

**IRSN**

INSTITUT  
DE RADIOPROTECTION  
ET DE SÛRETÉ NUCLÉAIRE

*Enhancing nuclear safety*

# Importance of redox interfaces regarding the fate and behaviour of radium in water impacted by NORM



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# Introduction

## Context and arising issues



- Mining operations increase the **flux of contaminants** to the surrounding environment
- **Radium** : specific contaminant of NORM industries
  - Derives from uranium + coal mining activity, oil + gas production
  - Removal of radium from wastewaters by co-precipitation into **radiobarite**
  - Barite is suspected to be dissolved under sulphate-reducing conditions

➤ **Long-term** effectiveness of radium trapping in water reservoir ?

➤ **Radium behavior** and **mobility** 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 barium and radium (up to 300 Bq L<sup>-1</sup>)
- Mixed with underground waters containing sulphate ions
- Much of the radium isotopes trapped into radiobarite [(Ba,Ra)SO<sub>4</sub>] 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)

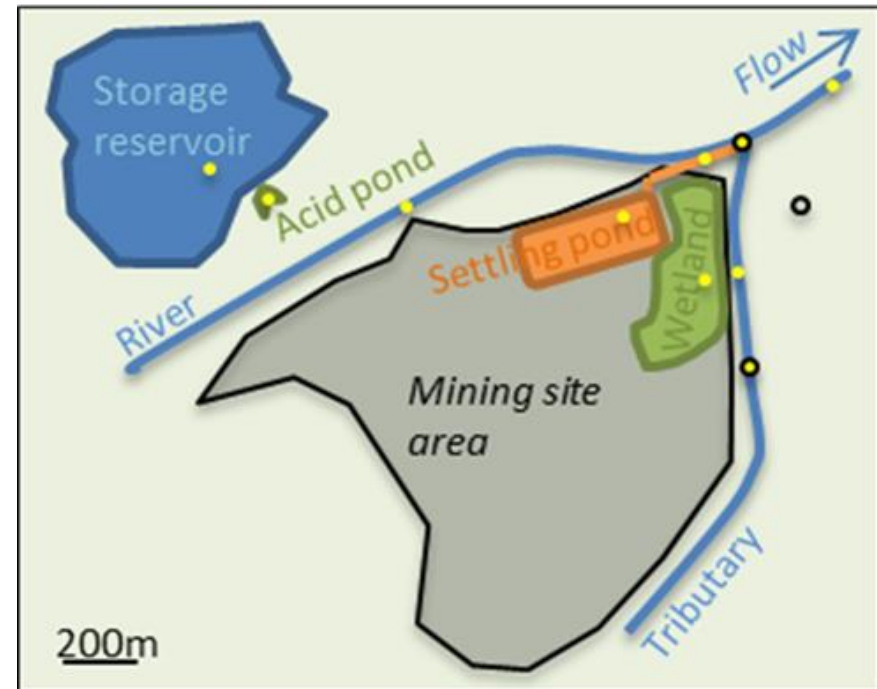
- Samplings and analyses

## Samplings

- 4 single campaigns 2014, 2015, 2016, 2018 (sampling points in yellow)
- Collection of sediment, water, sediment pore water, subsurface water

## Laboratory analysis

- Particulate and dissolved fractions
  - Gamma-emitters ( $\gamma$ -spectrometry)
  - Ra-226 and 228 (liquid scintillation)
  - Mineralogical composition (XRD)
  - Grain-size distribution (granulometry)
  - Major and trace elements (ICP-OES)





Coring sediment



$\mu$ -electrodes  
(oxygen,  
sulfide)



DET probe



Material  
transport



Suspended  
sediment



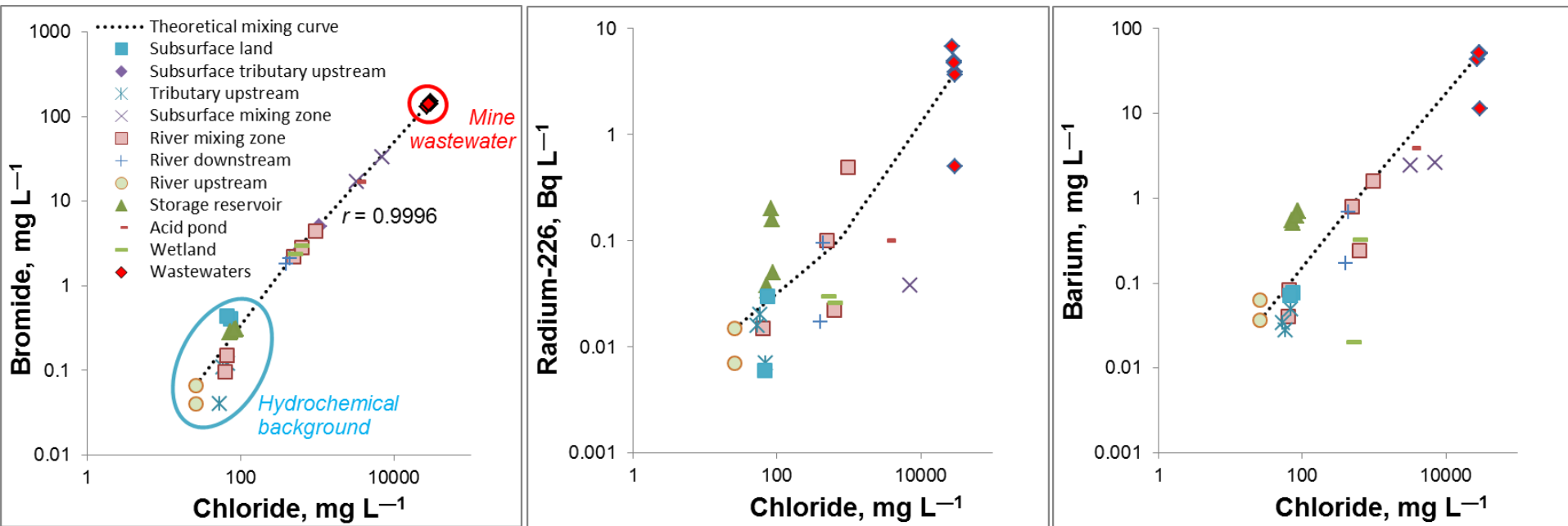
Sediment samples



Samplung  
works

# Results

## ➤ Mining area : surface and sub-surface waters

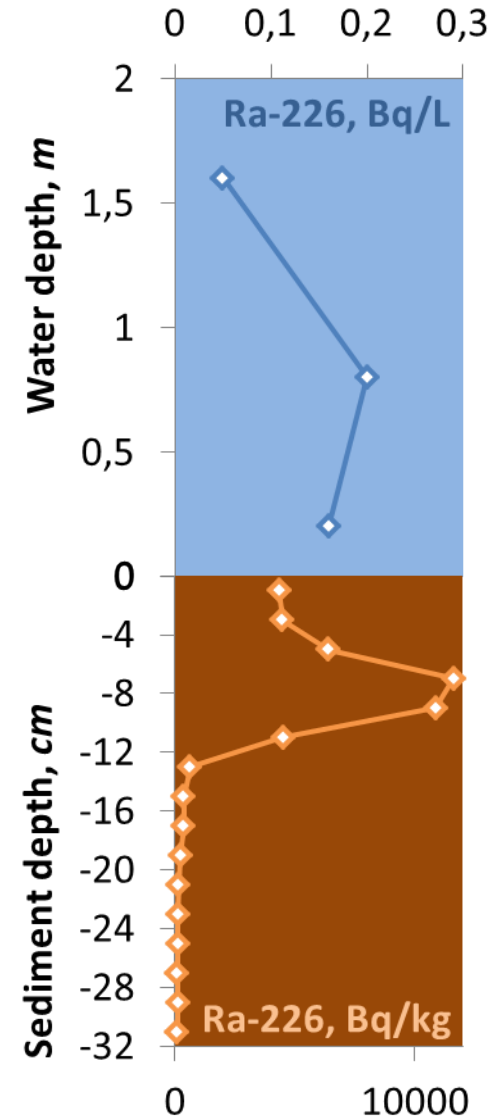
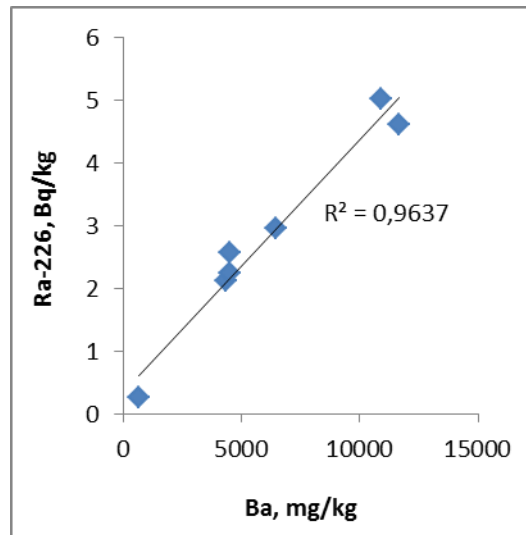
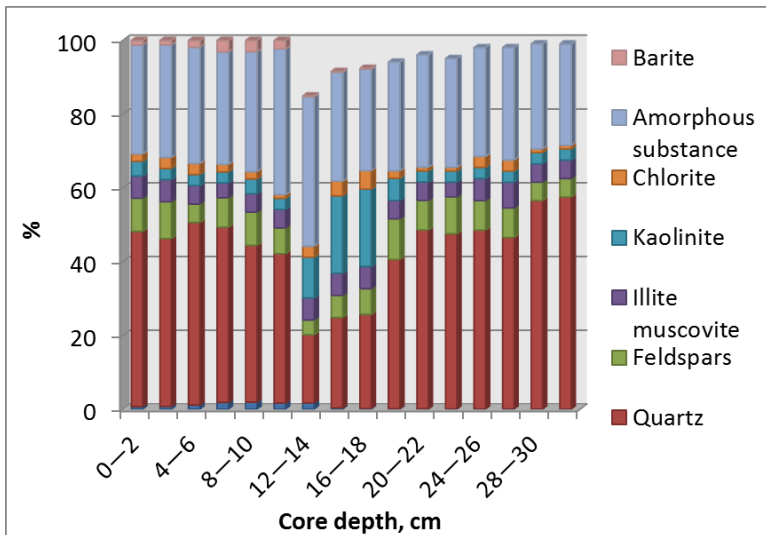


- Mixing processes between two term-sources [Courbet et al. IMWA 2016]
- Impact on river and subsurface waters ← direct and/or diffuse transfer pathways
- Ba and Ra removed from waters through precipitation + adsorption processes
  - Except the former settling pond : slight enrichment observed

## ➤ Role of the bottom sediment ?

# Results

## ➤ Former settling pond

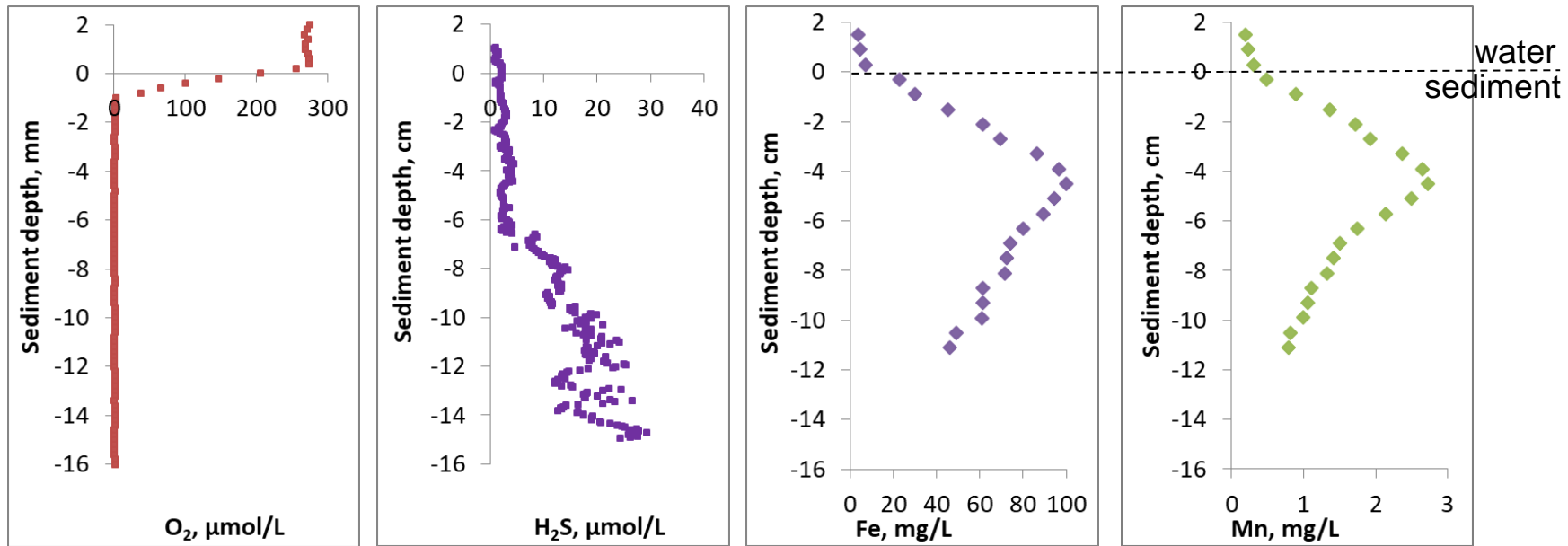


- Sediment composition : % barite < amorphous substances
- Correlation Ra with Ba
- Coupling chronological and geochemical investigations
  - Three age-periods of sediment accumulation = pre mining period, mining exploitation and on-going inputs

## ➤ Processes at the water-sediment interface ?

# Results

## ➔ Across the water-sediment interface



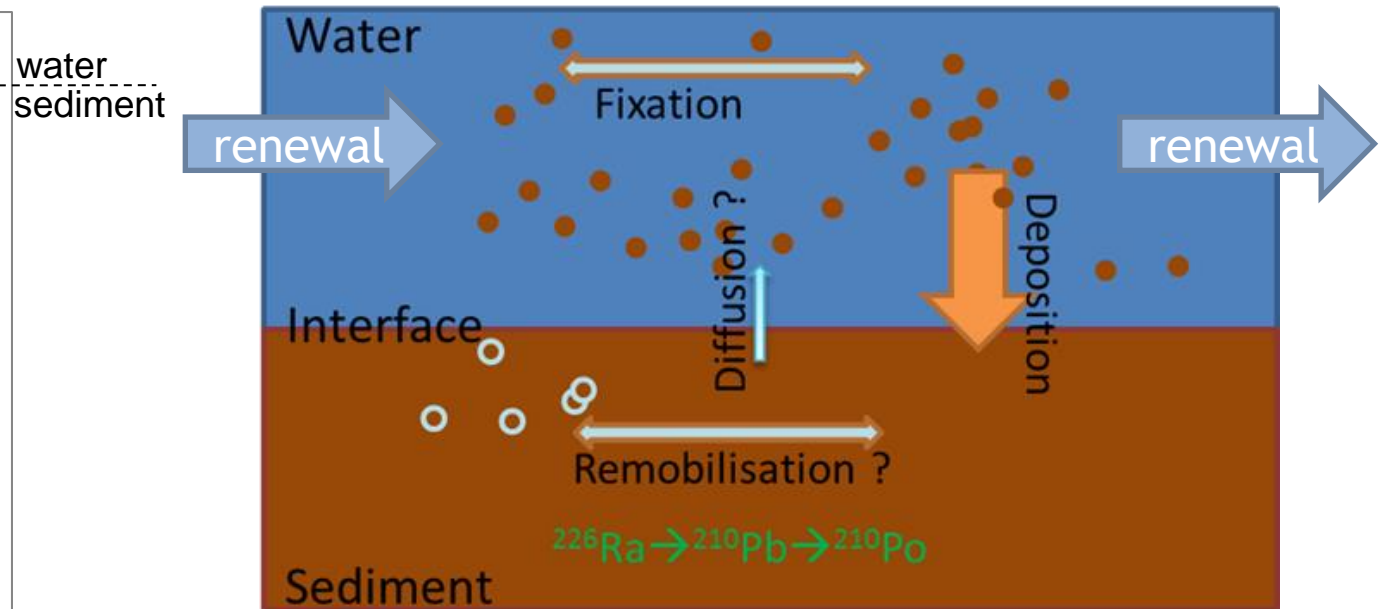
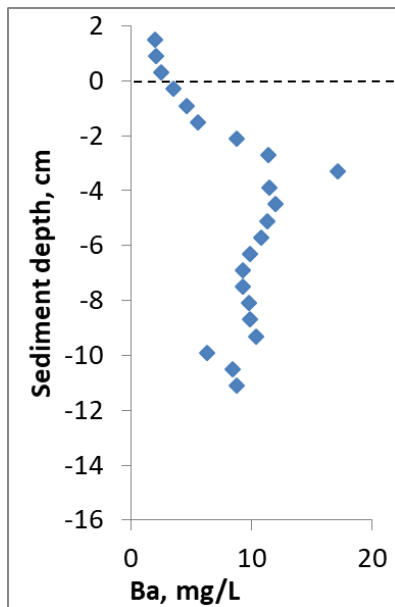
- High-resolution vertical profiles in the sediment pore water
  - Reduction zone below the interface → diffusive fluxes
- Below the water-sediment : Early diagenesis process
  - Oxygen consumption → organic matter degradation
  - Sulphide production (sulphate reduction)
  - Fe and Mn dissolution under reducing conditions

➔ Radium mobility ?



# Results

## ➤ Radium analogue : Barium



- Barium dissolution in sediment pore waters
  - Diffusive flux towards the overlying water (First Fick Law) =  $15 \text{ mg m}^{-2} \text{ d}^{-1}$
  - Estimation per day :  $\sim 1,2 \%$  of the total soluble Ba

## ➤ Management of waste storage covered by water

# Conclusion & perspectives

## Investigation on the long-term sustainability of the radium storage

- Empirical approach
  - Space scale of observation : mining area + surrounding environment
- Functioning of the ecosystem after its return to the wild state
  - Occurrence of diagenetic reactions
  - Diffusive fluxes through the water-sediment interface

## Further work to assess the radium mobility

- Acquisition of high resolution vertical profiles
  - Methodological and analytical developments
- Radium (and barium) speciation in sediment
  - Identification of Ra-bearing phases
- Site monitoring
  - Objective-specific survey period



# Acknowledgements

## Collaborators

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## Related projects and fundings

- RAMSES I project, funded from NEEDS program 2013
- RAMSES II project, funded from IRSN
- **TERRITORIES** project, part of the EJP CONCERT, funded from the Euratom program 2017-2020



<https://territories.eu/>