COST 631	Understanding and Modelling Plant-Soil Interactions in the Rhizosphere Environment
	HANDBOOK OF METHODS USED IN RHIZOSPHERE RESEARCH
	2.2. Elements in Soils: Total and Extractable Contents, Solid Phase Speciation
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Parameter	**(In situ) Elemental distributions, associations, and molecular speciation in solid phases**
Soil type	Techniques applicable to solid matrices
System	Material from field or laboratory systems
Method	**Synchrotron X-ray fluorescence (µ-SXRF) imaging and X-ray absorption fine structure (XAFS) spectroscopy**
Method description	*µ-SXRF imaging:* Soil samples (e.g., resin embedded thin sections) or solid materials are mounted onto an x,y sample stage positioned at 45˚ to a microfocused X-ray beam. The incident beam energy is fixed such that fluorescence signals from all elements of interest are simultaneously detected by a multi-element solid-state detector positioned at 90˚ to the incident beam. The sample is rastered in the beam path to generate a coarse map (typically 1 - 3 mm^2 map with 20 micrometer pixel resolution). Smaller step sizes (e.g., 5 micrometer) and longer dwell times can be used to optimize image resolution (fine map). The multi-element SXRF images are useful for observing (*in situ*) elemental distributions and associations in complex, heterogeneous systems at the micrometer scale (Fig. 1a). *XAFS spectroscopy:* Soil samples mounted for SXRF imaging can be utilized for µ-XAFS data collection. Points-of-interest (POIs) identified on the coarse and fine maps are selected for XAFS analysis, and spectra are collected from 200 eV below to 500 - 1000 eV above the designated edge energy (i.e., element specific). Data from the near-edge region (XANES) of the XAFS spectra can be used to investigate the oxidation state of redox-sensitive elements. Data reduction (i.e., background subtraction, normalization, chi extraction) of sample XAFS spectra (bulk and microfocused) and reference spectra is typically followed by principal components analysis (PCA) and linear least squares fitting (LLSF) to determine the primary components and their contribution to the set of sample spectra (Manceau et al., 2002). Molecular-scale information gleaned with XAFS is complemented by the multi-element SXRF images, and together they provide a detailed picture of *in situ* elemental distributions, associations, and molecular speciation in natural, heterogeneous systems (Fig 1a-d).
Do's, don'ts, potential limitations, untested possibilities	• Soil thin sections (~30 µm) are well suited to SXRF imaging and XAFS, but care must be taken with redox-sensitive elements to avoid beam-induced reduction or oxidation (interaction with resin, adhesives, or soil organic matter), which can be minimized by decreasing temperature, photon density, or exposure time. Alternatively, soil samples can be mounted by collecting the solid onto a filter paper and then sealing the entire cake between Kapton tape. Sieved soil can be mounted directly onto Kapton by a powder-tapping technique, which involves covering the mouth of a small vial (containing the sample) with Kapton, inverting several times to coat the tape, and tapping residual material off the tape.

	• These methods do not resolve the elements having a lower atomic number than sulfur (e.g., oxygen, nitrogen, carbon, or organic fractions). • Detection limits are beamline specific and dependent on the composition of the major constituents in the sample (range ~ 20 - 200 mg/kg). • Predictions for future developments to this technology include improved spatial resolution, detection of lighter (lower Z) elements, and lower detection limits. • Run time for most beamlines is limited and access is proposal driven and competitive.
References	Fendorf, S.E.; Sparks, D.L.; Lamble, G.M.; Kelley, M.J. 1994. Applications of X-ray absorption fine structure spectroscopy to soils. Soil Science Society of America J. 58:1583-1595. Manceau, A.; Marcus, M.A.; Tamura, N. 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. In: Fenter, P.; Sturchio, N.C. (Eds.). *Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science*, Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, DC, Vol. 49: 341-428. Nachtegaal, M.; M.A. Marcus; J.E. Sonke; J. Vangronsveld; D. van Der Lelie; D.L. Sparks. 2005. Effects of *in situ* remediation on the speciation and bioavailability of zinc in a smelter contaminated soil. Geochim. et Cosmochim. Acta 69:4649-4664. Roberts, D.R.; Scheinost, A.C.; Sparks, D.L. 2002. Zinc speciation in a smelter-contaminated soil profile using bulk and microspectroscopic techniques. Environ. Sci. Technol. 36:1742-1750.
Links	http://xraysweb.lbl.gov/uxas/Index.htm
Additional information	Complementary method for plant analysis by SXRF and XAFS (see **21_Tappero**).

c)

sample	atom	CN[a,d]	R (Å)[b,e]	σ^2 (Å²)[c]	atom	CN[f]	R (Å)[g]	σ^2 (Å²)
			first shell				second shell	
surface - spot 1[h]	Zn−O	4.0	1.97	0.0079	Zn−Fe/Zn	13.2	3.52	0.0091
surface - spot 2	Zn−O	4.1	1.98	0.0070	Zn−Fe/Zn	8.1	3.51	0.0100
subsurface - spot 1[i]	Zn−O	5.6	2.04	0.0049	Zn−Al	1.5	3.01	0.005[j]
subsurface - spot 2	Zn−O	5.1	2.00	0.005[j]	Zn−Fe	1.9	3.25	0.005[j]
subsurface - spot 3	Zn−O	3.4	1.98	0.005[j]	Zn−Fe/Mn	1.4	3.45	0.005[j]

[a] Coordination number. [b] Interatomic distance. [c] Debye-Waller factor. [d] Fit quality limits for parameters: ±20%. [e] ± 0.02 Å. [f] ± 40%. [g] ± 0.05

d)

	ZnFe₂O₄	ZnS	Zn-ferrihydrite	Zn-birnessite	Zn-gibbsite	Zn-aq
			(%)[a]			
surface, spot 1	100	0	0	0	0	0
surface, spot 2	85	0	15	0	0	0
subsurface, spot 1	0	0	15	0	50	35
subsurface, spot 2	0	0	40	0	15	45
subsurface, spot 3	0	0	35	25	15	25

Figure 1. μ-SXRF images for subsurface soil from a Zn smelter (a), Zn-XAFS k³-weighted chi and corresponding Fourier transforms (b), μ-XAFS parameters for soil samples (c), and linear combinations of fit results for soil samples (d) (adapted from Roberts et al., 2002).