Phytostabilization of a mining soil by a legume pioneer plant and associated grasses: 10 years of field experiment

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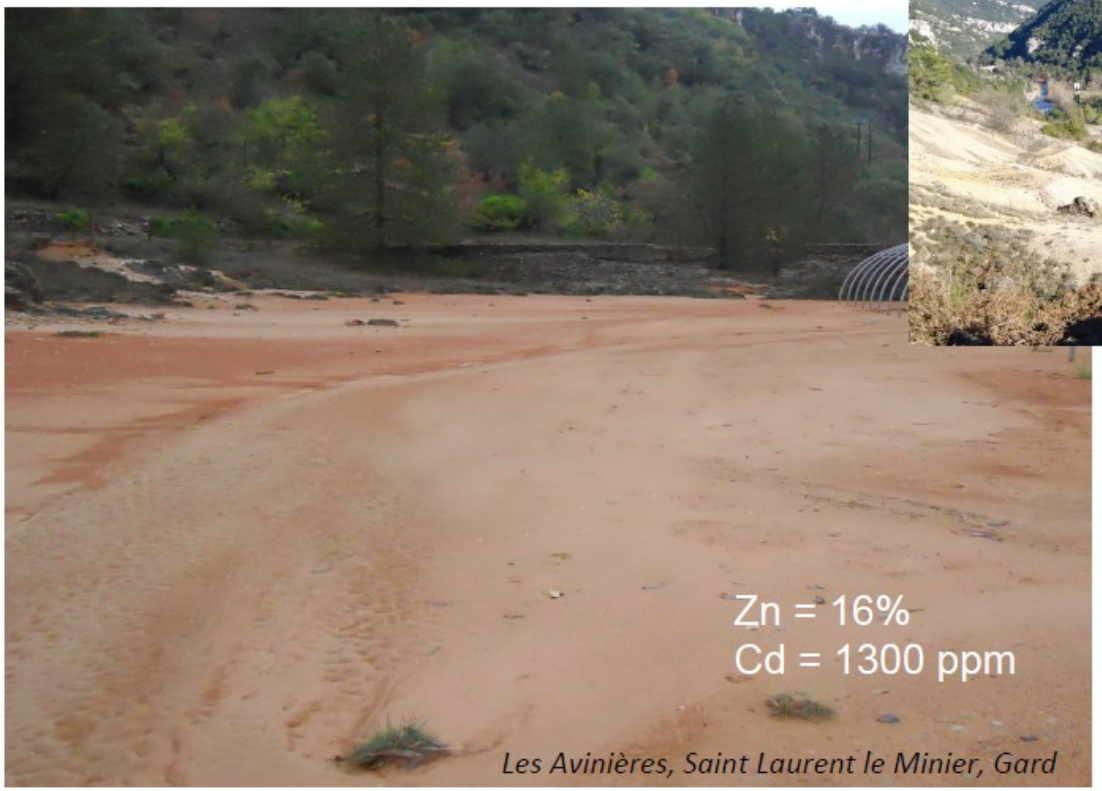
Pau university

- Université de Pau et des Pays de l'Adour (UPPA) : 13 000 students
- Our lab : IPREM (CNRS/University)
  - Speciation of metals and metalloids in the environment
  - Techniques : mass spectrometry, isotopic techniques, X-ray techniques

Context

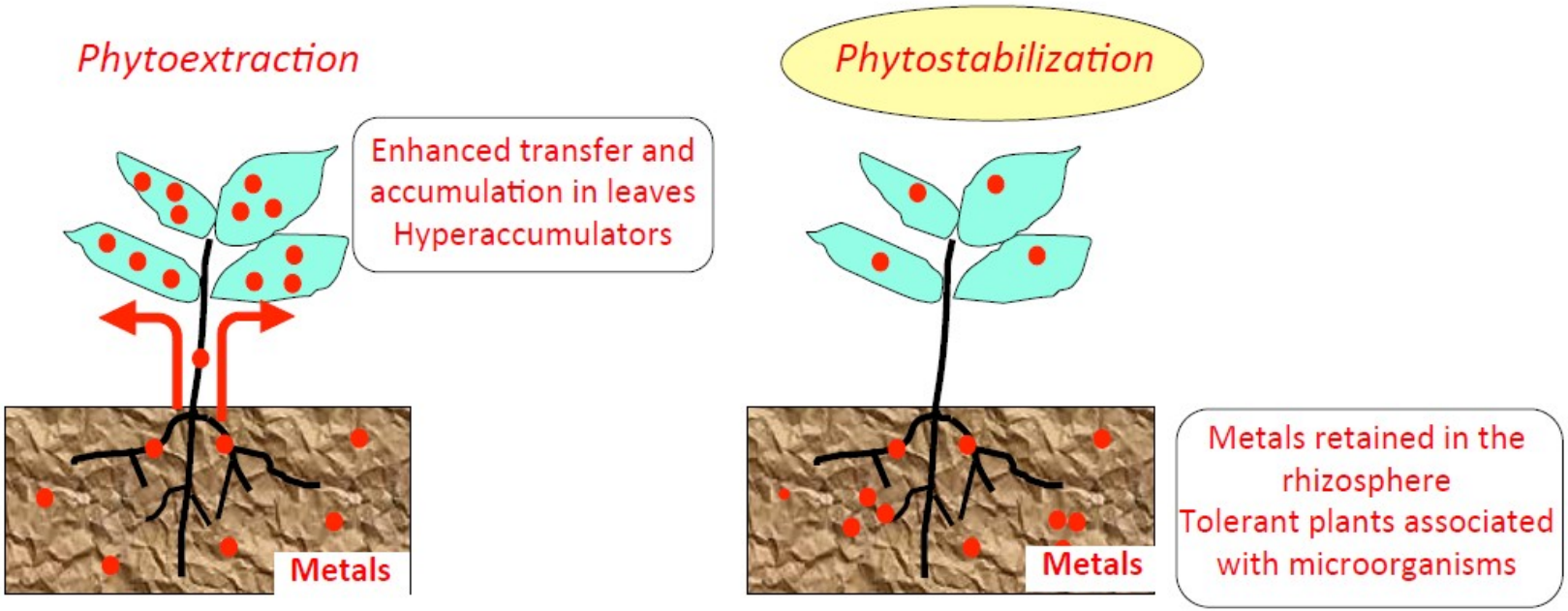
- Mining soils highly contaminated with metals, large areas with scarce vegetation



Les Avinières, Saint Laurent le Minier, Gard

Context

- Phytostabilization appears as an alternative technique for such mining soils



Context

- Native metal-tolerant plants are necessary

- *Anthyllis vulneraria ssp carpatica* (legume plant, *Fabaceae*) has been identified as a pioneer plant in the mining site Les Avinières

  On site metal concentrations in the shoot : 40 $\mu g.g^{-1}$ Cd, 7000 $\mu g.g^{-1}$ Zn DW

  => Not considered as a hyperaccumulator (Escarré et al. 2011; Soussou et al. 2013)

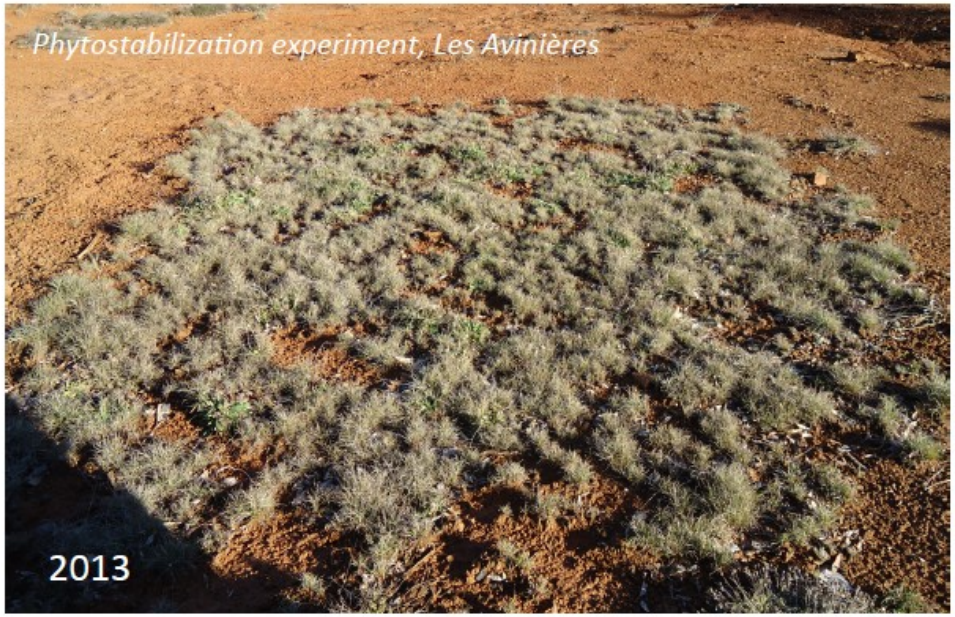



- Key point : symbiotic association with rhizobium bacteria root nodules which transform atmospheric N_2 into bioavailable nitrogen

  => stimulation of soil fertility, development of plant cover

Context and Objective

- Phytostabilization *in-situ* experiment with *A. vulneraria* since 2003 (Frérot et al., 2006)

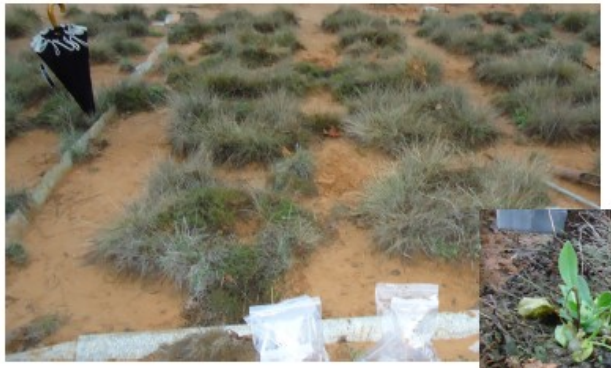


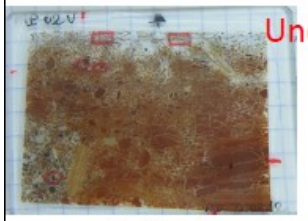
- Development of a plant cover with *A. vulneraria* and grasses (*Festuca arvernensis*) without any care for 10 years

➡ Objective : to determine the impact of the plant cover on Cd and Zn contained in the soil

Experimental

- Sampling campaign at the experimental site





Undisturbed samples (thin sections)

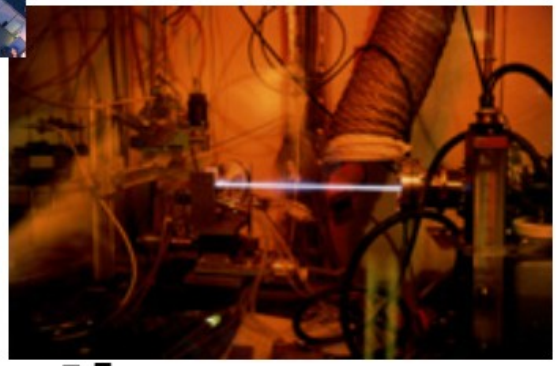
Bulk samples

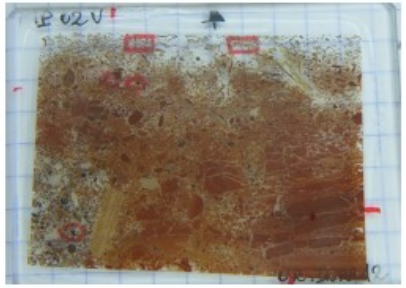
Soil (0-10 cm and 10-20 cm) around *A. vulneria* roots (rhizospheric soil) and in non-vegetalized soil (bare soil)

Bulk soil and undisturbed soil for thin sections

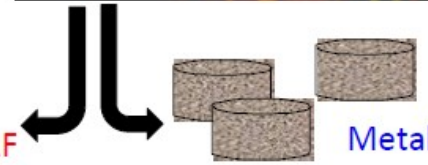
- Soil characterization (granulometry, pH, metal extraction…)

Experimental – Synchrotron experiments





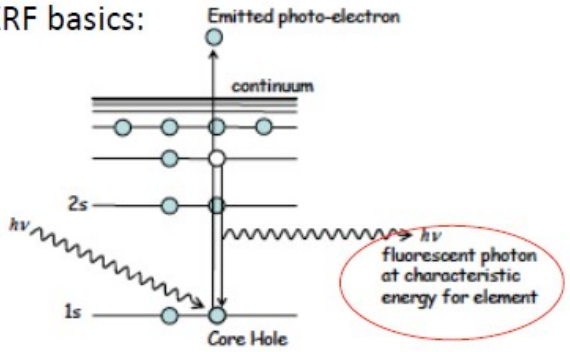
Undisturbed thin sections of soils => Metal distribution by µXRF
Metal speciation by µXAS

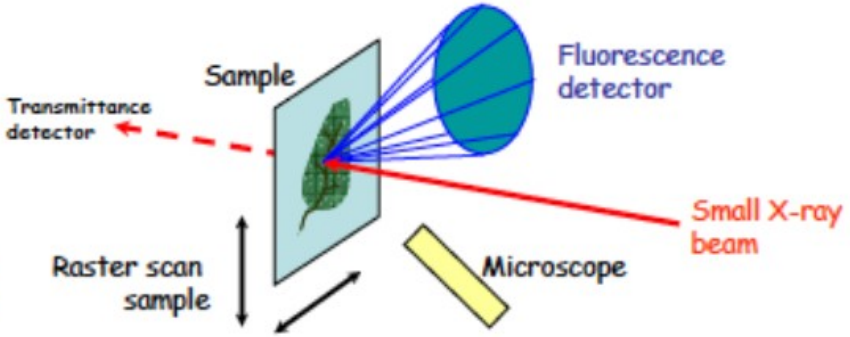


Bulk soils
Metal speciation by XAS

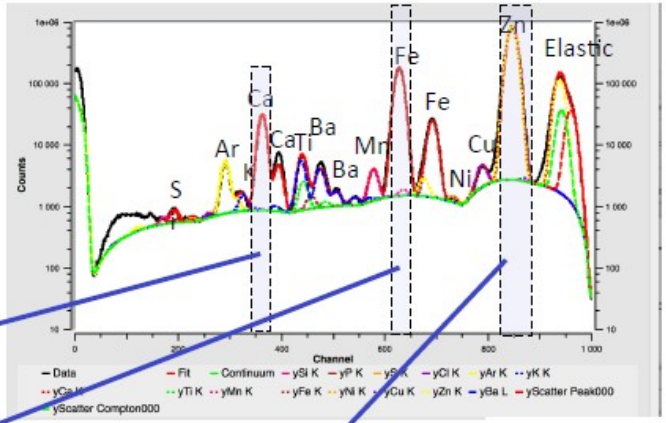
- Metal localisation by Chemical imaging : micro X ray Fluorescence (µXRF)

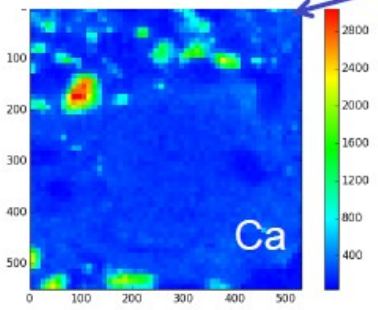
XRF basics:

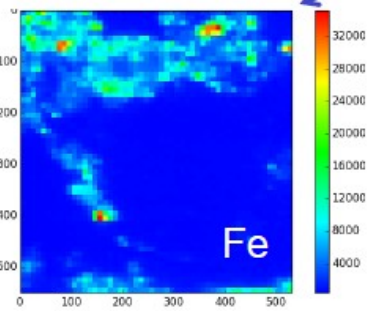


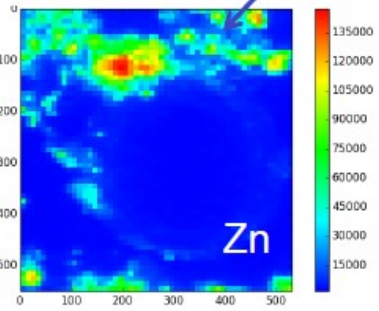


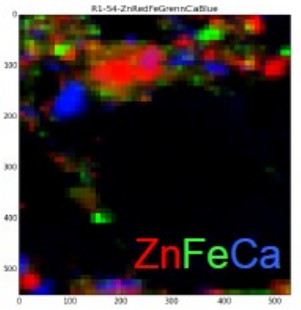
- Sensitivity << ppm
- Lateral resolution (< 1 µm to a few µm)



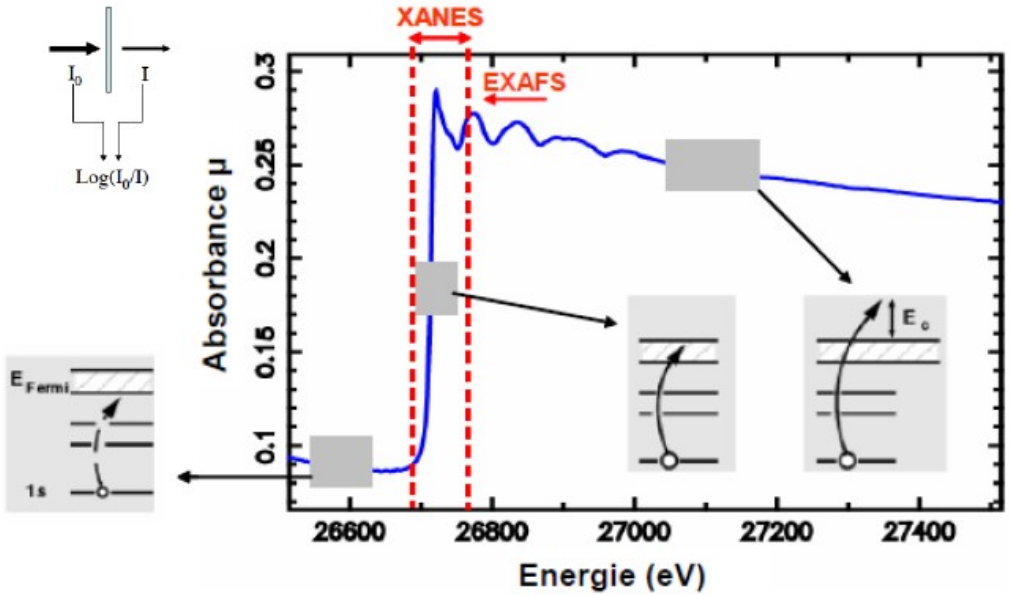


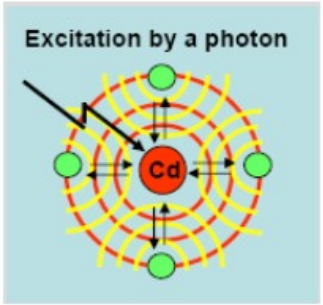


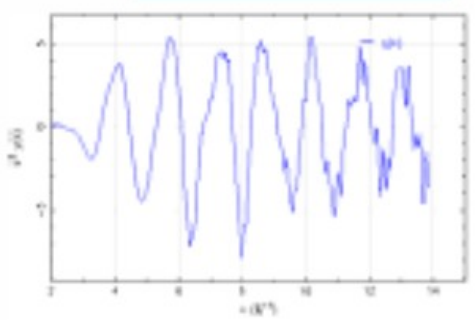


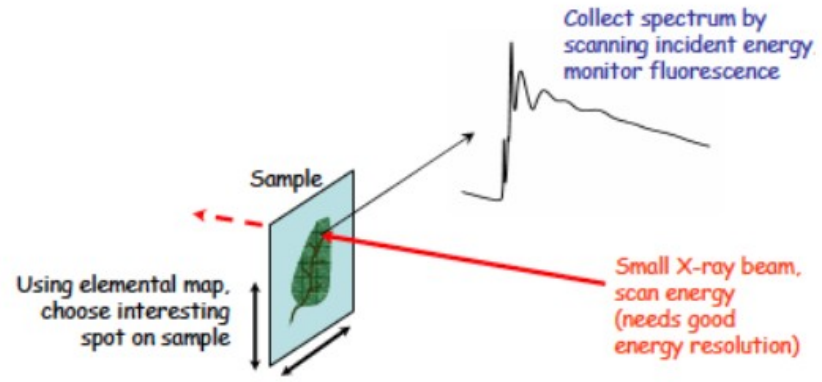


- Metal speciation: X-ray Absorption Spectroscopy (XANES, EXAFS, µXANES, µEXAFS)





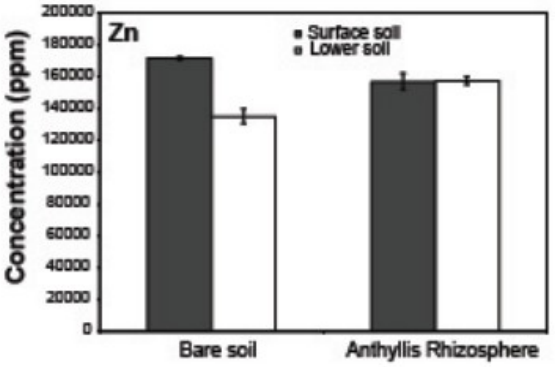


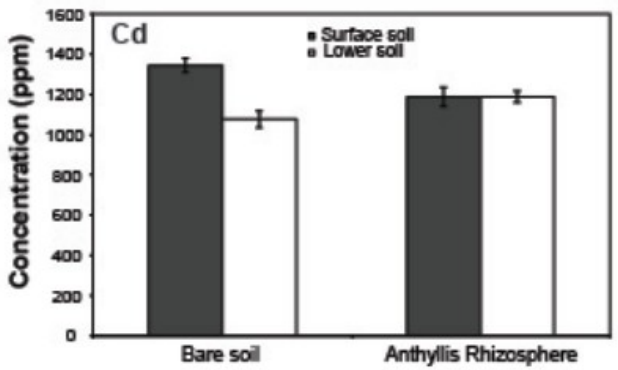


Fingerprint approach : comparison with model compounds

Results- Soil characterization

	Bare soil	Rhizospheric soil
Fractional weight (%)		
Coarse sands / 2000-200 µm	17.5	9.9
Fine sands / 200-50 µm	15.8	16.0
Silts / 50-2 µm	60.6	64.2
Clays / <2 µm	6.1	9.9
pH	7.6	7.6
Total $CaCO_3$ (%)	41	39
Cd/Zn extracted with water (%)	0.2 / 0.01	0.2 / 0.02
Cd/Zn extracted with EDTA (%)	19.1 / 12	27.5 / 15
Mineralogy (XRD)	Smithsonite, goethite, dolomite, calcite	



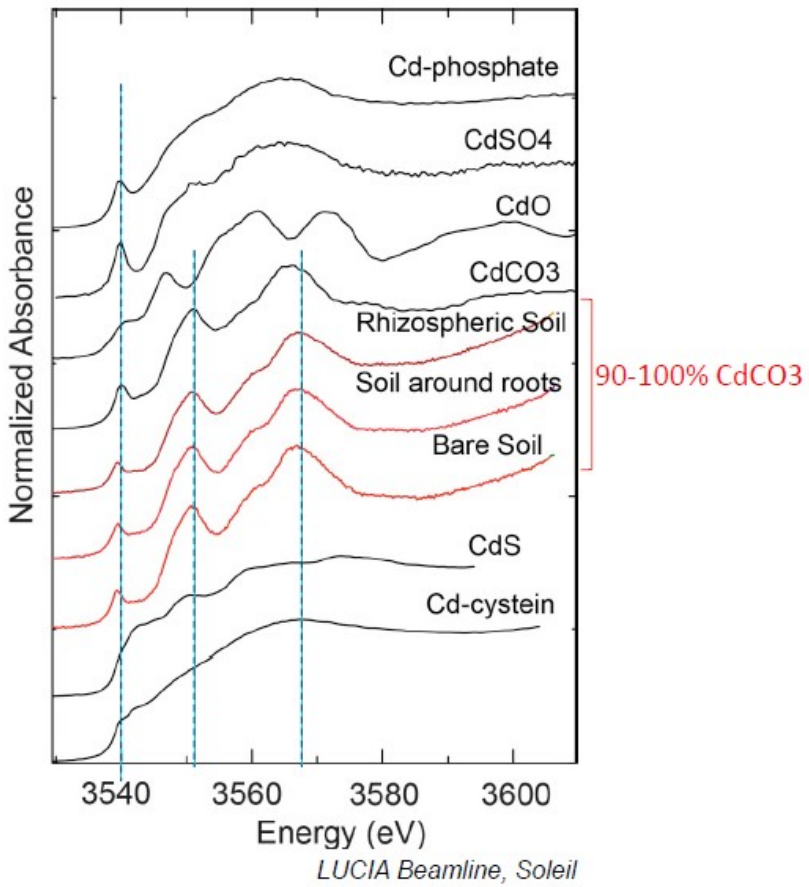


0-10 cm

10-20 cm

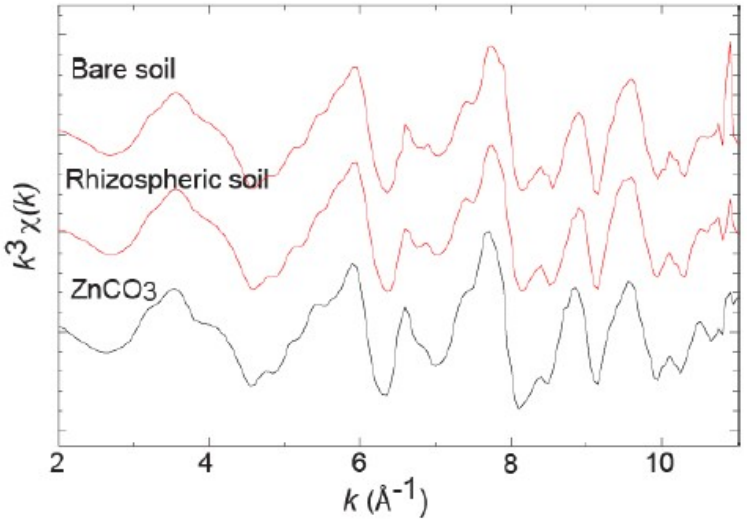
Results- Metal speciation in the bare and rhizospheric soils

Bulk XANES Cd L_{III} -edge



LUCIA Beamline, Soleil

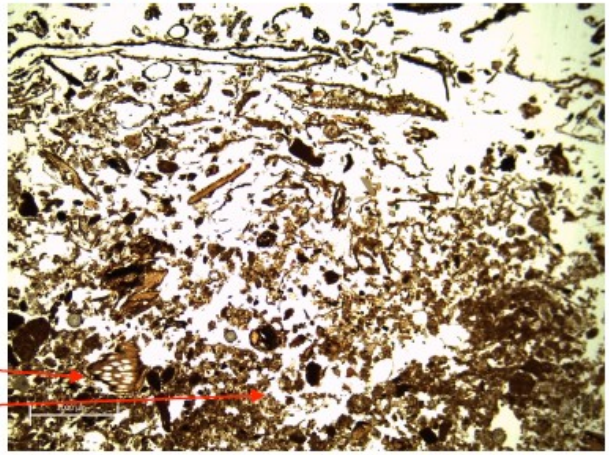
Bulk EXAFS Zn K -edge



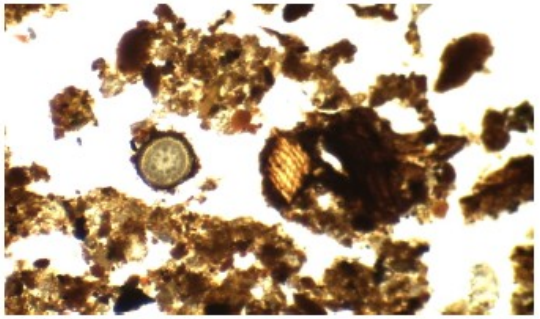
FAME Beamline, ESRF

At the root level? … Thin sections of soils

Vegetalized upper soil

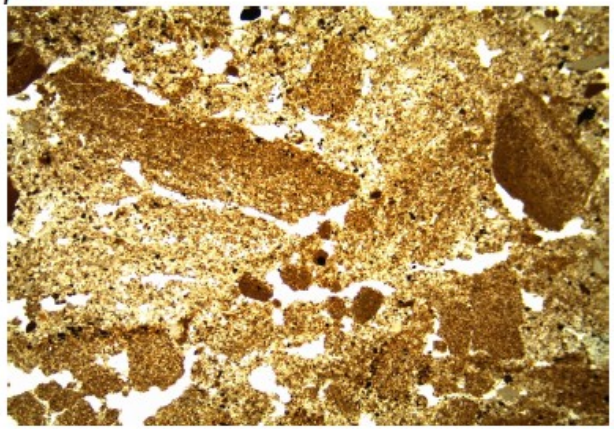


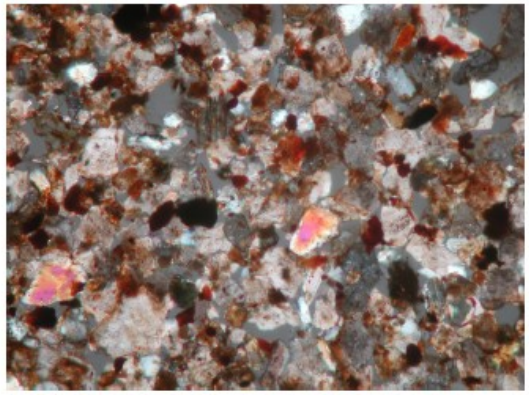
Organic matter
plant debris and mature OM



Carbonate matrix

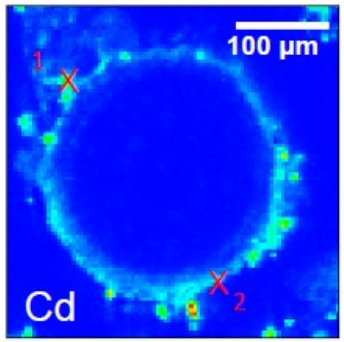
Bare upper soil

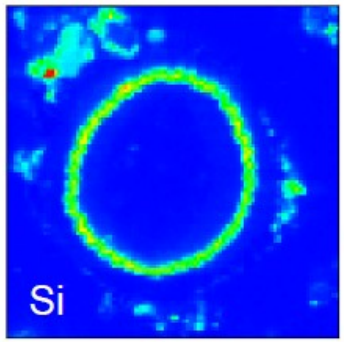


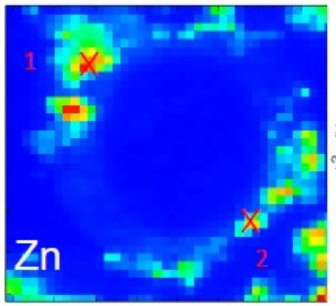


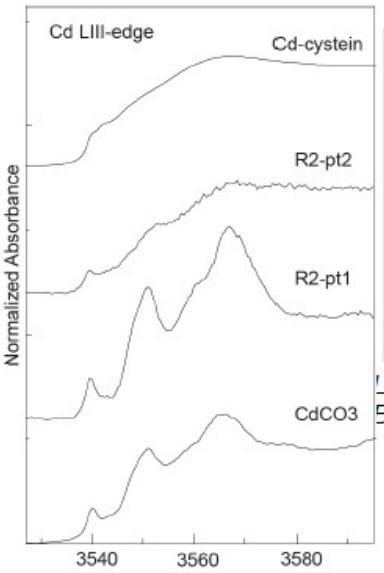
Carbonate matrix with iron oxides and some clay layers

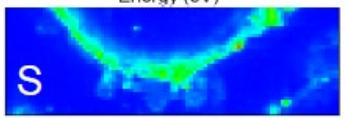
Chemical imaging by µXRF and Speciation by µXAS

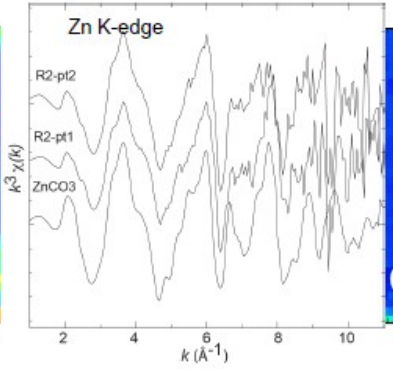


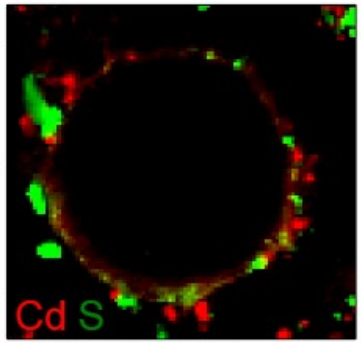




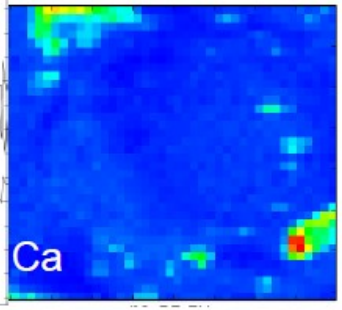


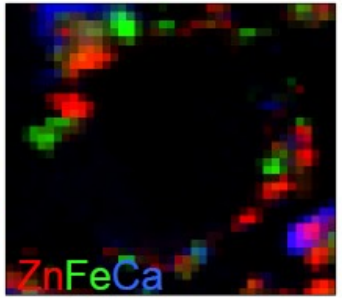






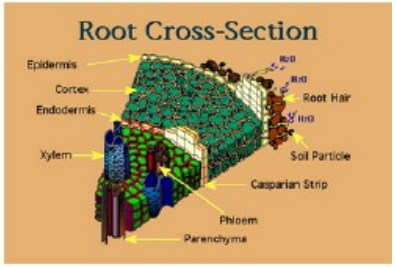
Lucia Beamline, Soleil
Beamsize: 5 µm (H) x 4 µm (V)





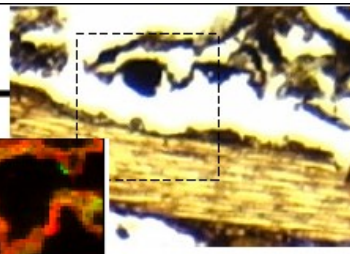
Max

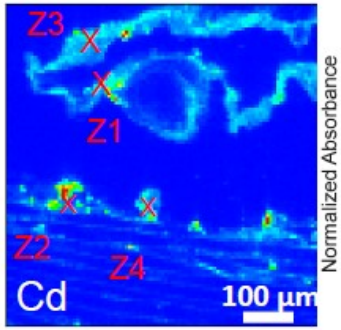
Min

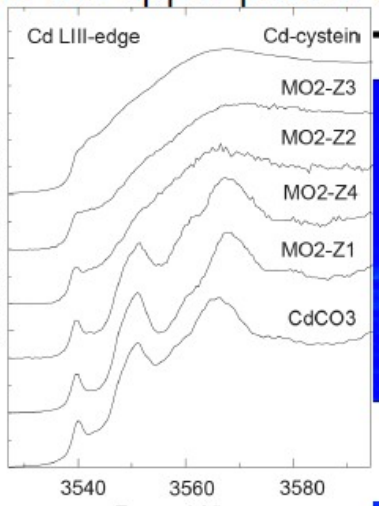


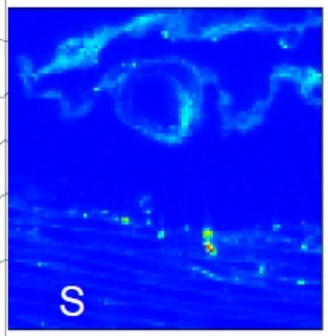
Diffabs Beamline, Soleil,
Beamsize: 9 µm (H) x 6 µm (V)

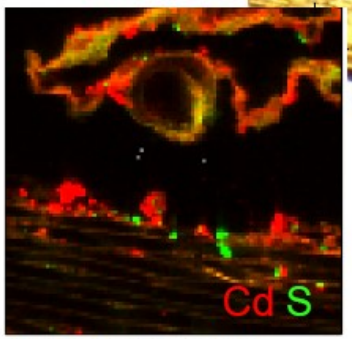
In organic matter in the upper part of the soil ?







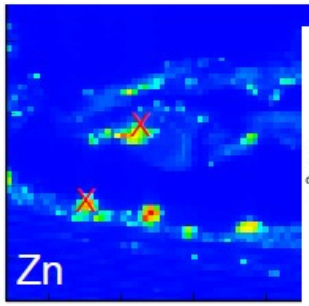


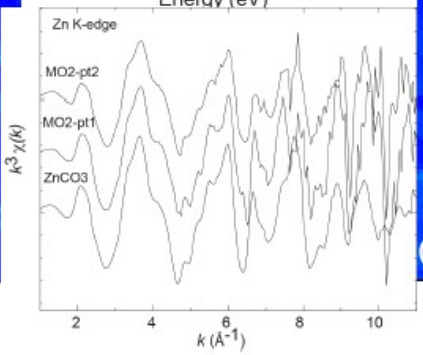


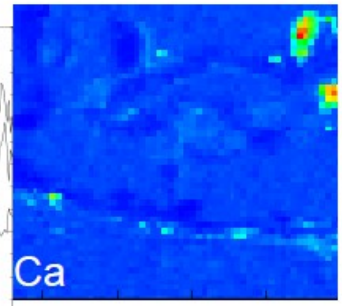
Lucia Beamline, Soleil
Beamsize: 5 µm (H) x 4 µm (V)

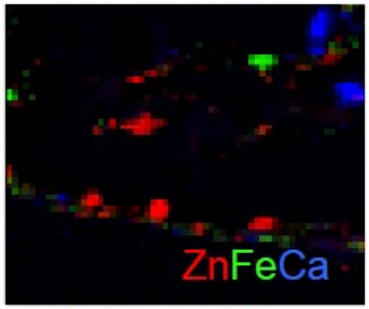
Max

Min









Diffabs Beamline, Soleil
Beamsize: 9 µm (H) x 6 µm (V)

Conclusion

- *Anthyllis vulneraria* has low if no effect on metal speciation in the bulk soil

- At the close vicinity of the root, we still identified $CdCO_3$ and $ZnCO_3$ particles and no other mineral precipitation was identified (but Cd-thiol in the root epidermis and OM)

- Recycling of Cd coming from plants and/or readsorption on OM thiol ligands, but restricted to the upper centimeters.

- Finally, in this case of carbonate soils, the phytostabilisation process protects against erosion and slightly impacts metal speciation in the rhizosphere.
- Increases the OM in soils

Acknowledgements

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Thank you for your attention...