INTRODUCTORY PART
WEATHERING & SOIL CHEMISTRY
ENVIRONMENTAL RN CHEMISTRY
LL RADIOACTIVE WASTES & TENORM
IN FRANCE

LLW Repositories in France

SECTORS PRODUCING RADIOACTIVE WASTE - France :

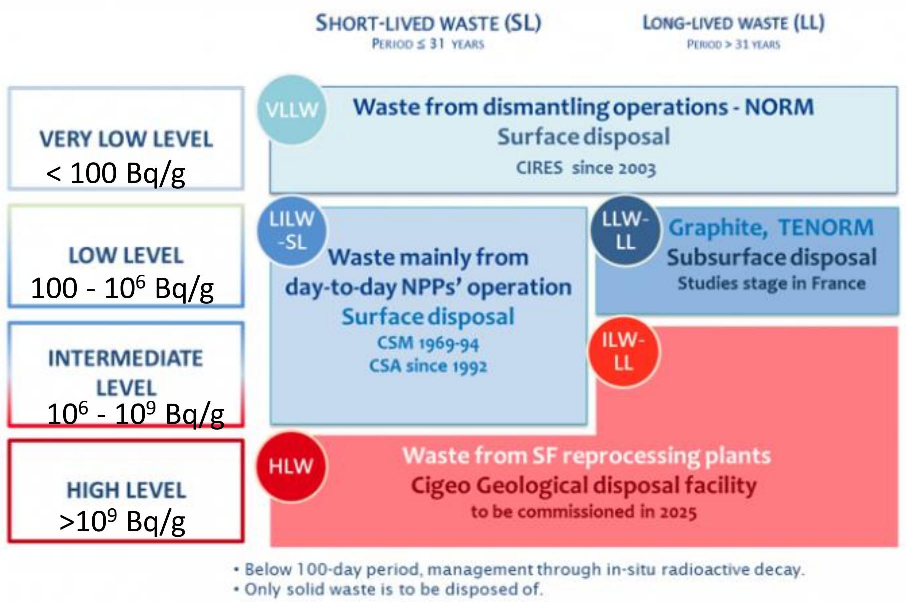
- Electronuclear cycle : 60%
- Defense : 9%
- Industry : 3%
- Medical : 1%

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 $^{60}C0$ 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

LILW-SL disposal at the Aube Disposal Facility (CSA). ANDRA

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.

Waste disposal

393 000 waste packages in 2018

LILW-SL disposal at the Aube Disposal Facility (CSA) of ANDRA

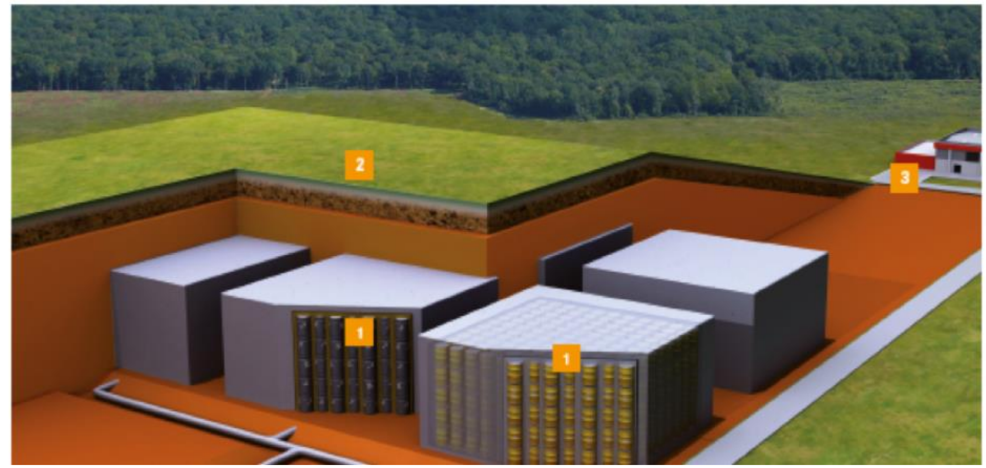
LLW Repositories in France

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

impermeable clay layer covered by a draining layer of sand (on which the disposal structures are built) constitutes a natural barrier to protect the environment in case of accidental releases of radioactive elements towards the groundwater table.



LILW-SL disposal at the Aube Disposal Facility (CSA). ANDRA

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

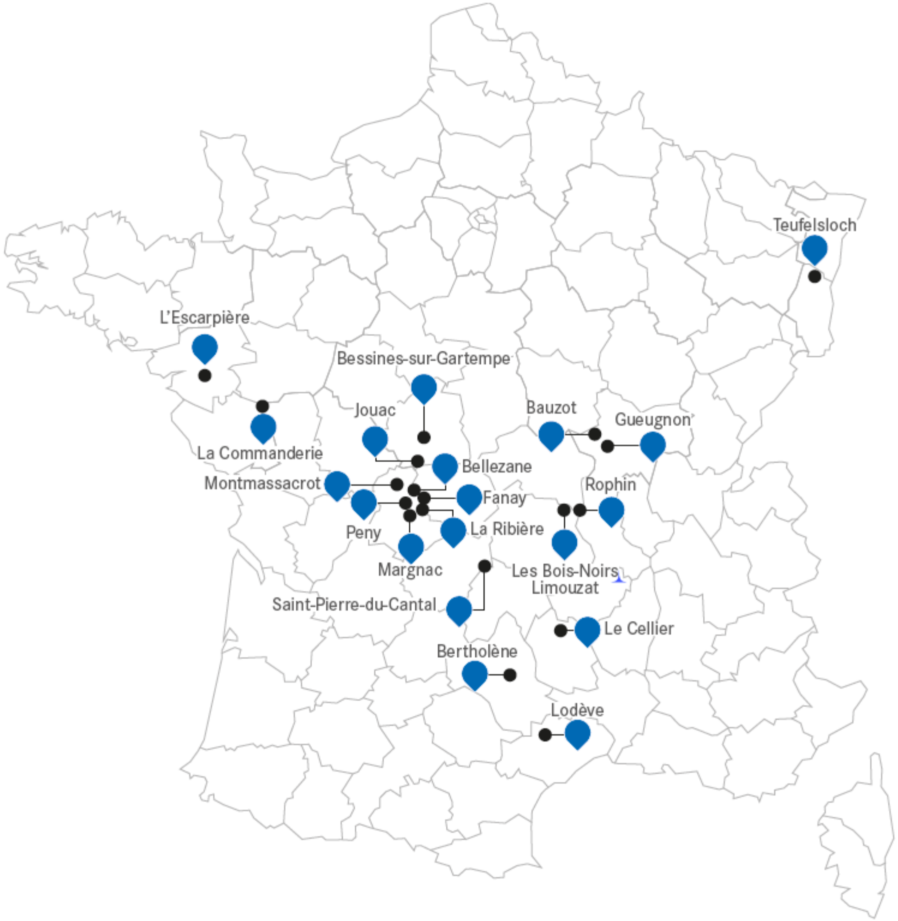
All the sites are described in the National Inventory of uranium mining sites « MIMAUSA) made by IRSN

Sites under the responsability 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 responsability of ORANO are being made, including the mill tailing storage sites



ZATU (Zone Atelier Territoires Uranifères) & Rophin site

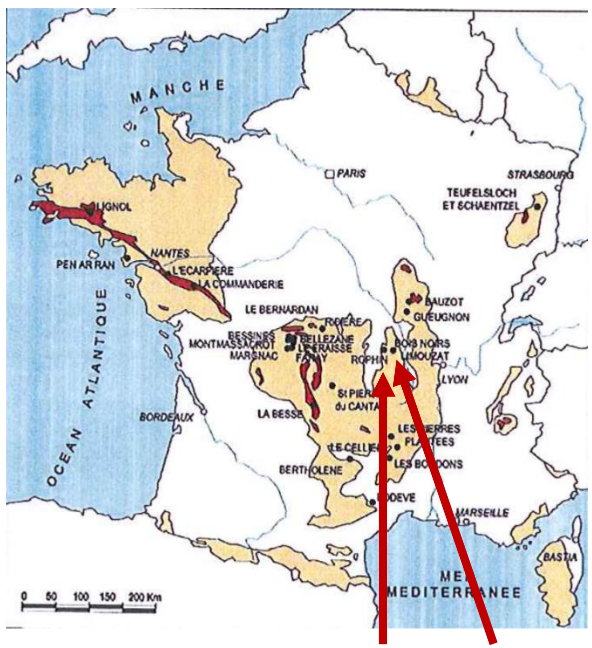
Long Term Socio Ecological Research

- 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

Zones Ateliers
LTSER FRANCE TERRITOIRES URANIFERES



ROPHIN BOIS NOIRS

- 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)

ZATU (Zone Atelier Territoires Uranifères) & Rophin site

Zones Ateliers
LTSER FRANCE TERRITOIRES URANIFERES

- **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…)

GEOLAB Géographie Physique et Environnementale

BECQUEREL le réseau IN2P3/CNRS de mesure de la radioactivité

Laboratories

LPC Laboratoire de Physique de Clermont

Subatech

Laboratoire Microorganismes : Génome et Environnement

IPHC Institut Pluridisciplinaire Hubert CURIEN Strasbourg

Institut de Chimie de Nice

CENBG

CHRONO ENVIRONNEMENT UNITE MIXTE DE RECHERCHE 6249

brgm

Lemna Laboratoire d'Economie et de Management Nantes-Atlantique

IRSN Institut de Radioprotection et de Sûreté Nucléaire

cea

LPCV Grenoble
BIAM Aix-Marseille

Other actors

DREAL

Conservatoires d'espaces naturels

asn Autorité de Sûreté Nucléaire

ACRO Association pour le contrôle de la radioactivité dans l'Ouest

orano

CHATELDON

LACHAUX

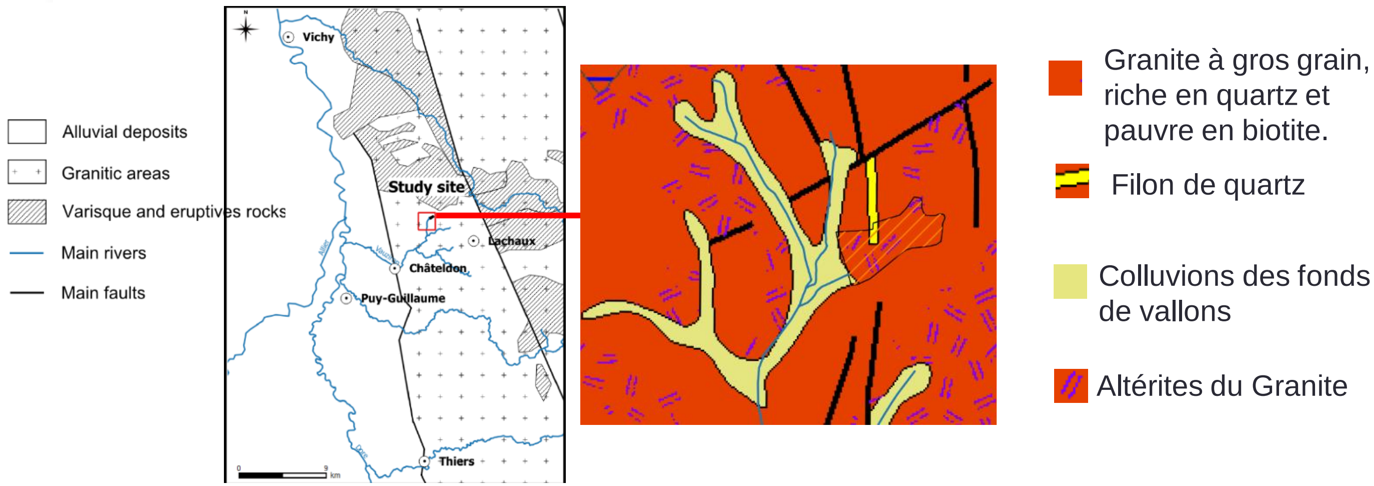
RIS

PUY-DE-DÔME CONSEIL GENERAL

Allier le Département

GEOCHEMICAL CONTEXT AND ISSUES

Rophin's site



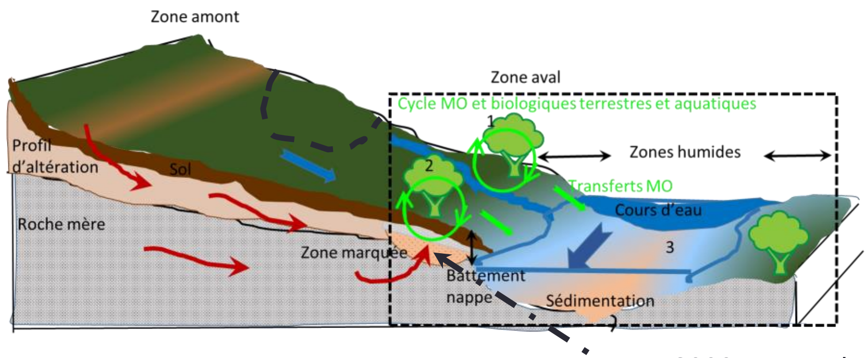
- A small watershed (circa 2 ha) in the Forez Massif (hydrog. basin : Allier)

- 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 [$Pb_2(UO_2)(PO_4)2 \cdot 2H_2O$] and autunite [$Ca(UO_2)_2(PO_4)_2 \ . \ 8\text{-}12\ H_2O$]

GEOCHEMICAL CONTEXT AND ISSUES

Rophin’s site : NORM issues



Up to 2000 ppm U, locally

- 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

GEOCHEMICAL CONTEXT AND ISSUES

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, ie, 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

Zones Ateliers
LTSER FRANCE TERRITOIRES URANIFERES

Rophin Site

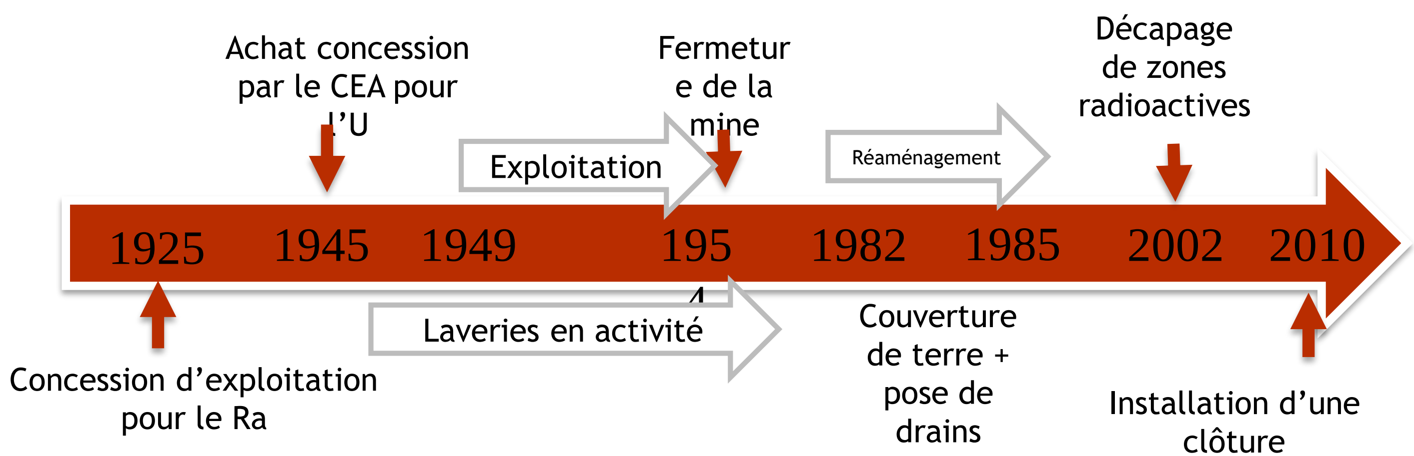
HISTORICAL CONTEXT AND ISSUES

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*



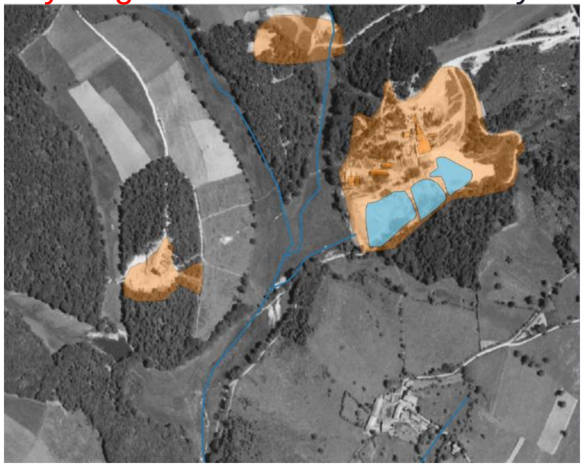
HISTORICAL CONTEXT AND ISSUES

Vue de la laverie chimique de Rophin en août 1950 (fond Orcel, MNHN)

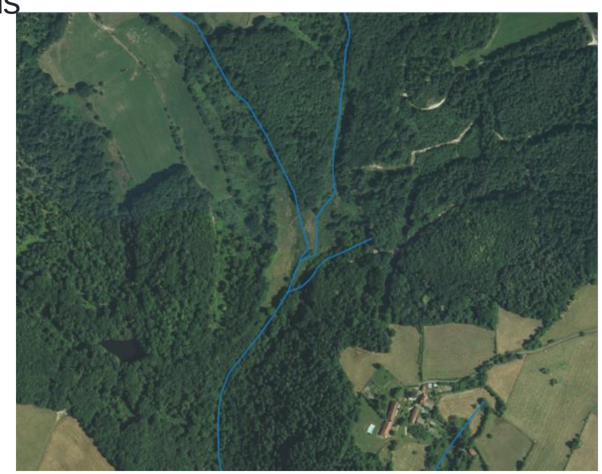
Vue générale de la laverie mécanique de Rophin en 1953 (photo CEA)

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

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



During exploitation

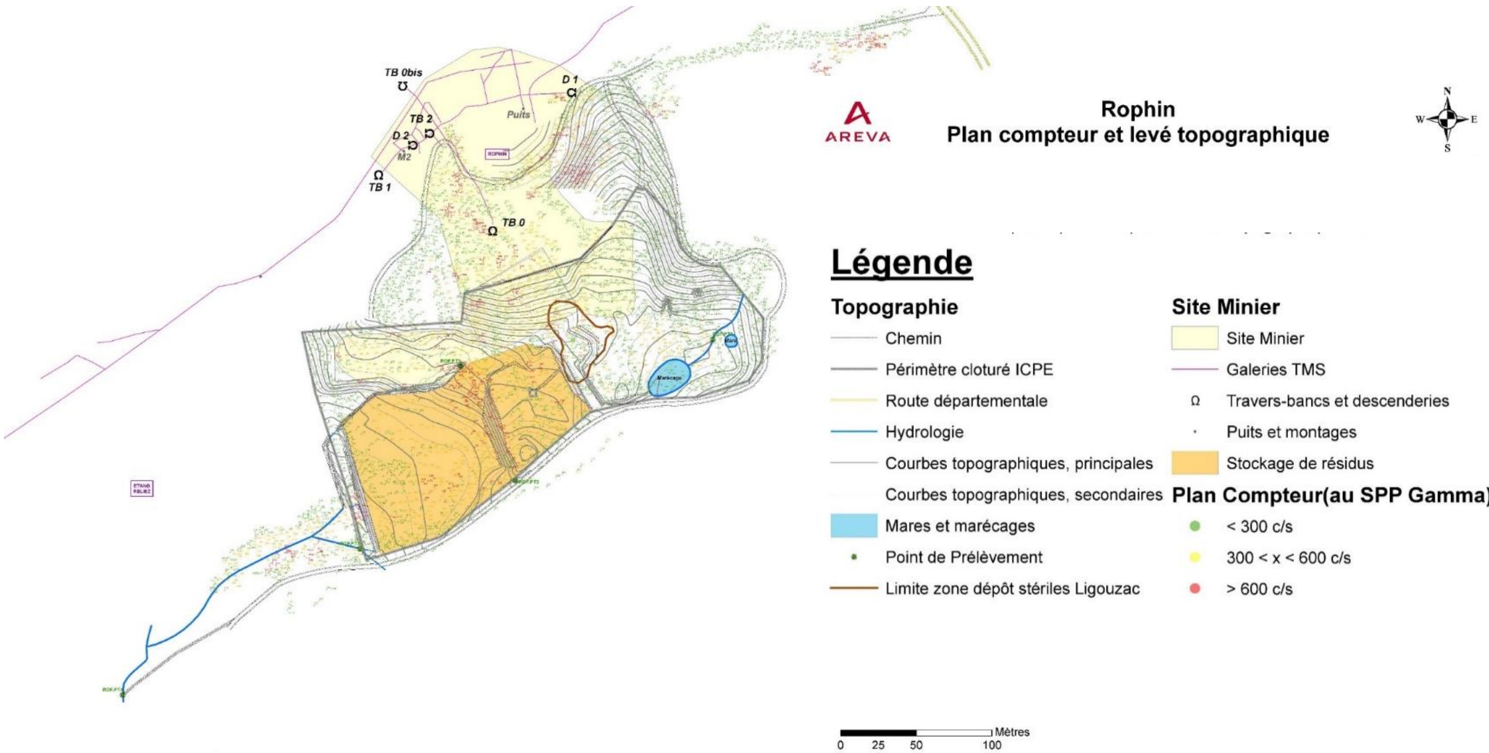


In 2015

HISTORICAL CONTEXT AND ISSUES

Rophin's site : TENORM issues

Potentially 2 sources of RNs and heavy metals :
- Storage site (anthropic)

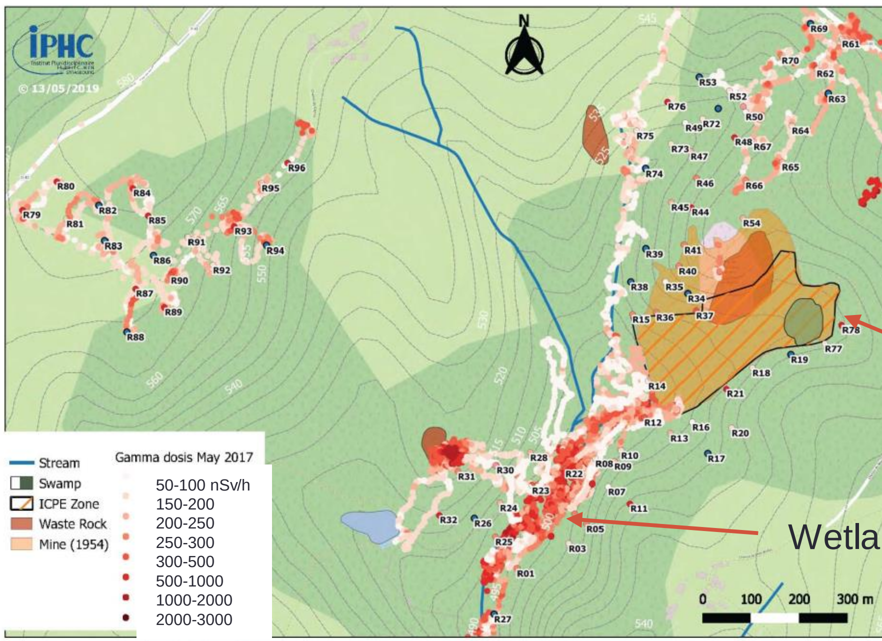


HISTORICAL CONTEXT AND ISSUES

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]



Mill tailings storage

Wetland

Zones Ateliers
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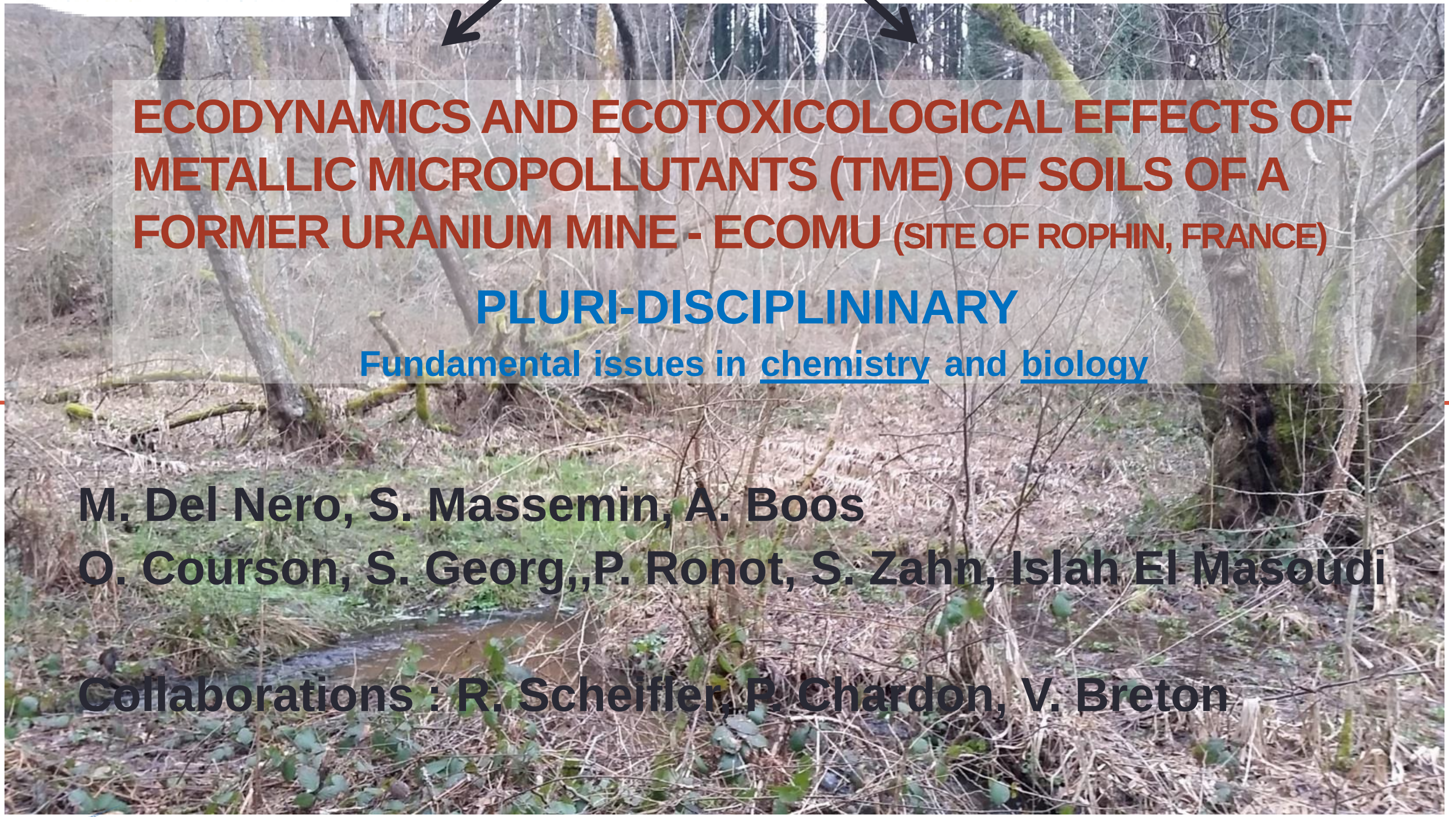
MECHANISMS ?



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. Scheifler, P. Chardon, V. Breton

IPHC Institut Pluridisciplinaire Hubert CURIEN STRASBOURG
CHRONO ENVIRONNEMENT
LPC
cnrs IN2P3 Les deux infinis
Ecosphère Continentale et Côtière
interreg Oberrhein Rhin Supérieur

ECOMU PROJECT

- Brief general presentation
- Soil-water chemistry
- Ecotoxicology

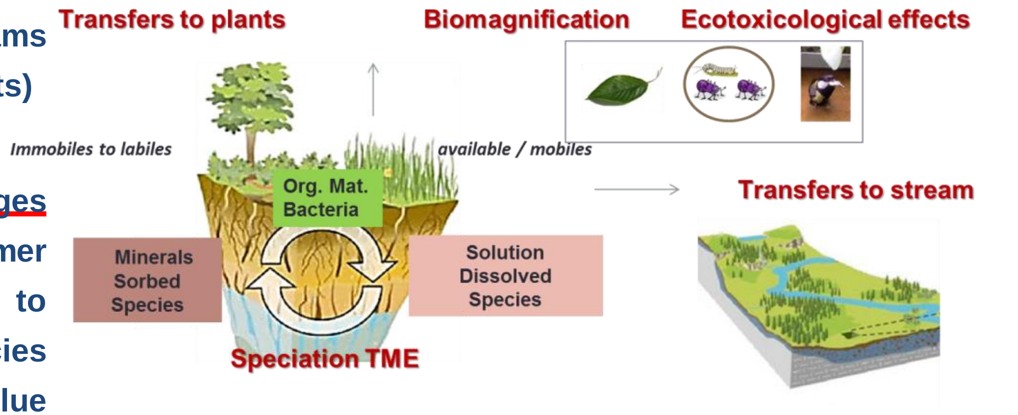
BRIEF GENERAL PRESENTATION

ECOMU PROJECT

- 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



Measurements

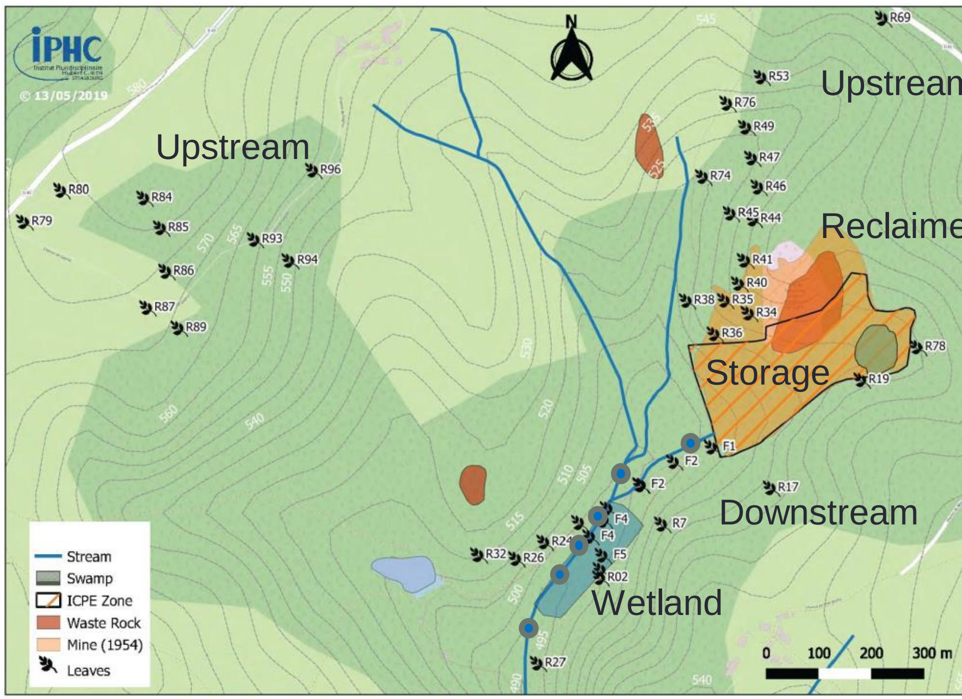
Fundamental issues

Zones Ateliers LTER FRANCE

The Rophin site

Soil studies

Soil studies

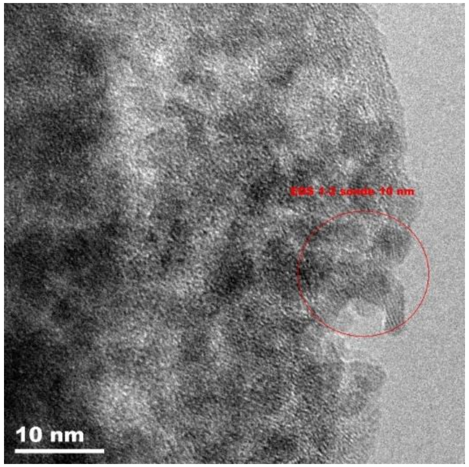


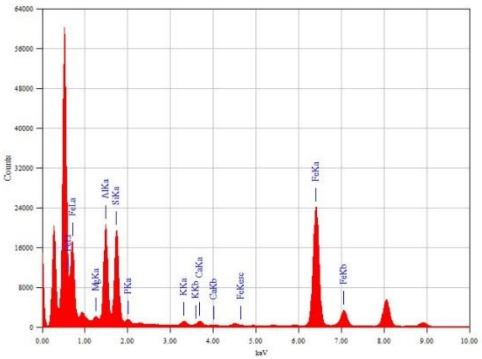
Collection of soil, water and leave samples

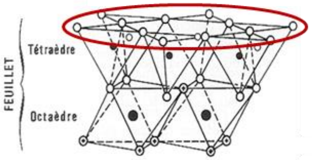
Mineralogical analysis

Soil studies

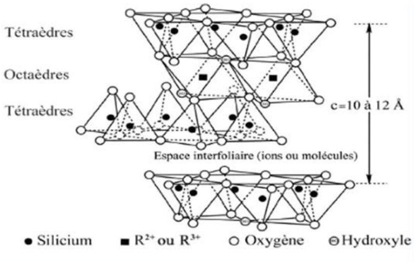
KAOLINITE (TO)







SMECTITES (TOT)



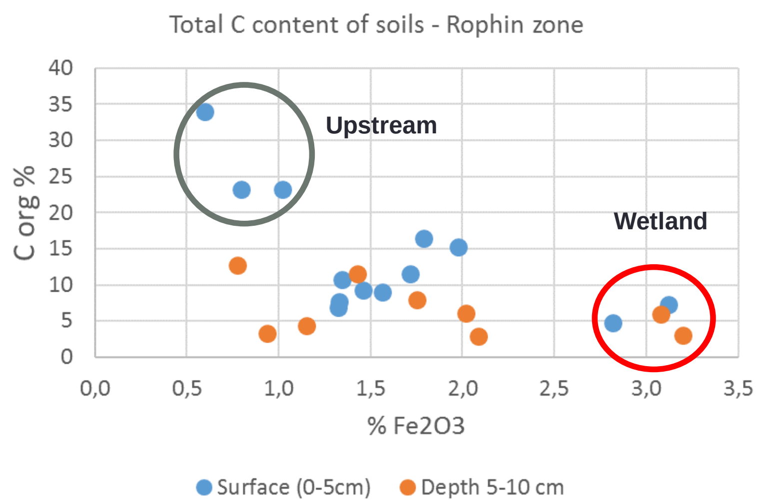
Main minerals of soils are K-felspars, quartz and clays; Kaolinite and illite clays predominate in upstream soils

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)

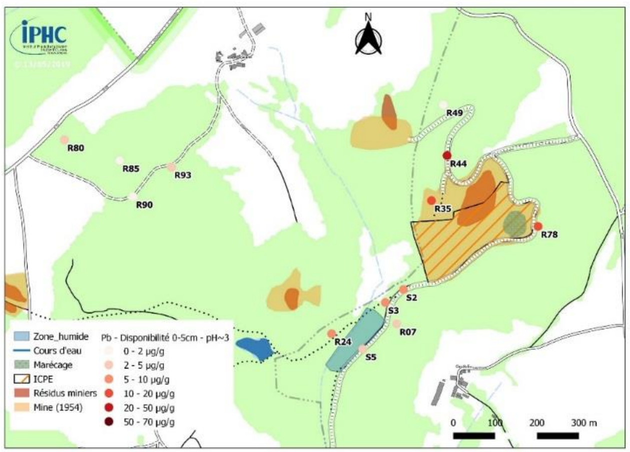


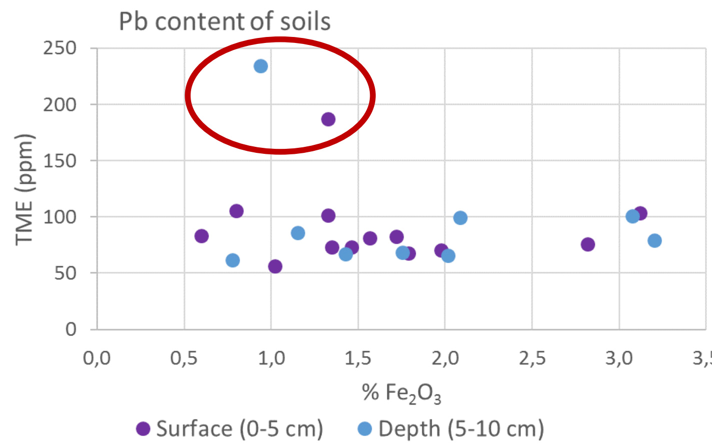
Upstream surface soils have higher content in OM

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

Soil studies

Chemical analysis





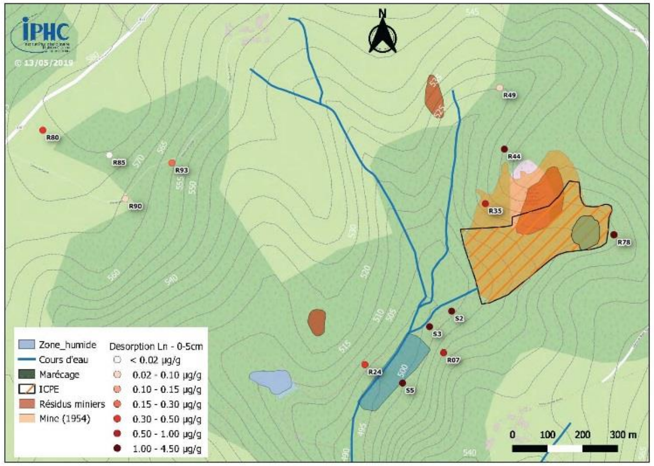
High content of Lead in soils upstream or downstream (like for Zn)

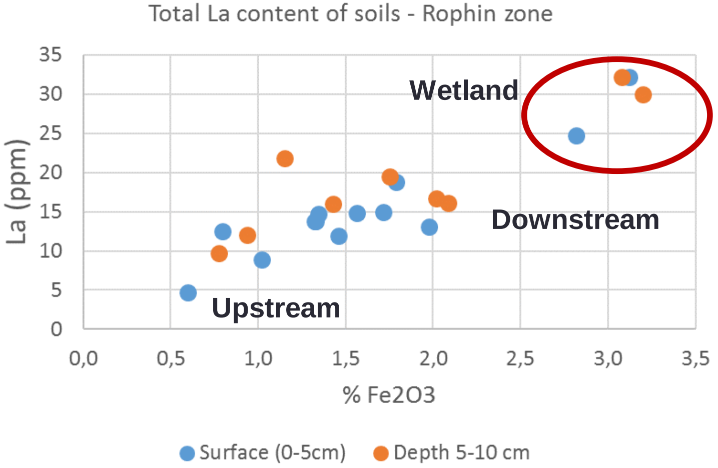
Anomalous soil samples around storage site (past mining activities)

Different desorption depending on a soil !

Soil studies

Chemical analysis





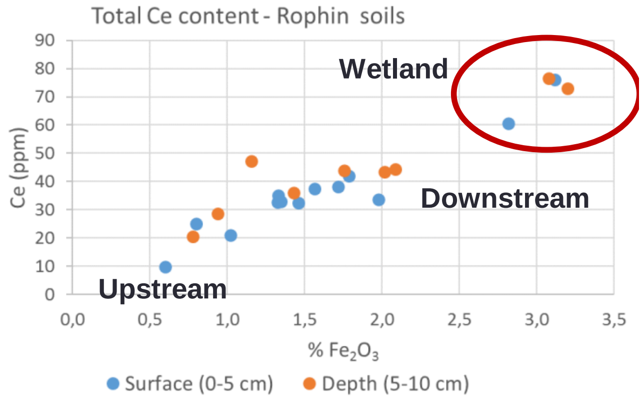
Increase of La with Fe_2O_3 content of soils from upstream to downstream

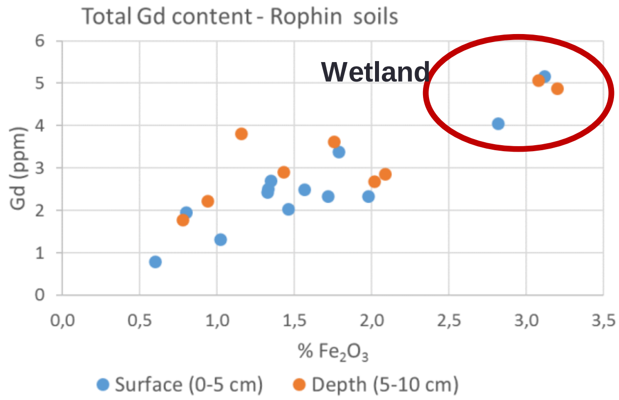
Soils of wetland are natural accumulation zones of Fe and La

Different desorption rates, not only dependent on the total concentration

Soil studies

Chemical analysis



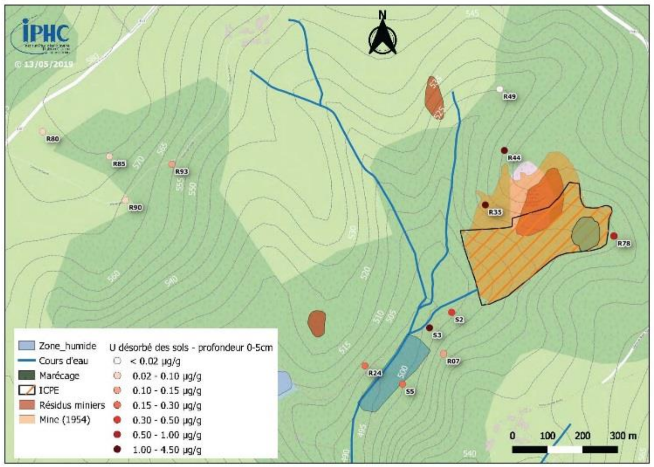


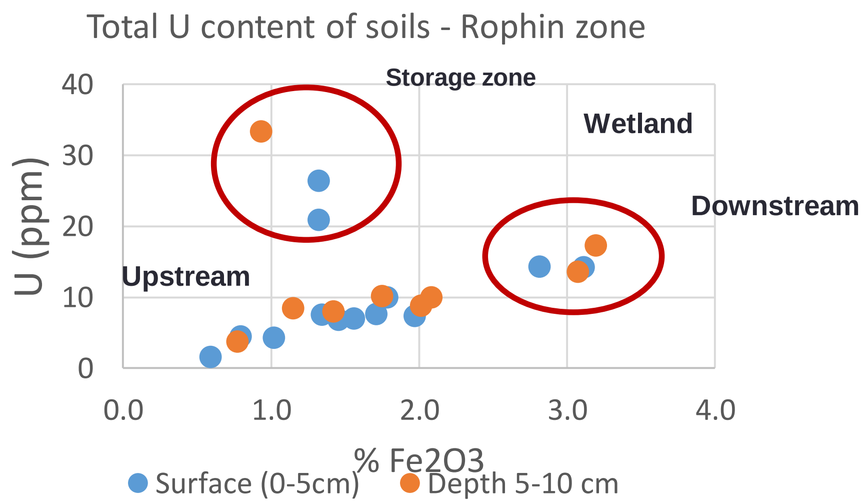
Increase of all elements of Ln series with Fe_2O_3 content of soils from upstream to downstream

Soils of wetland are natural accumulation zones of Fe and Ln

Soil studies

Chemical analysis





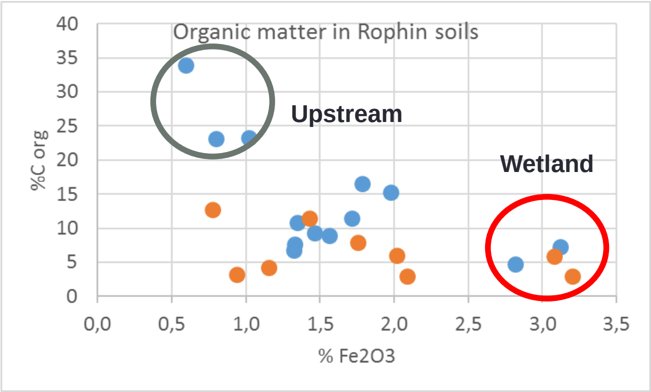
Increase of U with Fe_2O_3 content of soils from upstream to downstream

Anomalous soil samples around storage site (past mining activities)

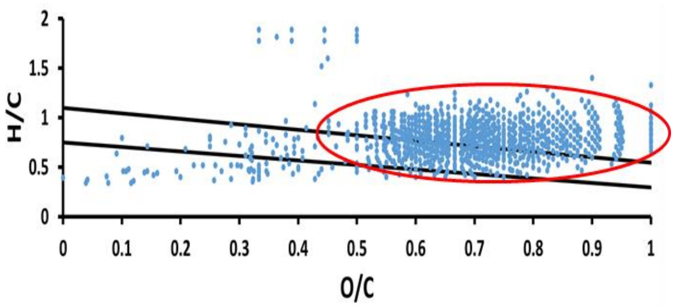
Soils of wetland are natural accumulation zones of Fe and TMEs like U and Ln

Soil studies

Elemental and molecular analysis of organic matter (OM)



Composition of the specific soil molecules of the wetland as analysed by ESI-FTMS



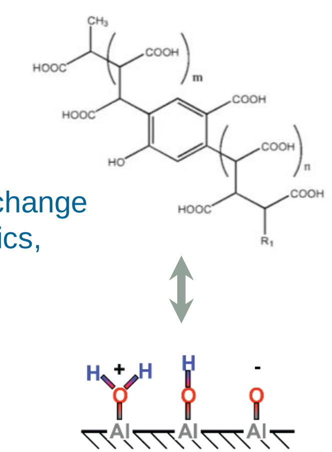
Upstream soils have higher content in OM - Thousands of organic molecules of various structures and compositions (aliphatic, aromatic, condensed aromatics) were analysed

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

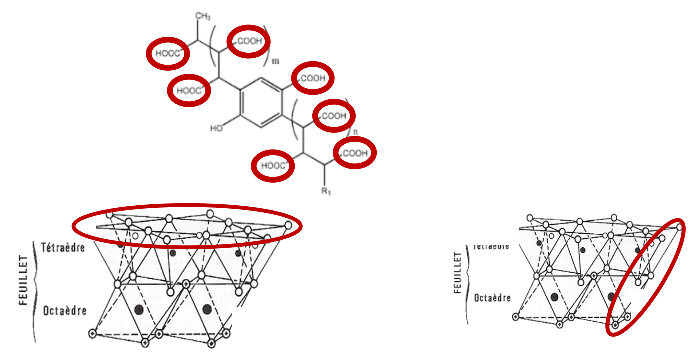
- **Molecule acidity is** the main chemical parameter governing the sorptive fractionation of FA (aliphatics and NC aromatics): surface ligand exchange
- Both **molecular acidity** and **degree of hydrophobicity** control the degree of sorption of polycyclic aromatics on Al/Fe oxides
- Increasing FA-to-hematite ratio favours preferential retention of most acidic PAC whereas aliphatics and NCA are left in solution



Surface ligand exchange (acidic NC aromatics, aliphatics, PAC)

Kaolinite

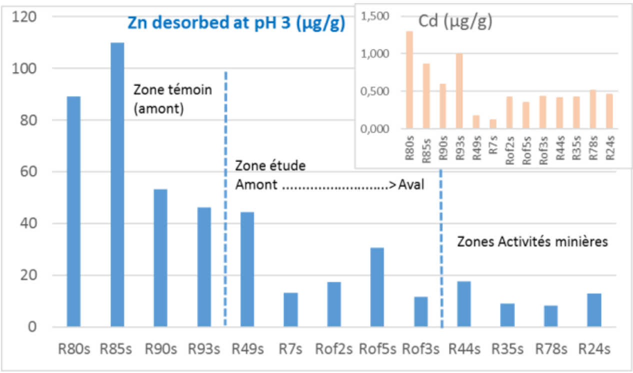
- **Weak selectivity** of the kaolinite surface towards FA molecules
- Poor sorption of PACs O/C < 0.2
- H-bonding of the FA molecules at weak sites (aluminol groups and silanol groups) on the basal plane of kaolinite is a good candidate

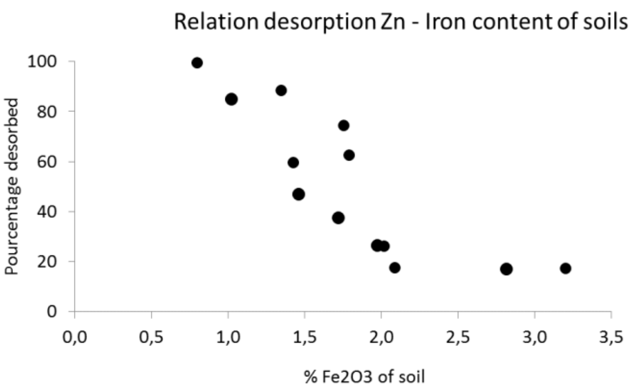


H-bonding at basal planes

Soil studies

Desorption experiments of
TME from Rophin soil samples





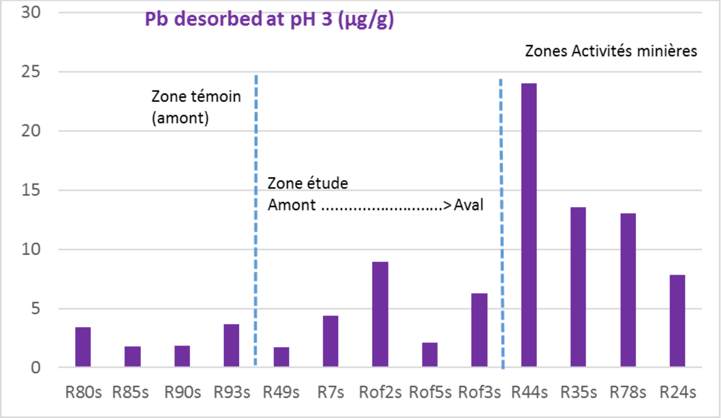
Desorption % : Zn (90-5%) > Pb (20-5%) > U (18%-<5) – Ln (5%-<5%) <u>except in wetland</u>

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



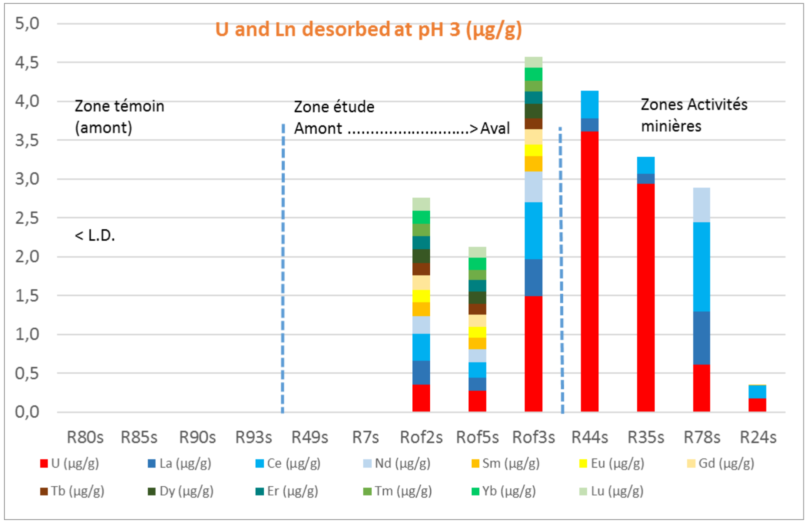
Release of TME % : Zn > Pb (> U – Ln) <u>except in wetland</u>

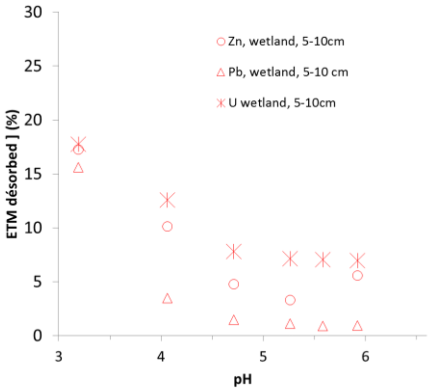
Pb is more released from downstream soils and wetland, particularly in depth (although not accumulated) than from upstream surface soils (reverse of Zn) → OM favours a strong retention of Pb

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 areaccumulated 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_2O_3 content of soils from upstream to downstream

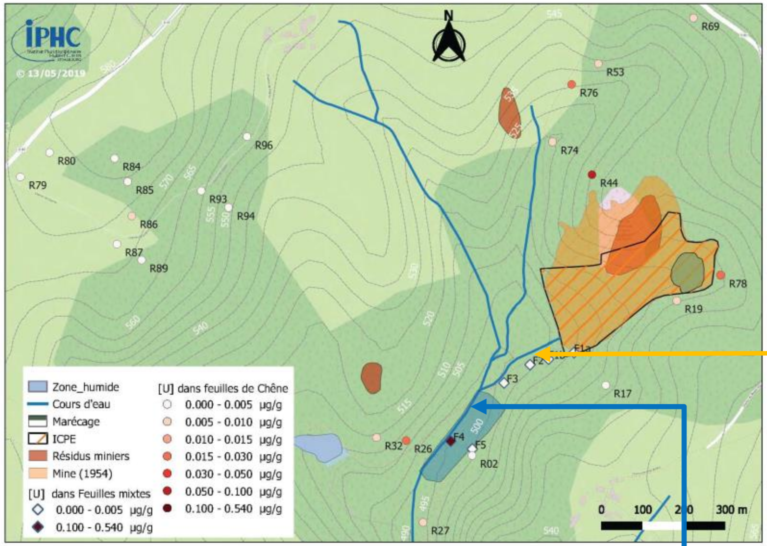
Desorption depend on a TME and on a soil (not only concentration) → Different cocktails potentially bio available depending on a TME speciation

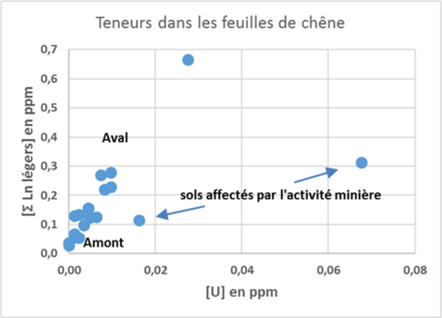
Soils of wetland are natural accumulation zones of Fe and TMEs like U and Ln, but U, Ln and Pb are potentially more mobile in wetland (% desorbed)

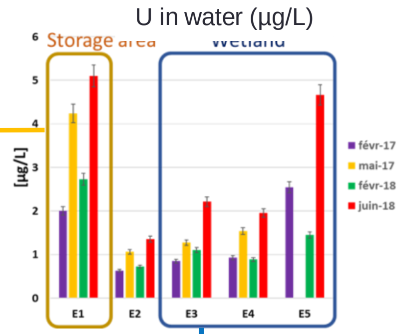
Anomalous soil samples around storage site (past mining activities) : potentially high desorption rates of Pb, Light Ln, U (and Ba)

Transfers

Transfers



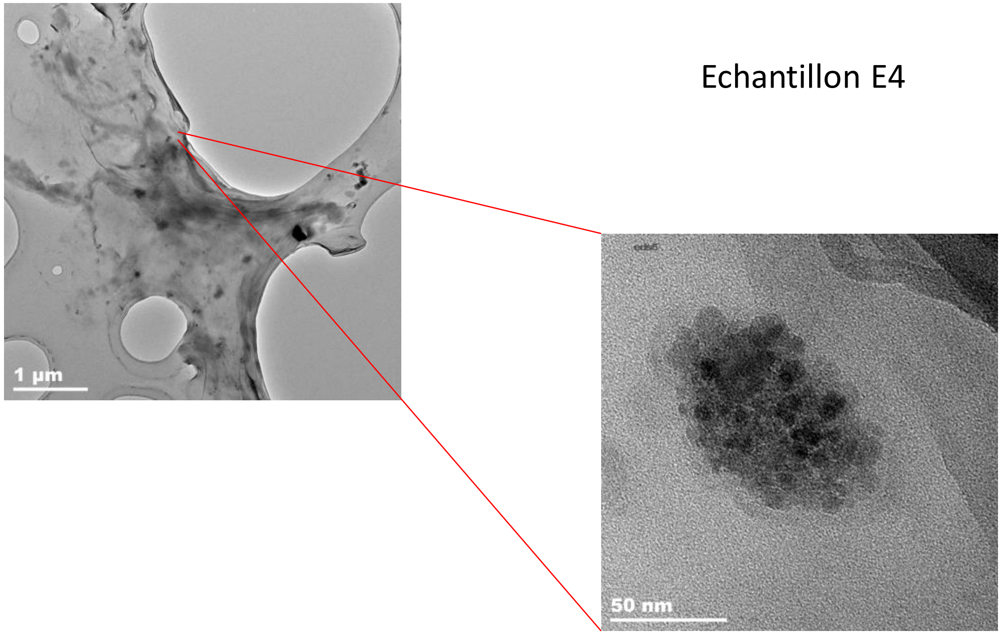


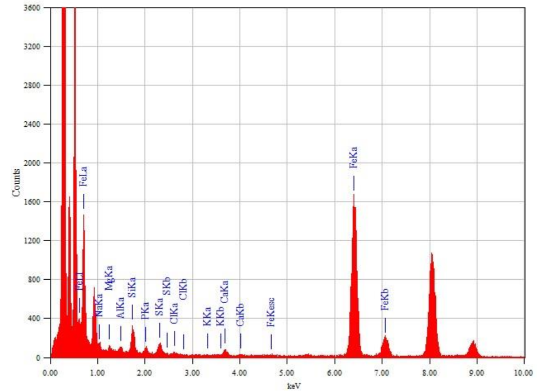


- U, Ln and Pb are transferred to plants of the wetland possily due to a specific metallo – organic speciation
- Soils affected by past mining activites may transfer higher amounts of U to plants
- Storage zone and wetland are potential sources of higher concentrations of U, Ln and Pb in waters, too

Colloids: vectors of U / Ln mobility?

Echantillon E4





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

ECOTOXICOLOGY

ECOTOXICOLOGY

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?

Operophtera brumata

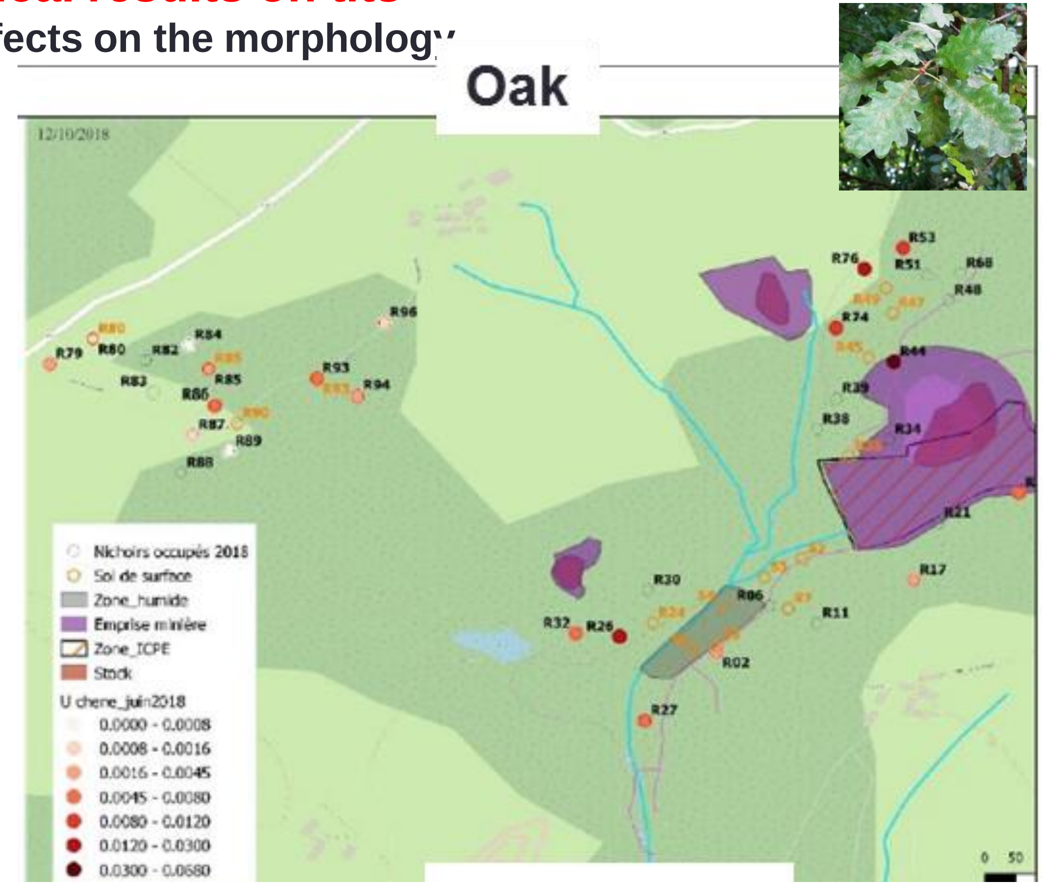
Misumena vatia

No relationship with any Me

ECOTOXICOLOGY

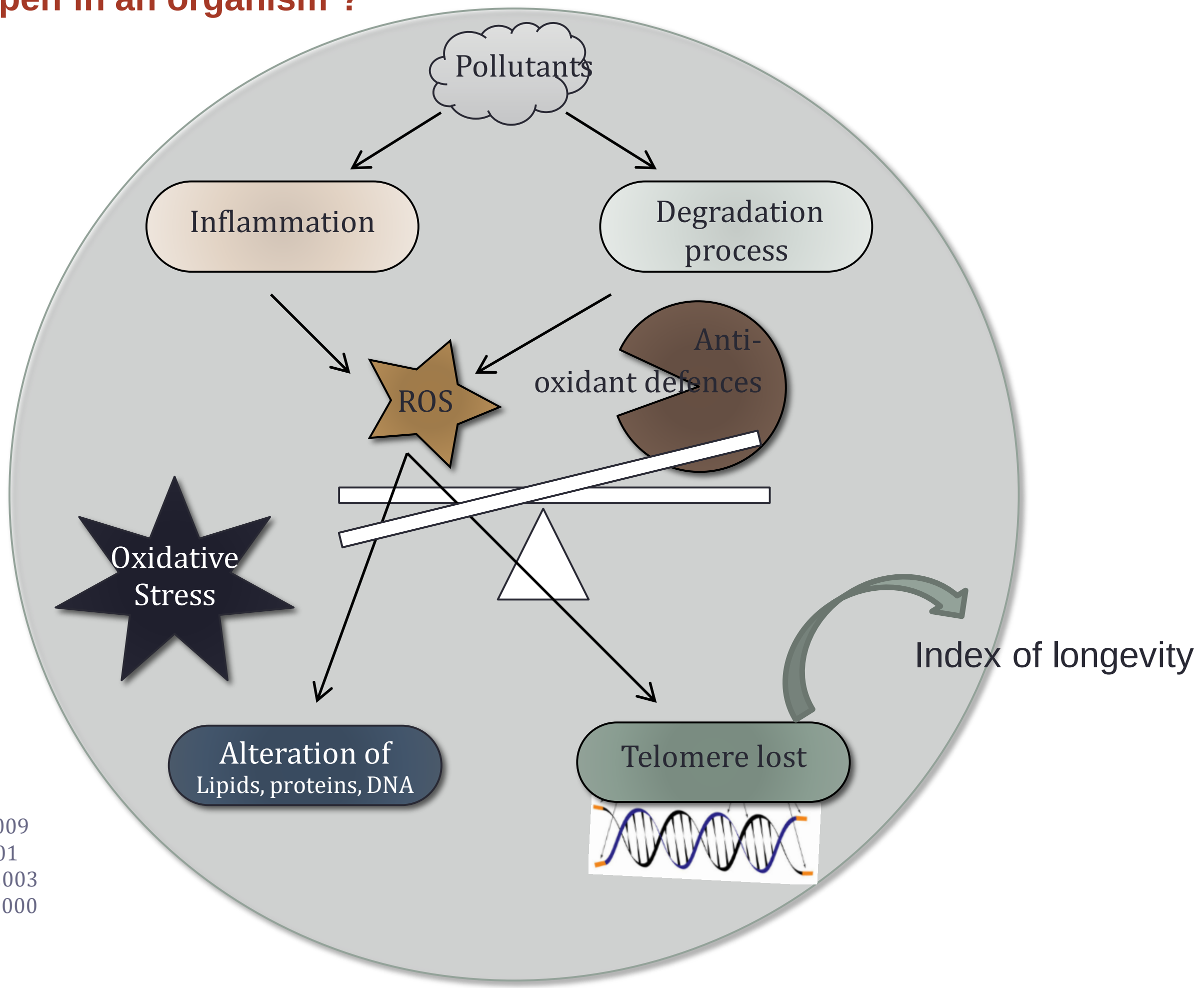
Biological results on tits

2. Effects on the morphology



ECOTOXICOLOGY

What's happen in an organism ?



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

Koivula et al. 2011
Berglund et al. 2007

Oxidative stress

Immune response
Snoejs et al. 2010

Physiological parameters

Negative on nestlings
No change in female adults

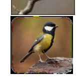
Telomeres
Stauffer et al. 2016

Our study

No effect

Telomeres decrease with U-Cd

Telomeres increase with Lanthanides-Pb



Telomeres decrease with Lanthanides-Pb

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

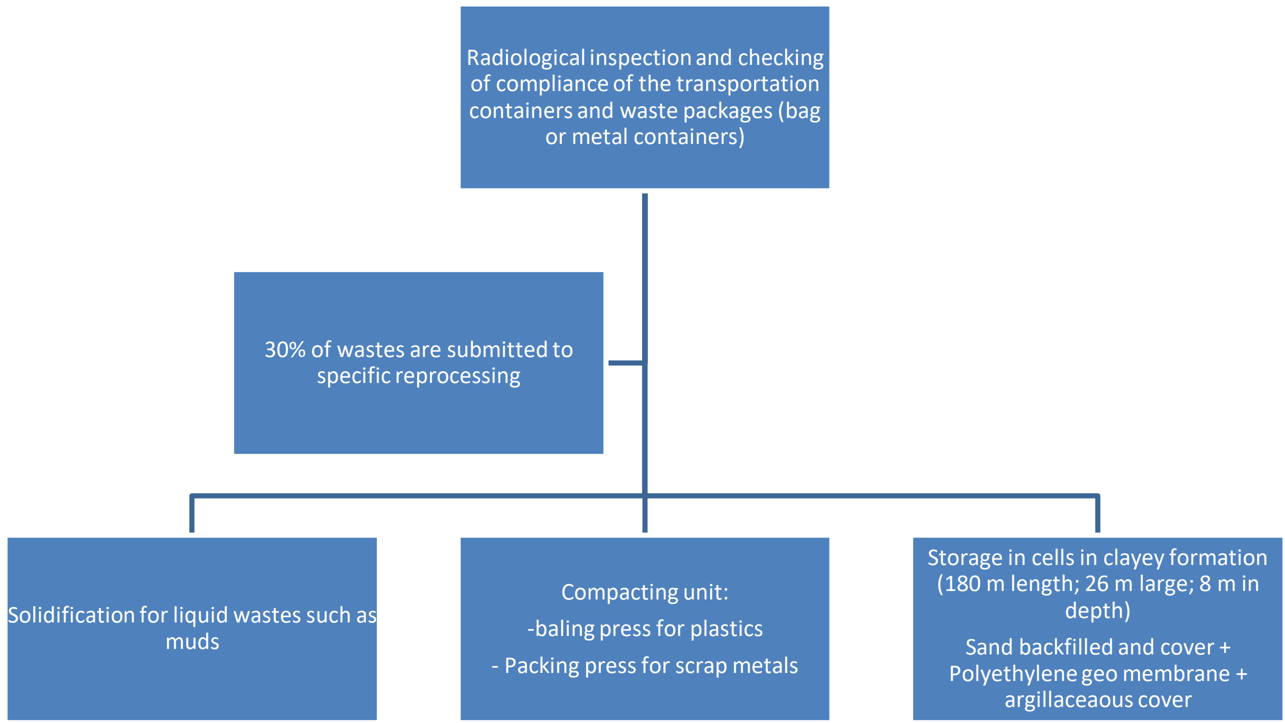
LLW Repositories in France

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 montored during 300 years