INTRODUCTORY PART
WEATHERING & SOIL CHEMISTRY
ENVIRONMENTAL RN CHEMISTRY
LL RADIOACTIVE WASTES & TENORM IN FRANCE
LLW Repositories in France

SECTORS PRODUCING RADIOACTIVE WASTE - France:

- Electronuclear cycle: 60%
- Defense: 9%
- Industry: 3%
- Medical: 1%

1000 producers/holders beside EN cycle: hospitals, university, industries, individual people

Operational facilities for Very low level wastes (VLLW) and Low Intermediate Level Wastes

Short Lived: stored in surface repositories (CIRES & CSA)

There are also 180 past mining sites

300 M tons of mill tailings are stored and environment is monitored

Radioactive waste management by ANDRA
LLW Repositories in France

The Aube disposal facility stores low- and intermediate level, short-lived radioactive wastes since 1992 (after CSM Manche)

Located in the Aube department
Radionuclides like $^{60}$Co or $^{137}$Cs or limited amounts of long-lived - 393 000 waste packages in 2018

Wastes :
Technological waste : produced during maintenance or repair works (metal, filters, cables, rubble, plastic, glass…)
Process waste : cleaning of ventilation and primary or secondary water circuits : water filters, air filters, ion-exchange resins, evaporator concentrates, sludge
Heavy maintenance waste : exceptional maintenance operations, such as vessel heads, primary pumps, parts of fuel assemblies
Decommissioning waste : scrap metal, rubble, earth and sludge

More than 60% of total volume of radioactive wastes ; 0.02% of total activity of French radioactive wastes
LLW Repositories in France

The Aube disposal facility (CSA) stores low- and intermediate level, short-lived radioactive wastes since 1992 (after CSM Manche)

- Wastes treated (compacted, solidified) by producer/holder and conditioned in concrete containers or in metal steels
- Waste packages transport to CSA - Checking for radiological level and compliance at arrival
- **Waste package grouting unit** block by mortar all bulk waste contained in 5 and 10 m³ metal containers to form a solid and non-dispersible, radioactivity-confining 5 cm thick matrix around the waste.
- **Waste package compaction** 200 L drums filled with "soft" waste; the waste pucks obtained are then cemented in a 450 L drum with hydraulic binder.

393 000 waste packages in 2018

*LILW-SL disposal at the Aube Disposal Facility (CSA) of ANDRA*
LLW Repositories in France

The Aube disposal facility (CSA) stores low- and intermediate level, short-lived radioactive wastes since 1992 (after CSM Manche).

Geological formation: Aptian sands covered by Aptian clay.

Designed for one million cubic meters of short-lived low or intermediate-level radioactive waste.

1) Vaults (concrete filled for perishable waste container - such as metal drums or boxes, gravel filled for non-perishable waste containers - such as concrete shells and boxes)
2) Cover system (filling materials, drainage layers, top-soil cover with grass)
3) Treatment and other auxiliary buildings
TE-NORM Wastes in France

250 sites for exploration, mining and treatment of U ore in France

All the sites are described in the National Inventory of uranium mining sites « MIMAUSA) made by IRSN

Sites under the responsibility of ORANO

17 mill tailing storage sites

ORANO has made impact studies for all the sites, which has been examined by PNGMDR (National plan on management of radioactive materials and waste) 2013-2015

Environmental diagnosis of all the mining sites under the responsibility of ORANO are being made, including the mill tailing storage sites
Long Term Socio Ecological Research

- ZATU belongs to LTER in France (created in 2000) and ILTSER (International Long Term Socio Ecological Research Network)

- Supported by CNRS / INEE

- 15 “Zones Ateliers” on different types of structural units, e.g., a river basin, a former-mine…

- Develop long-term fundamental and applied research in the field of the environment

Concept: An iterative framework bridging the social and bio-physicochemical sciences
ZATU (Zone Atelier Territoires Uranifères) & Rophin site

- Naturally Occurring Radioactive Material NORM (territories of Hercynian Arc in France) and TENORM (Technologically-Enhanced)

- Pluridisciplinary approach with 3 main Research Axes:
  - Risk trajectories
  - Traces & footprints (mechanistic: Radionuclides RN & trace metal elements TME transfers and accumulation, organisms responses)
  - (TE)NORM & Biocenosis (mechanistic & effects of low doses)

- Transversal: Instrumentation, sensors and data management

Several « open » sites, Rophin: GPS: 46°0'31.84"N, 3°33'10.86"E (Puy de Dôme)
Research topics: Naturally Occurring Radioactive Material NORM and Technologically-Enhanced TENORM
- Created in 2015. LPC Coordinator (V. Breton till 2018, D. Biron)
- A steering committee with a representative from labs, IRSN and CEA (2019)
- Financial supports: CNRS (and calls: EC2CO, Region, ANR, INTERREG...)

Laboratories

Other actors

ZATU (Zone Atelier Territoires Uranifères) & Rophin site
GEOCHEMICAL CONTEXT AND ISSUES

Rophin’s site

• A small watershed (circa 2 ha) in the Forez Massif (hydrog. basin: Allier)

• Parent-rock: Granite (quartz, K-feldspars, plagioclase, micas as primary minerals)

• Natural radionuclides (RN) ie, U-238, U-235, Th-232, and other trace metal elements (TME) like Ln, Pb…

• U ores emplaced at the end of Hercynian orogeny as lodes. Rophin lodes are oxidized and consist of low-temperature silica / quartz with parsonite \( \text{Pb}_2(\text{UO}_2)(\text{PO}_4)2\cdot2\text{H}_2\text{O} \) and autunite \( \text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{-}12\text{ H}_2\text{O} \)
Rophin’s site: NORM issues

• Rophin site: a forested area, humic soils developed on granite and a wetland including stream sediments, variation in soils composition at landscape scale

• Humic soils and wetlands are known to concentrate RNs and TMEs (U>1000 ppm in wetlands) due to past transfers over thousands of years

• Soils and wetlands are potential point sources of RNs/TMEs for waters and organisms

• Transfers and bioavailability of RNs and TMEs depend on their speciation which is poorly known in complex systems such as soils and wetlands and is a NORM issue
Rophin’s site : NORM issues

- RNs impact living organisms according to two main processes: external gamma irradiation, and internal irradiation and chemical toxicity following transfer of RN into organisms, e.g. by ingestion.

- The second process is considered to be more impactful for NORM and is related to the RNs availability in soil, which directly relates to the chemical forms of the RNs in the environment, i.e., their chemical speciation.

- Ecotoxicological effects of RNs and TMEs are moreover poorly known due to complex cocktails effects and trace level concentrations, and are another main issue of NORM.
Rophin Site

The inheritance from the First uranium mine exploitation in France

LACHAUX - 9 Avril 1947
Mme Joliot-Curie
HISTORICAL CONTEXT AND ISSUES

Rophin’s site : TENORM issues

- Rophin is one of sites of U mill tailings storage in France (MIMAUSA database).

- In the vicinity of Rophin mine, several other ore bodies were exploited: Gagnol, Etang du Reliez, Reliez and Bancherelle.

- Mill tailing waste (30 000t on 6000m$^2$) has been stored in situ.
During exploitation

In 2015

HISTORICAL CONTEXT AND ISSUES

- Ponds rejected downstream white and contaminated argilaceous residues during floodings events

Since storage, the vegetation is left to grow on the storage site, potentially recycling radionuclides and heavy metals
HISTORICAL CONTEXT AND ISSUES

Rophin’s site: TENORM issues

Potentially 2 sources of RNs and heavy metals:
- Storage site (anthropic)
HISTORICAL CONTEXT AND ISSUES

Rophin’s site: TENORM issues

Potentially 2 sources of RNs and heavy metals:
Storage site (anthropic) & Wetland (natural + anthropic)

Changes in speciation of RNs in soils and hence of mobility and bio-availability due to mining
ECODYNAMICS AND ECOTOXICOLOGICAL EFFECTS OF METALLIC MICROPOLLUTANTS (TME) OF SOILS OF A FORMER URANIUM MINE - ECOMU (SITE OF ROPHIN, FRANCE)

PLURI-DISCIPLININARY
Fundamental issues in chemistry and biology

M. Del Nero, S. Massemin, A. Boos
O. Courson, S. Georg, P. Ronot, S. Zahn, Islah El Masoudi

Collaborations: R. Scheffler, P. Chardon, V. Breton
ECOMU PROJECT

- Brief general presentation
- Soil-water chemistry
- Ecotoxicology
Acquire knowledge on both:

- Chemical speciation of TME (Ln, U, Pb...) in complex systems (soils), and the link with transfers to streams and to trophic chain (plants)

- Ecophysiological damages (oxidative stress, telomer length, a longevity index) to a terrestrial animal species (a vertebrate: the great/blue tit) due to biomagnification of TME cocktails
The Rophin site

Soil studies
Soil studies

Collection of soil, water and leaf samples
Main minerals of soils are K-feldspars, quartz and clays; Kaolinite and illite clays predominate in upstream soils

Association of Ferric smectite clay and iron oxides of colloidal sizes (cf. Figures) only in downstream soils and wetland

A natural evolution of soils at the landscape scale due to a more intense leaching of Fe and primary silicate minerals in soils richer in organic matter upstream
Soil studies

Elemental analysis of organic matter (OM)

Upstream surface soils have higher content in OM

Fe was leached with OM from upstream soils and accumulated downstream and in wetlands: formation of Fe-smectite and iron oxides
Soil studies

Chemical analysis

High content of Lead in soils upstream or downstream (like for Zn)

Anomalous soil samples around storage site (past mining activities)

Different desorption depending on a soil!
Soil studies

Chemical analysis

Increase of La with Fe$_2$O$_3$ content of soils from upstream to downstream

Soils of wetland are natural accumulation zones of Fe and La

Different desorption rates, not only dependent on the total concentration
Soil studies

Increase of all elements of Ln series with Fe$_2$O$_3$ content of soils from upstream to downstream

Soils of wetland are natural accumulation zones of Fe and Ln
Soil studies

Chemical analysis

Increase of U with Fe$_2$O$_3$ content of soils from upstream to downstream

Anomalous soil samples around storage site (past mining activities)

Soils of wetland are natural accumulation zones of Fe and TMEs like U and Ln
Soil studies

Elemental and molecular analysis of organic matter (OM)

Upstream soils have higher content in OM - Thousands of organic molecules of various structures and compositions (aliphatic, aromatic, condensed aromatics) were analysed

Soils of wetland have lower contents in OM but specific highly-oxygenated molecules

Probably U and Ln were leached with OM from upstream soils and accumulate downstream due to interactions between these highly oxygenated organic molecules and Fe-minerals
**Fe / Al oxides**

- **Molecule acidity** is the main chemical parameter governing the sorptive fractionation of FA (aliphatics and NC aromatics): surface ligand exchange.

- Both **molecular acidity** and **degree of hydrophobicity** control the degree of sorption of polycyclic aromatics on Al/Fe oxides.

- Increasing FA-to-hematite ratio favours preferential retention of most acidic PAC whereas aliphatics and NCA are left in solution.

**Kaolinite**

- **Weak selectivity** of the kaolinite surface towards FA molecules.

- Poor sorption of PACs O/C < 0.2.

- H-bonding of the FA molecules at weak sites (aluminol groups and silanol groups) on the basal plane of kaolinite is a good candidate.
Soil studies

Desorption experiments of TME from Rophin soil samples

Desorption %: Zn (90-5%) > Pb (20-5%) > U (18%<5) – Ln (5%<5%) except in wetland

Zn desorption shows huge variations in desorption with pH in upstream surface soils

Zn is more released in upstream than downstream soils and wetland (although not accumulated) → loosely bound to clays upstream and tightly bound to Fe-oxides downstream
Soil studies

Desorption experiments of TME from Rophin soil samples

Release of TME %: Zn > Pb (> U – Ln) except in wetland

Pb is more released from downstream soils and wetland, particularly in depth (although not accumulated) than from upstream surface soils (reverse of Zn) → OM favours a strong retention of Pb

Anomalous desorption rates from soils affected by mining activities
Soil studies

Desorption experiments of TME from Rophin soil samples

- U and Ln are more released (quantity and %) from downstream than upstream soils

- Release of TME in wetland %: Zn – U > Pb – Cu > Ln: U and Ln are accumulated but potentially accessible and mobile in wetland soils

- Anomalously high desorption of U and Ln (only light Ln) in soils affected by past mining
Soil studies

Increase of U, Ln, As with Fe$_2$O$_3$ content of soils from upstream to downstream

Desorption depend on a TME and on a soil (not only concentration) → Different cocktails potentially bio available depending on a TME speciation

Soils of wetland are natural accumulation zones of Fe and TMEs like U and Ln, but U, Ln and Pb are potentially more mobile in wetland (% desorbed)

Anomalous soil samples around storage site (past mining activities) : potentially high desorption rates of Pb, Light Ln, U (and Ba)
Transfers
- U, Ln and Pb are transferred to plants of the wetland possibly due to a specific metallo–organic speciation.
- Soils affected by past mining activities may transfer higher amounts of U to plants.
- Storage zone and wetland are potential sources of higher concentrations of U, Ln and Pb in waters, too.
Colloids: vectors of U / Ln mobility?

TEM Measurement: Observation of the fraction 0.45μm-0.08μm after filtration
ECOTOXICOLOGY
Food availability

→ 75% of food

→ Invertebrate sampling at each occupied nest

What about the effects of Me on the number and mass of these both types of preys?

No relationship with any Me
2. Effects on the morphology

ECOTOXICOLOGY

Biological results on tits
ECOTOXICOLOGY
What’s happen in an organism?

Pollutants

Inflammation

Degradation process

ROS

Anti-oxidant defences

Oxidative Stress

Alteration of Lipids, proteins, DNA

Telomere lost

Index of longevity

Andersson et al. 2009
Bonvallot et al. 2001
Haussmann et al. 2003
Livingstone et al. 2000
Saito et al. 1984
**Biological results on tits**

**Effects on the physiology of tits**

- **Oxidative stress**
  - Koivula et al. 2011
  - Berglund et al. 2007

- **Immune response**
  - Snoejs et al. 2010

- **Physiological parameters**
  - Negative on nestlings
  - No change in female adults
  - Telomeres decrease with U-Cd
  - Telomeres increase with Lanthanides-Pb
  - Telomeres decrease with Lanthanides-Pb

**Our study**

- No effect
Conclusion

* Some soils of Rophin site presents higher concentrations of U-Pb-As-Zn (wetland)
* Bioavailability of Me is heterogeneous in Rophin. Idem for the Leaf/prey concentrations
* Hatching success is affected by Pb
* Body size is negatively associated to lanthanides-Pb
* Telomeres in adults vary depending on a Me
* Different sensitivity between great and blue tits

Me Pollution has differential effects on reproductive success, morphological and physiological parameters in great and blue tits
Further research (wetland)

* Relation between RN speciation and RN lability
* Link between OM-microorganisms-plants-mineral interactions and RN speciation
  * Action retro-actions between RN and microorganisms
* Relations between RN speciation and uptake by plants (biogeochemical cycle)

Consortium of research teams from CNRS, CEA and IRSN
LLW Repositories in France

The Industrial facility for grouping, sorting and Very-Low Level waste (VLLW) disposal facility (CIRES):

Located in the Aube department

Wastes from dismantling operations, or non nuclear industries using naturally radioactive materials, or from cleaning of legacy sites historically contaminated

27% of total volume of radioactive wastes

VLLW Radioactive waste management at CIRES by ANDRA
LLW Repositories in France

The Industrial facility for grouping, sorting and Very-Low Level waste (VLLW) disposal facility (CIRES):

Every year, around 30,000 m³ of waste is disposed of in the trenches dug out in the clay.

Environment is planned to be monitored during 300 years.