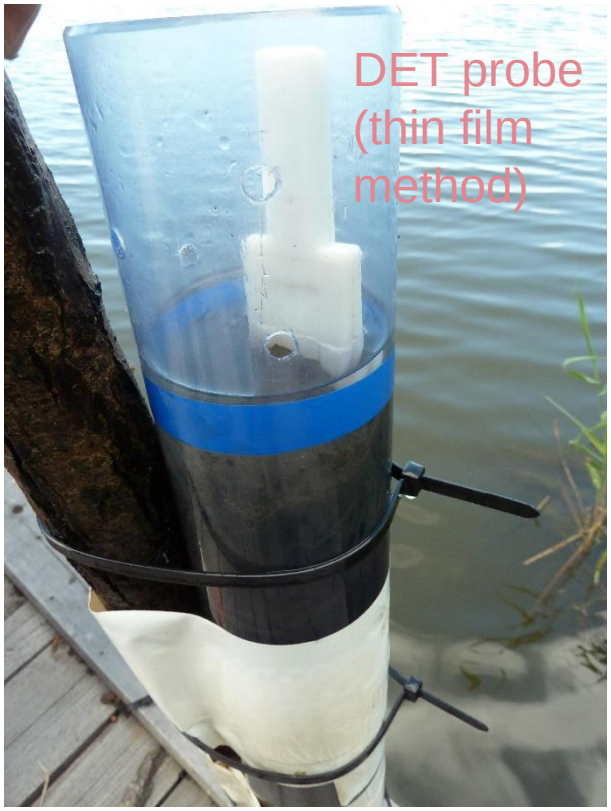
- Samplings
  - 4 single campaigns 2014, 2015, 2016, 2018
  - 11 sampling points in yellow on the scheme
  - Collection of sediment, water, sediment pore water, subsurface water

- Laboratory analysis
  - ➢ Particulate and dissolved fractions
    - Gamma-emitters (γ-spectrometry)
    - Ra-226 and 228 (liquid scintillation)
    - Mineralogical composition (XRD)
    - Major and trace elements (ICP-OES)
    - *Ra-226 by ICPMS (in progress)*




Coring sediment


µ-electrodes (oxygen, sulfide)


DET probe (thin film method)


Material transport

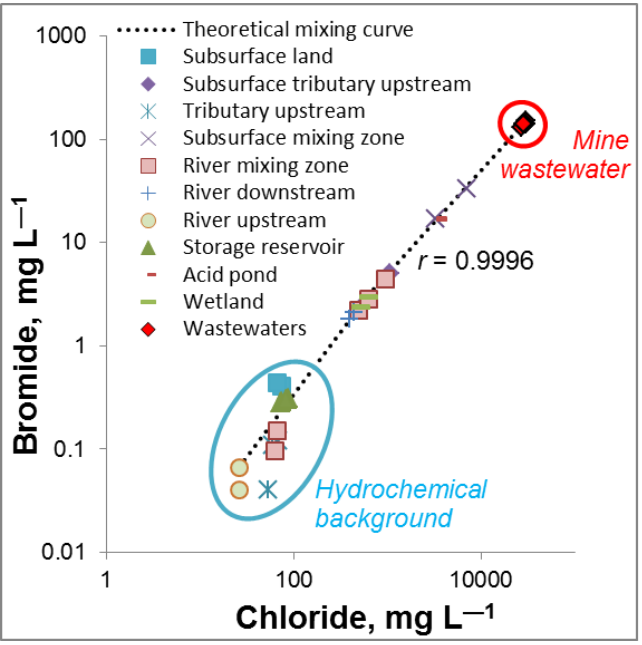

Suspended sediment

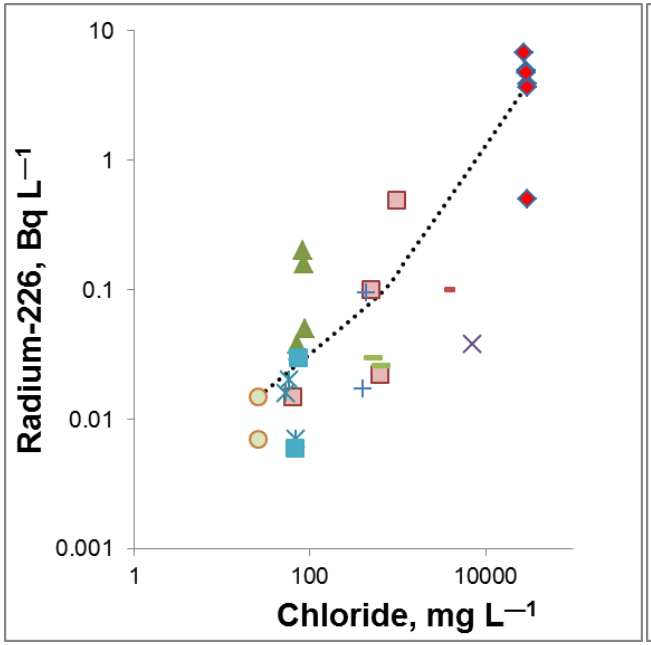

Sediment samples

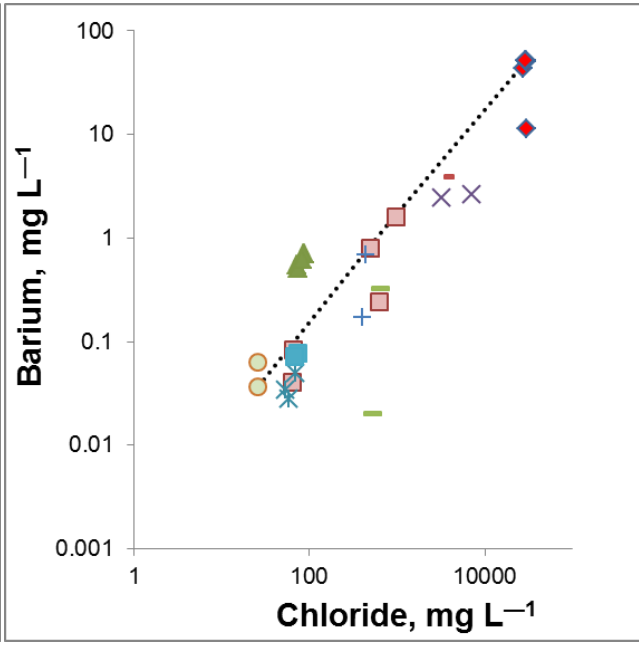

Sampling works

Results

↗ Mining area : surface water and groundwaters





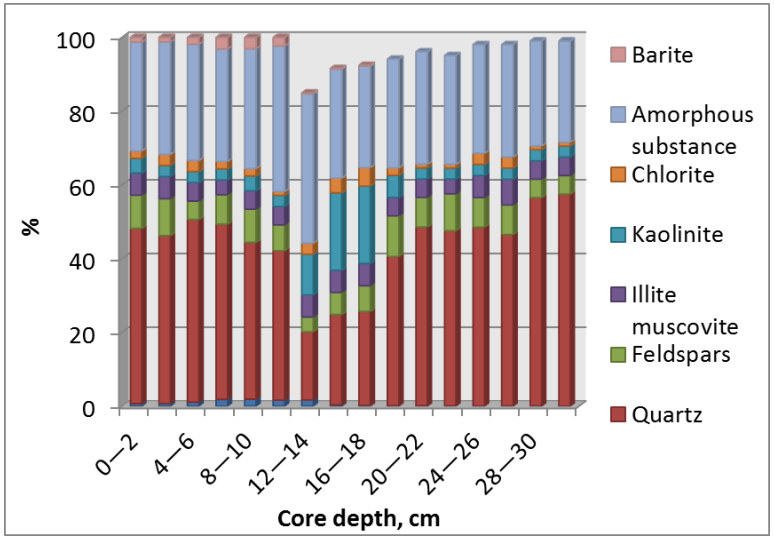


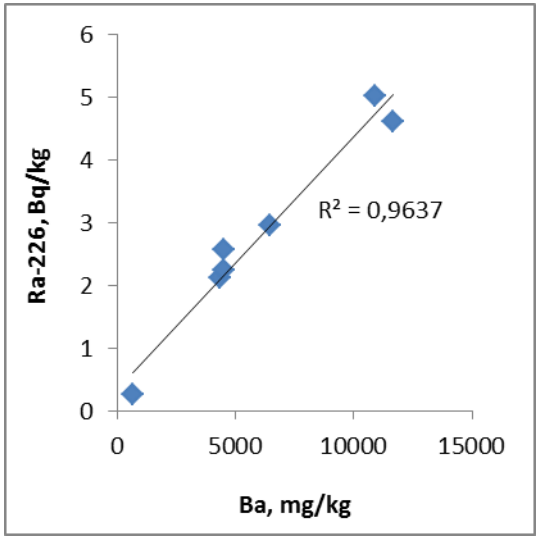
- Mixing processes between two term-sources [Courbet et al. IMWA 2016]
  - Mine wasterwater / hydrochemical background
- Ba and Ra removed from waters through precipitation + adsorption processes
  - ➢ Except the former settling pond : slight enrichment observed

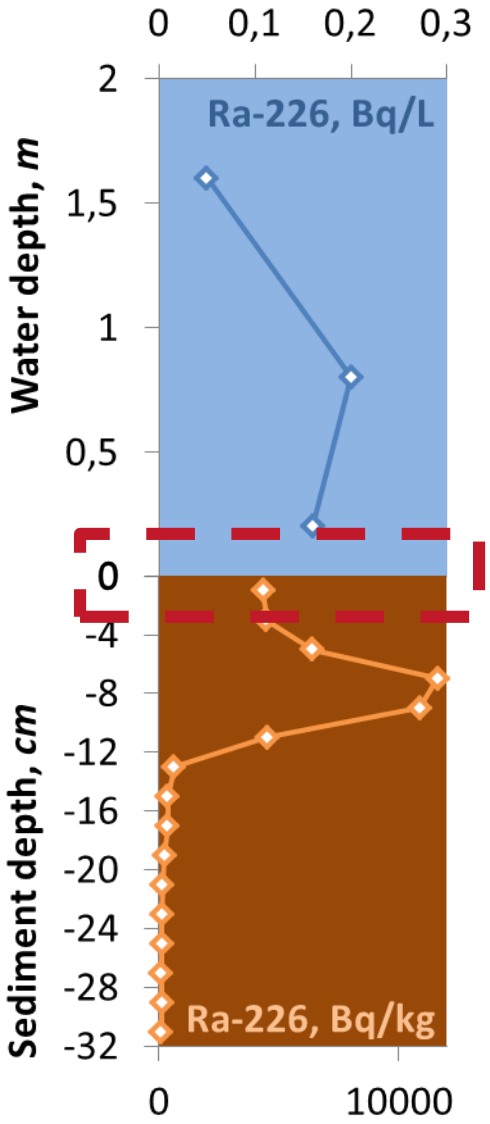
↗ Role of the bottom sediment ?

Results

↗ Former settling pond





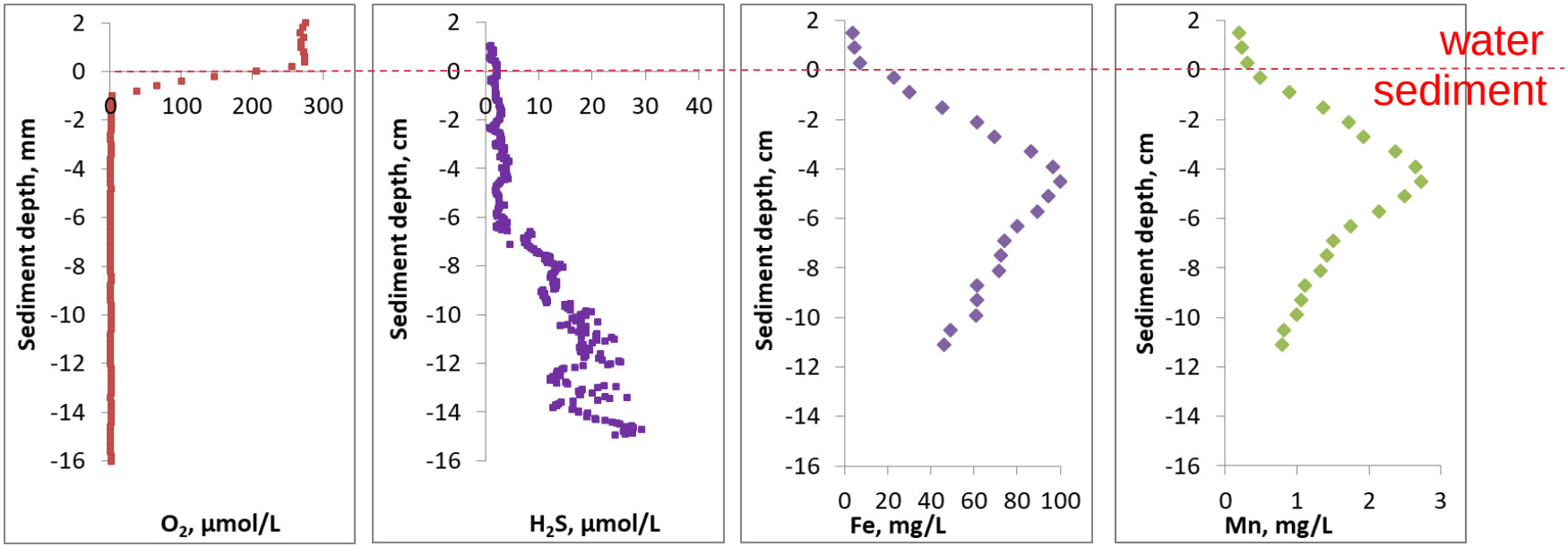


- Sediment composition
  - Ra-226: up to **11 kBq/kg** at 7 cm of depth
  - % Barite < 5
  - Correlation Ra with Ba → same origin/behavior
- Pond water : up-down gradient Ra-226

↗ Processes at the water-sediment interface ?

Results

↗ Across the water-sediment interface

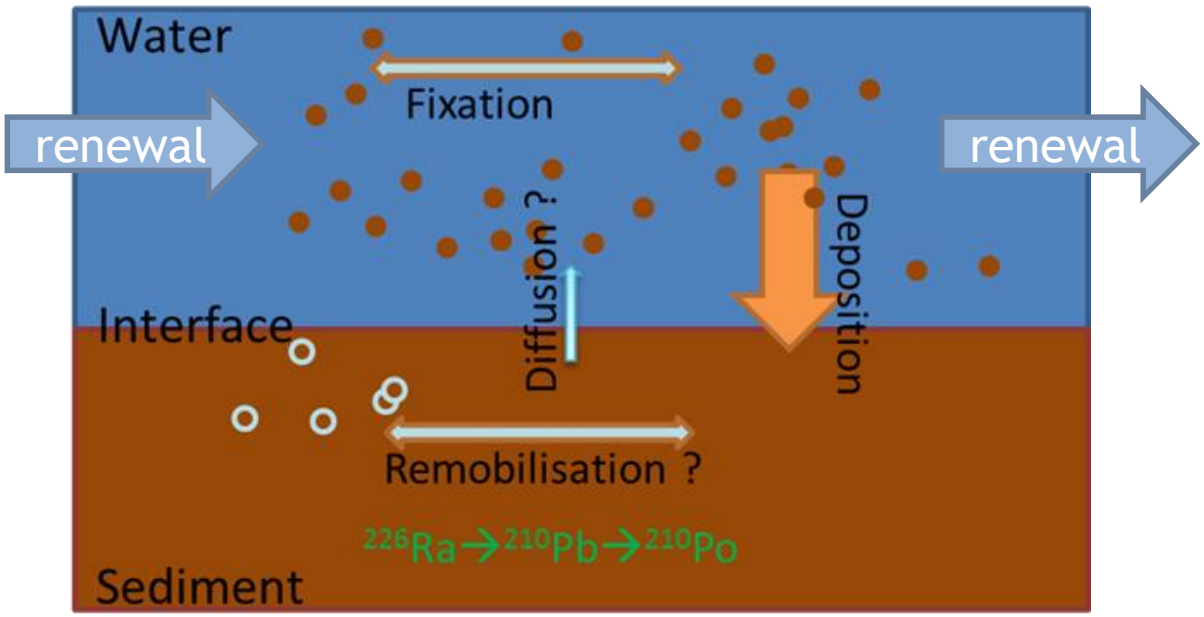


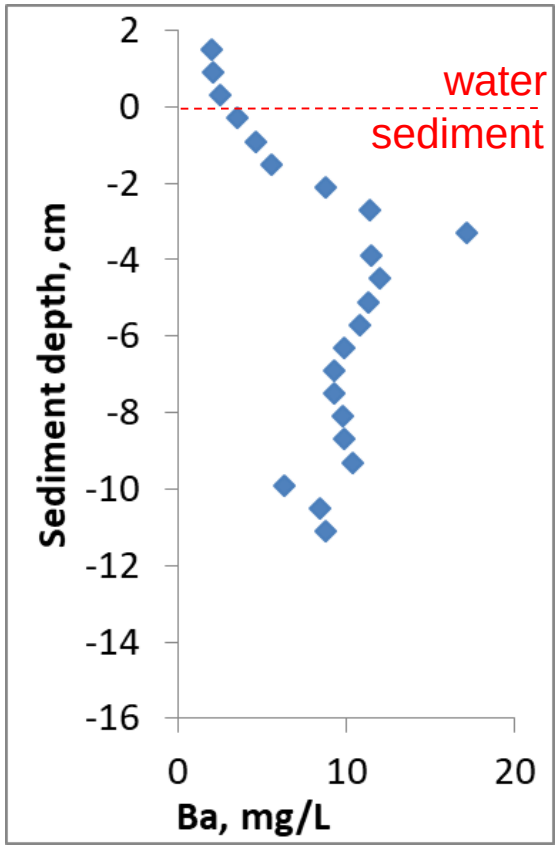
- High-resolution vertical profiles in the sediment pore water
  - ➢ Oxygen consumption ← organic matter degradation
  - ➢ Sulphide production ← sulphate reduction
  - ➢ Fe and Mn oxides dissolution under reducing conditions

↗ Early diagenesis process : fate of Ra ?

Results

↗ Ra analogue : Ba





- Determination of Ra in sediment pore water by **ICPMS** : *in progress*
- Ba remobilization in sediment pore water
  - ➢ In the zone of the reducing dissolution zone of Fe/Mn oxides
  - ➢ Diffusive flux towards the overlying water (First Fick Law) = 15 mg m^{-2} d^{-1}

Conclusion & perspectives

- Investigation on the fate and behaviour of Ra in a former settling pond displaying NORM bottom deposits
  - Empirical approach
  - Functionning of the ecosystem after its return to the wild state
    - Occurrence of diagenetic reactions
    - Diffusive fluxes through the water-sediment interface (Ba = Ra)

- Further work to assess the Ra behaviour
  - Acquisition of high resolution vertical profiles
  - Ra (and Ba) speciation in sediment
  - Ra-226 progeny (Po-210) ?

↗ **Long-term sustainable waste management strategy**

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GIG

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