



Speciating Soil Pb Contamination to Support Decision Making

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Introduction

- Total element concentration is generally a poor indicator of risk
- Chemical species: A chemical species is a specific form of a chemical element, defined as its molecular or complex structure, or oxidation state. Chemical species is important for overall risk and bioavailability.
- Speciation analysis: The analytical activity of identifying and measuring chemical species. Identifying and measuring includes strictly a clear identification of the species (elements and possibly binding partners) as well as an exact quantification in a representative sample
- Operationally or functionally defined species characterization is not chemical speciation analysis



Introduction

Chemical Speciation

Remediation

- Metal fate and transport
- Remediation strategy & effectiveness

Bioavailability/Risk

- Explains variability of uptake
- Demonstrates remediation

Chemical Speciation

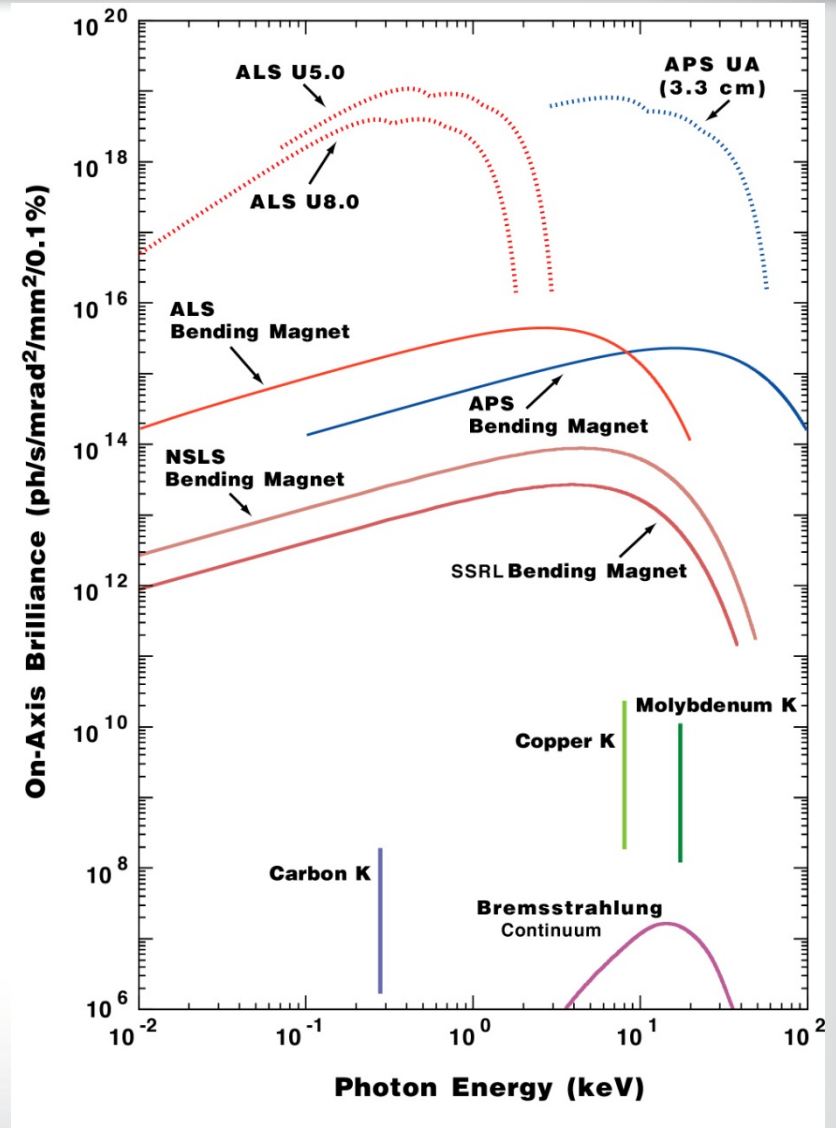
	XRD	XRF(EMPA)	XAS	Mössbauer	FTIR
Technique	X-Ray Diffraction	X-Ray Fluorescence Microprobe	X-Ray Absorption Spectroscopy	Mössbauer Spectroscopy	Fourier Transform Infrared Spectroscopy
Related Techniques	XPD		XANES, EXAFS, SEXAFS		
Incident (exciting) radiation	X-ray tube or synchrotron x-rays	XRF X-ray tube, XRFMP synchrotron x-rays only	Synchrotron and some rotating anode x-ray sources	Gamma rays	Infrared photons, wavelength 1-10 m
Particle emitted	Diffracted X-rays	Characteristic X-rays	Transmitted or characteristic X-rays	Gamma rays	Transmitted or reflected IR photons
Depth information	None	None	Yes, SEXAFS	None	0.5-2.5 mm
Spatial resolution	500 Å-10 mm synchrotron x-rays, none x-ray tube	500 Å-10 mm synchrotron x-rays, none x-ray tube	500 Å potential with synchrotron x-rays	None	1-10 mm
Detection limit	1-5% mixtures (XPD)	100-5000 ppm	~1 ppm	1-1000 ppm	0.1-0.5%
Detectable elements	Li-U	Li-U	Li-U	Isotopes with Mössbauer transitions, ~ 44 elements	Functional groups
Depth profiling	No	No	No	No	No
Chemical information	Yes, species identity and structure	No	Yes, oxidation state, species, coordination number, some structure	Yes, structure, bonding	Yes
Quantitative analysis	Yes, to 5-10%	Yes, high precision	Semiquantitative	Semiquantitative	Semiquantitative in bulk
Imaging	No	Yes	No	No	No
Mapping	No	Yes	No	No	No
Line traces	No	Yes	No	No	No
Molecules detected	Yes	No	Yes	Yes, chemical shifts	Yes, IR active molecules
Crystallographic information	Yes	No	Some	No	Some distinction between phases
Materials	Crystalline solids and polymers	Solids and non-volatile liquids	Solids and non-volatile liquids	Solids	Solids and organic liquids
Used on geological or environmental samples?	Yes	Yes	Yes	Yes	Yes
Applications and information obtained	Structure detn. and ID of major species in mixtures	Elemental composition	Coordination no., oxidation state, bonding of amorphous phases & ID	Site locations, bonding, structure	Compound identification on surfaces, of powders, liquids etc., functional group ID, bonding. GC detector
Advantages	In-situ, large library of patterns, non-destructive	Many elements, non-destruct., low detn. limits, in-situ, maps, imaging	In-situ, non-destruct., low detn. limits, species determination	Nondestructive, in-situ	Universal, good quantitation, moderate resolution, in situ, non-destructive
Disadvantages	Insensitive, only crystalline materials	Only elements, resolution 10 microns	Possible sample damage, not readily available	Limited no. of elements, need radioisotopes necessary, poor data analysis	Low sensitivity, only ok for solids, avoid aqueous solns.
Availability	Common	XRF/EMPA common, XRFMP at synch. facilities	Only at synchrotron facilities	Very uncommon	Common, micro. much less so



Chemical Speciation

Why use a synchrotron X-ray source?

- Orders of magnitude higher brilliance than tube source
- Translates into major improvements in sensitivity and spatial resolution for x-ray analyses
- Makes some spectroscopic techniques (XAFS) feasible with a tunable monochromator

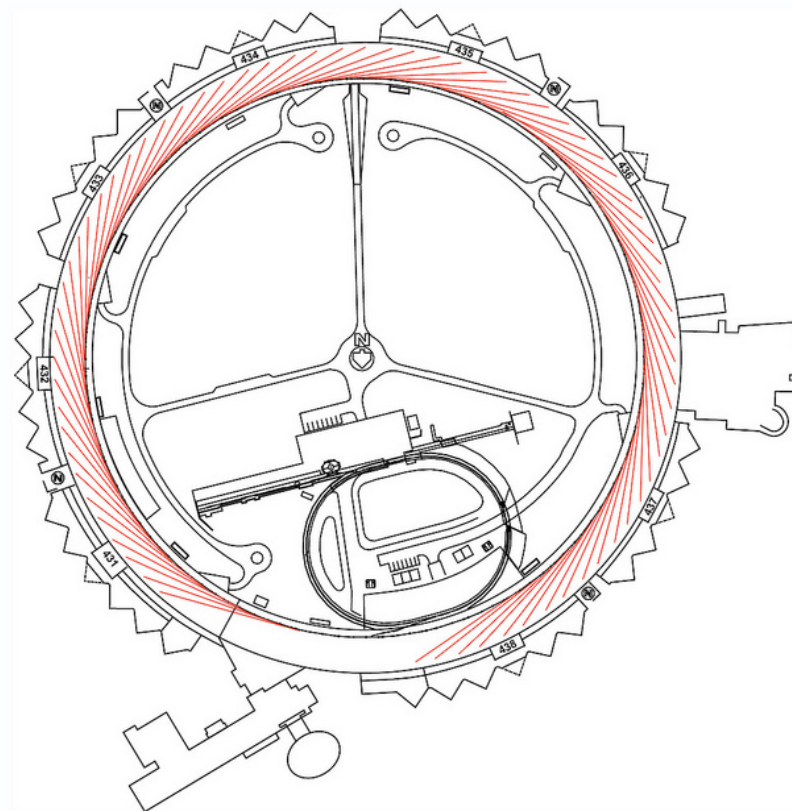




Chemical Speciation



~80 worldwide
12 in the US



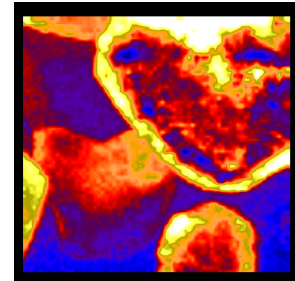


Chemical Speciation

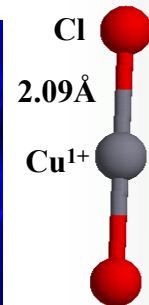
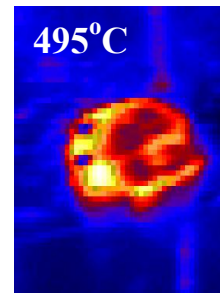
Principal Synchrotron Techniques Used in Environmental Science

- **X-ray Fluorescence (XRF):** chemical composition (quantification, mapping)
- **X-ray Absorption Fine Structure (XAFS) Spectroscopy:** chemical speciation (oxidation state, coordination, nearest neighbors)
- **Surface Scattering and Diffraction:** surface structure, sorption processes
- **Microtomography:** 3D imaging of internal microstructure (porosity, fluid flow, composition)

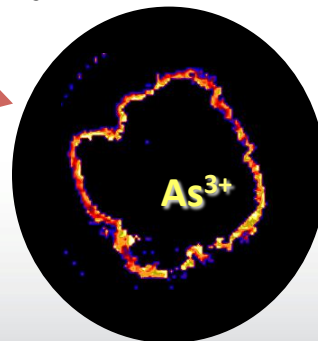
Arsenic on Bangladesh Biotite



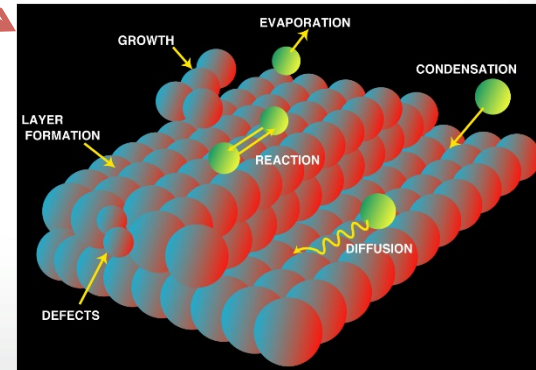
Copper Speciation in Fluid Inclusions



Arsenic in Cattail Root Plaque



Surface Reactions

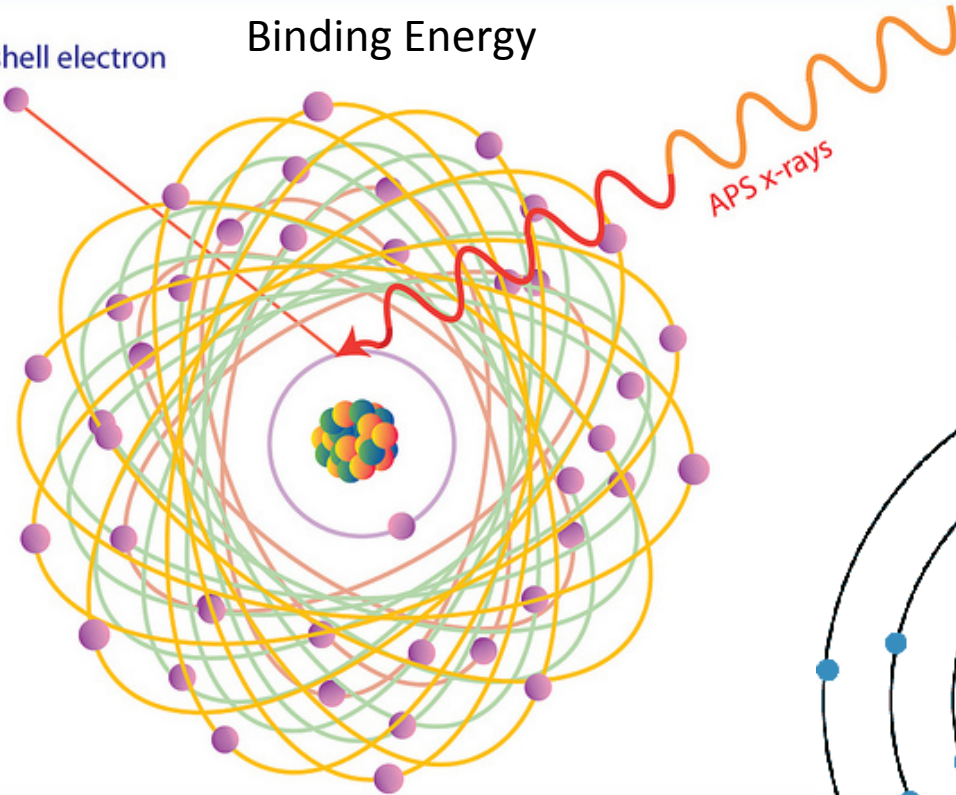




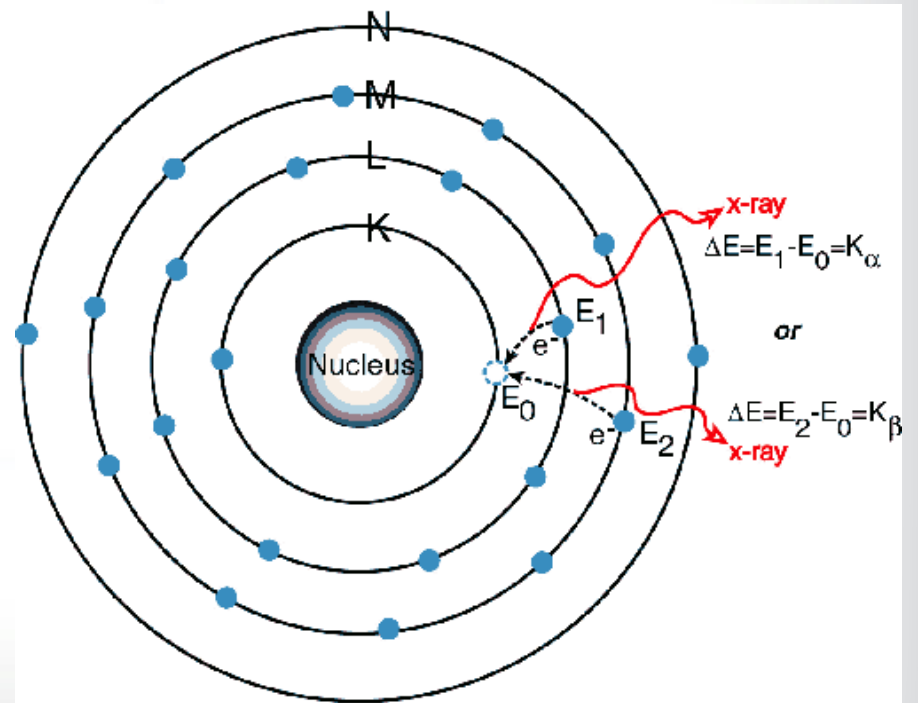
Chemical Speciation

Liberated K-shell electron

Binding Energy



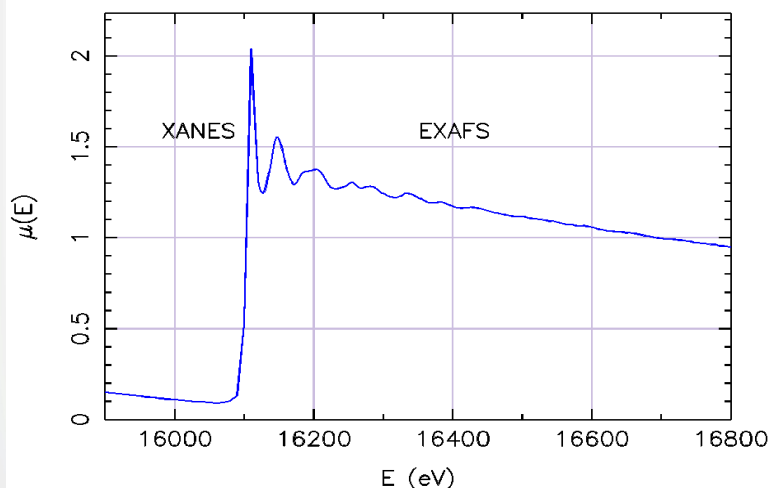
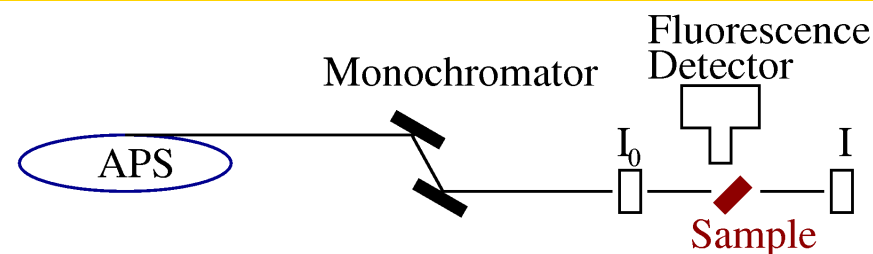
Emission Energy





Chemical Speciation

X-ray Absorption Spectroscopy: Measure energy-dependence of the x-ray absorption coefficient $\mu(E)$ [either $\log(I_0/I)$ or (I_f/I_0)] of a core-level of a selected element



XANES = X-ray Absorption Near-Edge Spectroscopy

EXAFS = Extended X-ray Absorption Fine-Structure

Element Specific: Elements with $Z > 20$ can be examined.

Valence Probe: XANES gives chemical state and formal valence of selected element.

Local Structure Probe: EXAFS gives atomic species, distance, and number of near-neighbor atoms around a selected element.

Low Concentration: concentrations down to 1 ppm for XANES, 10 ppm for EXAFS.

Natural Samples: samples can be in solution, liquids, amorphous solids, soils, aggregates, plant roots, surfaces, etc.

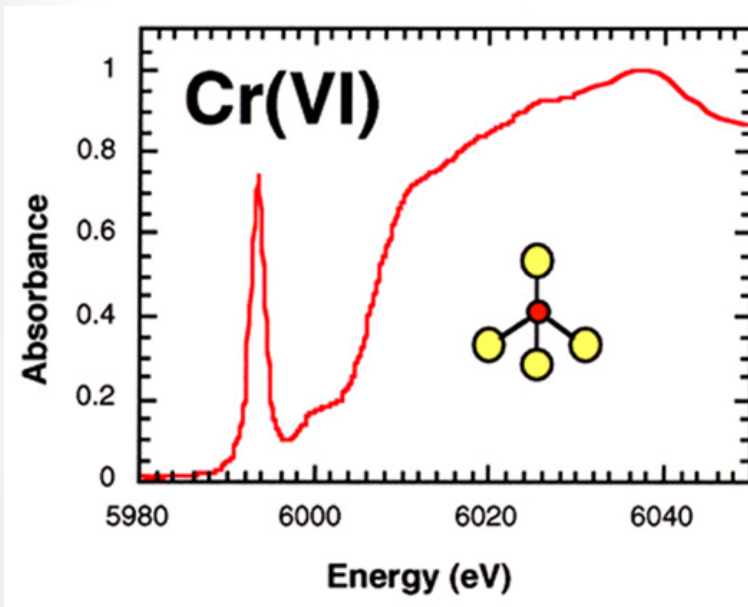
Small Spot Size: XANES and EXAFS measurements can be made on samples down to ~20 nanometers in size.



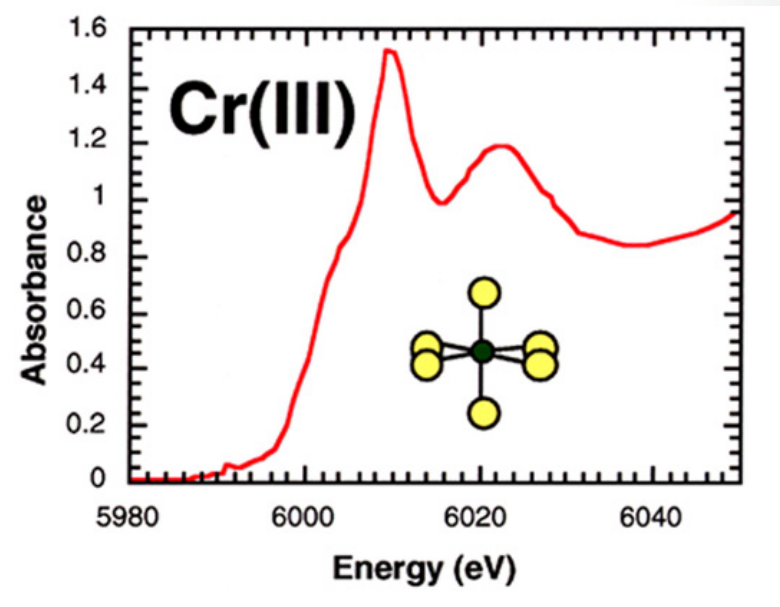
Chemical Speciation

Chemical state is critical in determining toxicity and mobility

Cr(VI) is highly carcinogenic and highly mobile in ground water.



Cr(III) is not carcinogenic or very toxic, and is not mobile in ground water.



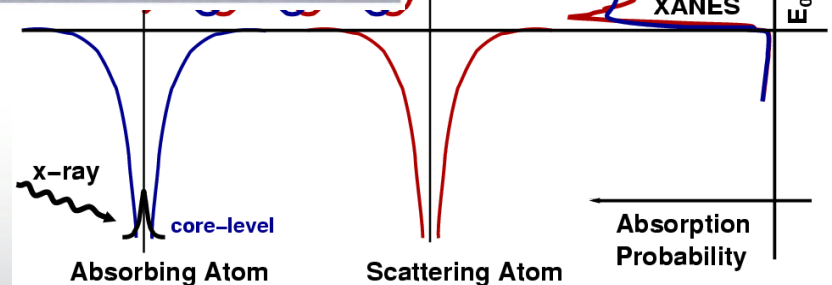
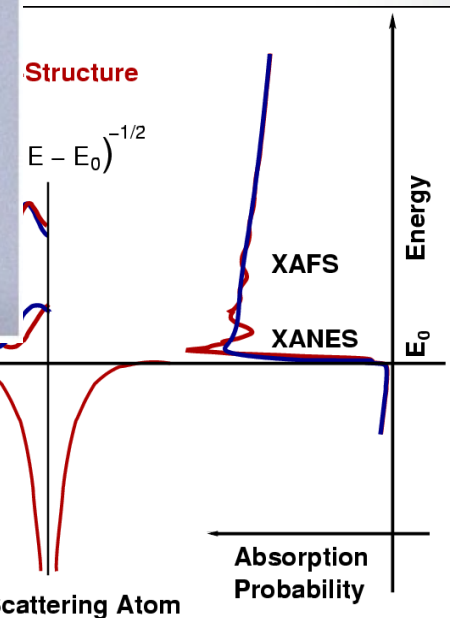
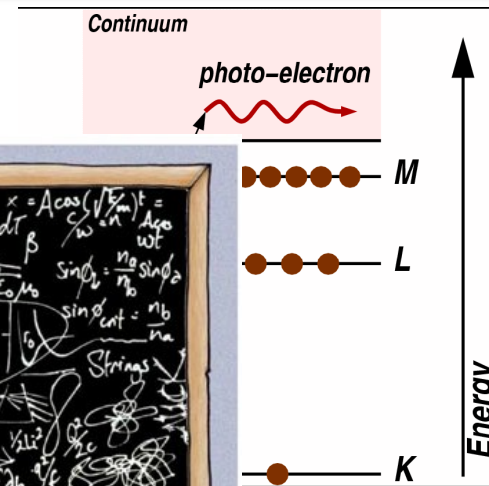
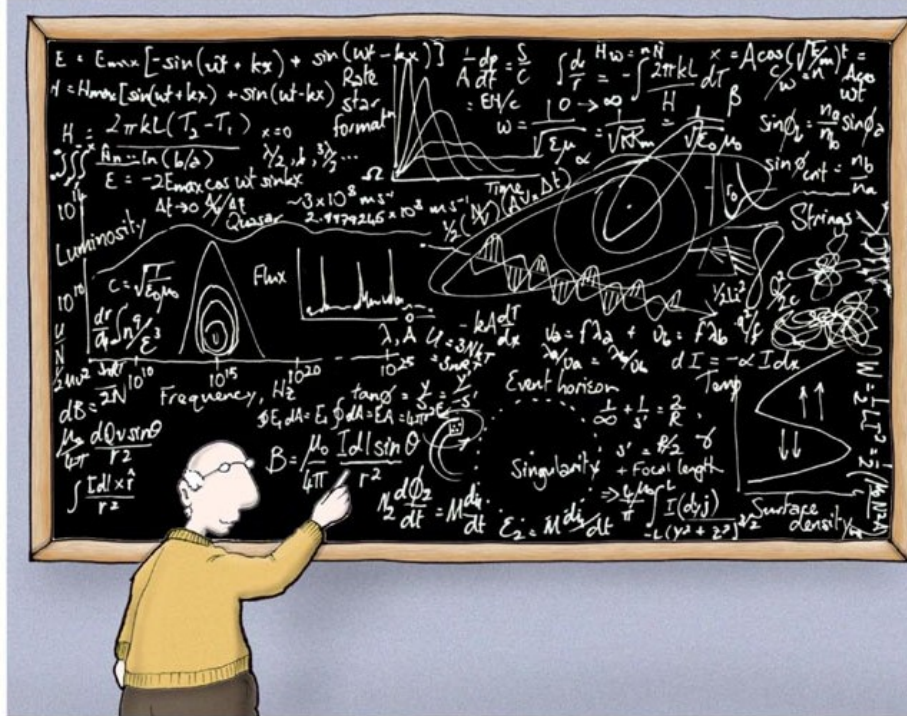
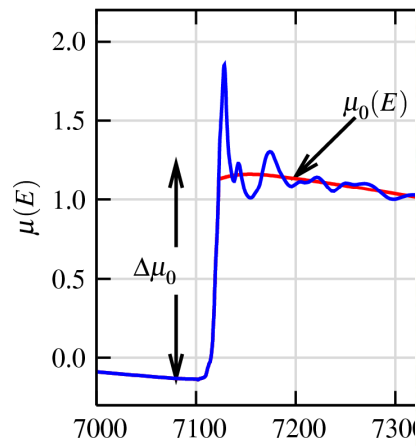


Chemical Speciation

Beer's Law:

$$I = I_0 e^{-\mu t}$$

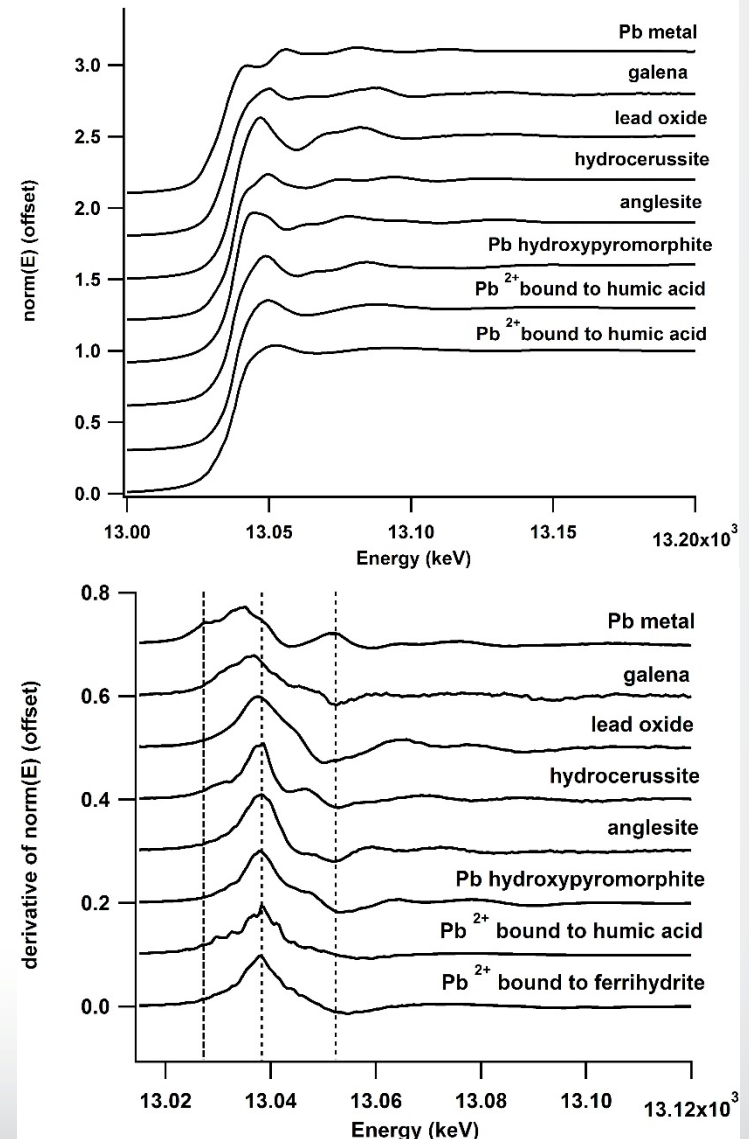
$$\mu \approx (\rho Z^4)/(AE^3)$$





Omaha Lead Superfund Site Lead Speciation

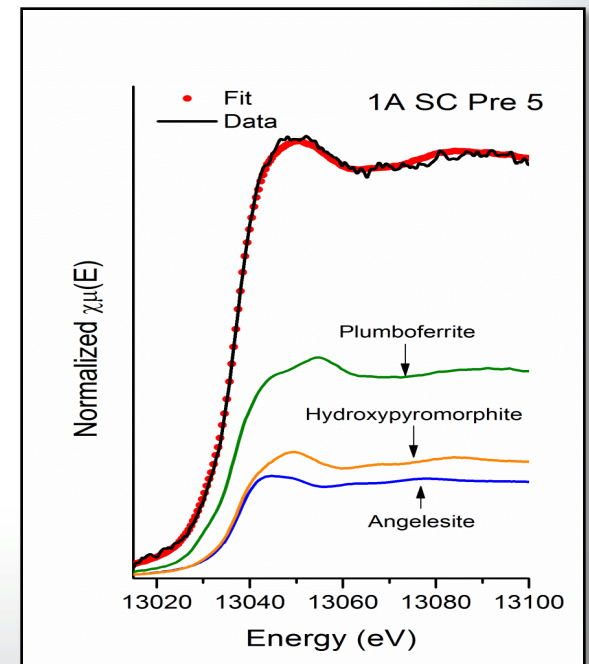
Pb Species	Industrial uses	Natural occurrence in soil
Pb metal	Solder, old pipes	Rare
Galena (PbS)	Lead ore	Rare
Lead oxide (PbO)	Lead glass, industrial ceramics, computer components	Rare
Hydrocerussite (PbCO ₃ ·Pb(OH) ₂)	'White lead', lead paint	Occurs naturally
Anglesite (PbSO ₄)	-	Common, weathering product
Lead hydroxypyromorphite	-	Common, very insoluble
Pb ²⁺ bound to ferrihydrite	-	Common
Pb ²⁺ bound to humic acid	-	common





Omaha Lead Superfund Site Project Objectives

- Investigate the redistribution of lead in previously remediated soils after intrusion into the subsoil (soil below the remediation interface)
 - Does soil mixing associated with normal homeowner excavation practices result in surface lead concentrations in excess of 400 mg kg^{-1} when the subsurface concentration of lead is high ($< 1200 \text{ mg kg}^{-1}$).
 - How well mixed is the soil after excavation
 - Is it possible to model the soil mixing process for risk assessment purposes
- Bonus Objective
 - Determine the speciation of lead in the subsoil of residential soils.





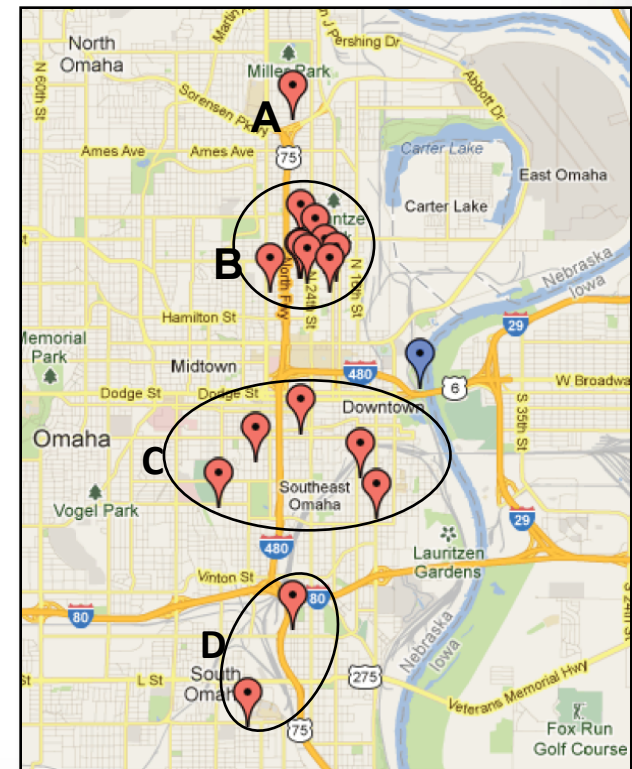
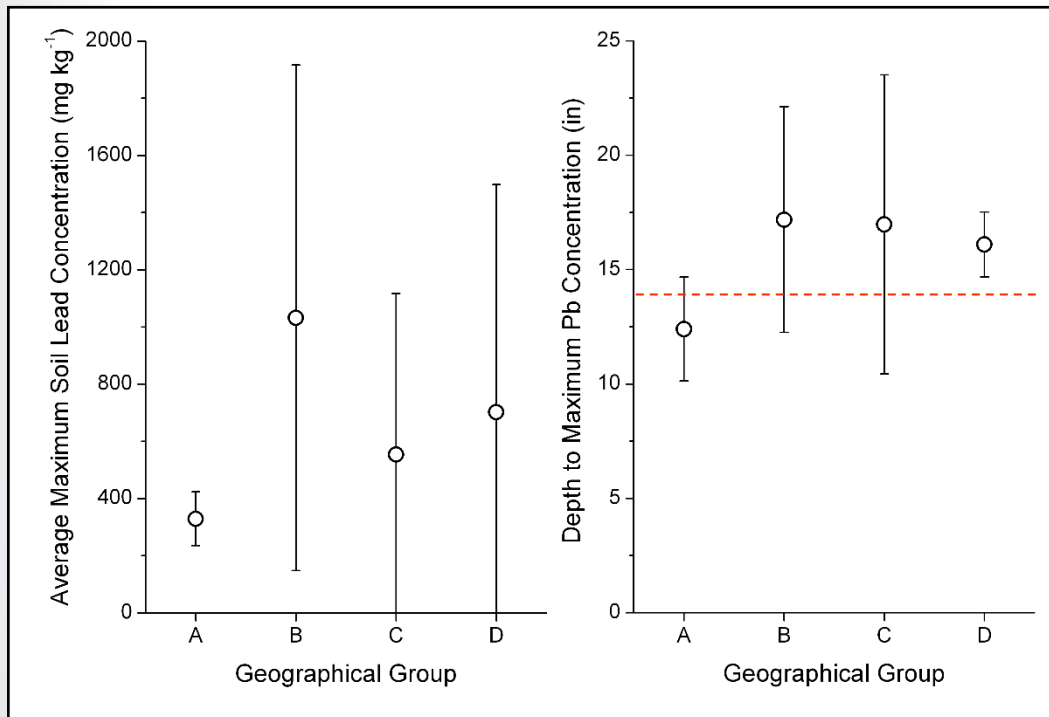
Omaha Lead Superfund Site Sampling Technique

- The two different techniques produced spoil with different properties
 - Homeowner
 - Larger irregularly shaped clods of variable size
 - Standardized
 - Small well formed granular clods, of low variability





Omaha Lead Superfund Site Geographic Lead Distribution



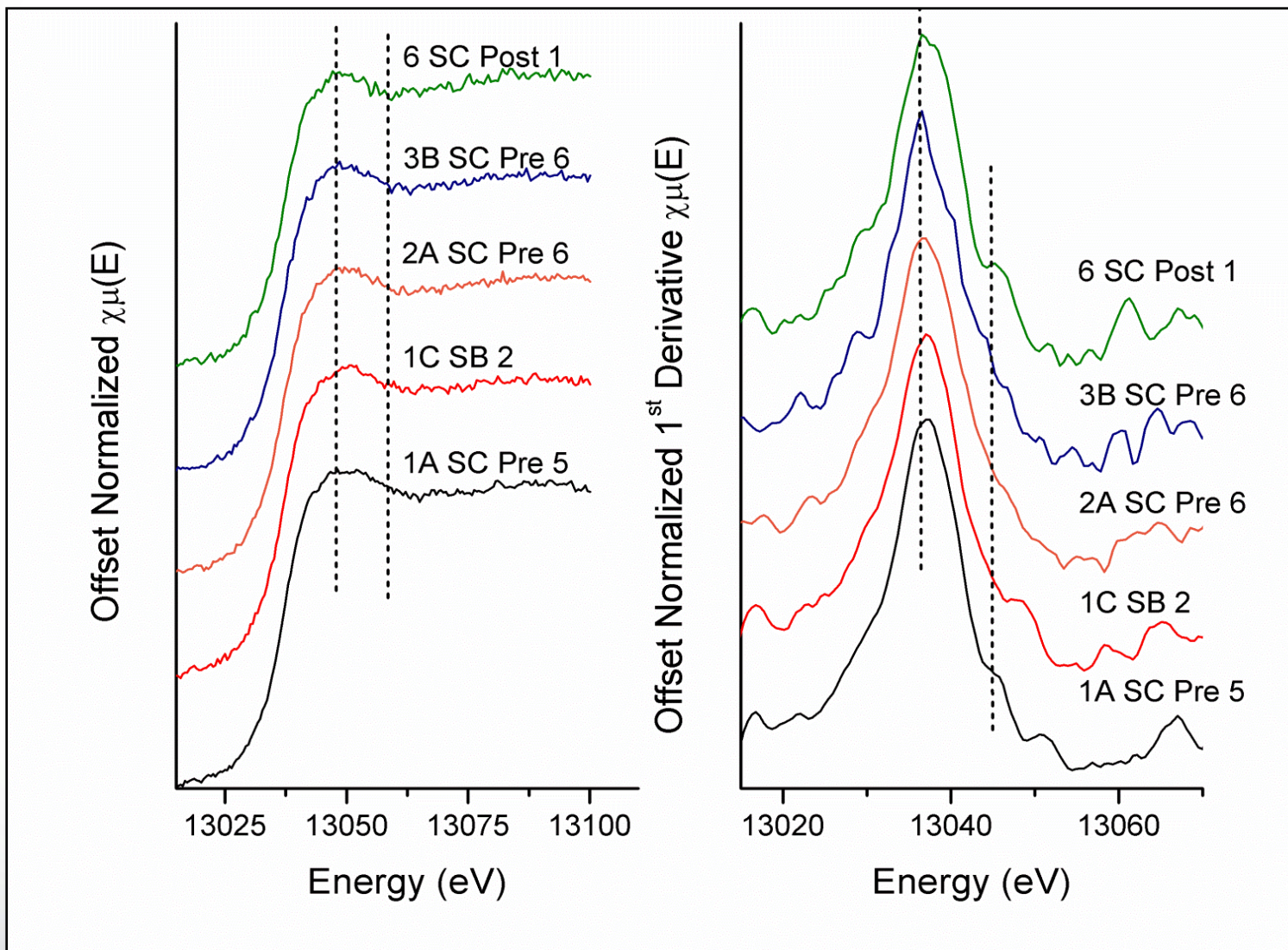


Omaha Lead Superfund Site Lead Speciation

- Five soil samples were analyzed by XAFS analysis to determine soil lead speciation
 - 3 pre-excavation core sections (1A, 2A, 3B)
 - 1 spoil pile (1C)
 - 1 post excavation surface soil (6)
 - Speciation was determined by linear combination fitting of the XANES and 1st derivative of the Pb L3 XANES data.
 - Linear combination fitting models the spectrum from a sample of unknown speciation with a linear combination of spectra from standards of known structure and composition that are candidate species within the sample.

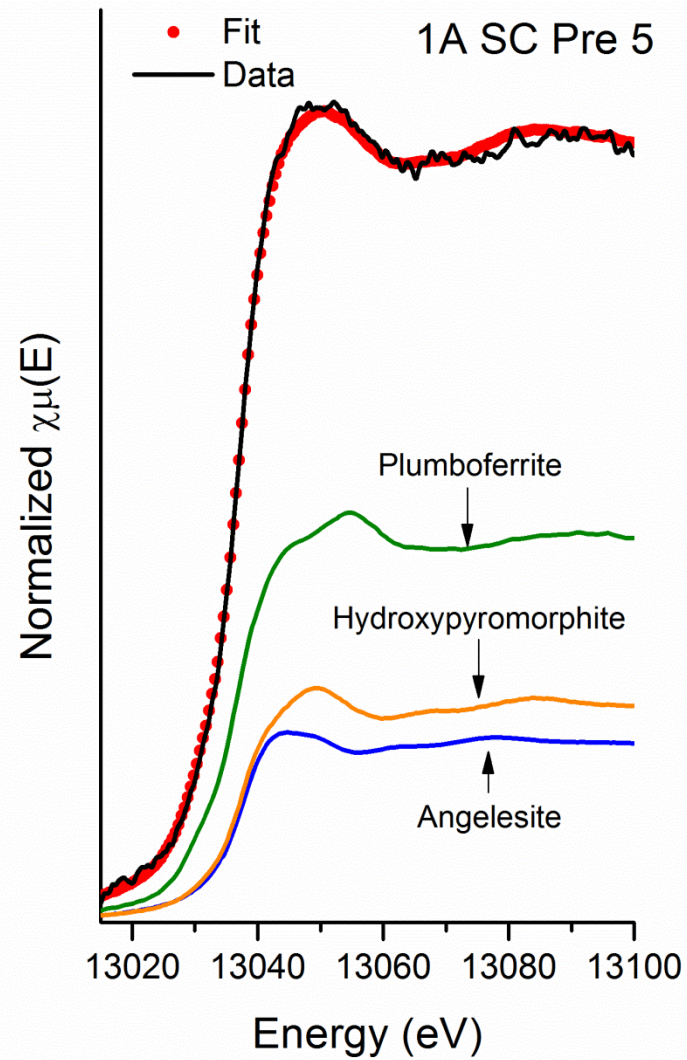


Omaha Lead Superfund Site Lead Speciation





Omaha Lead Superfund Site LCF Results





Omaha Lead Superfund Site LCF Results

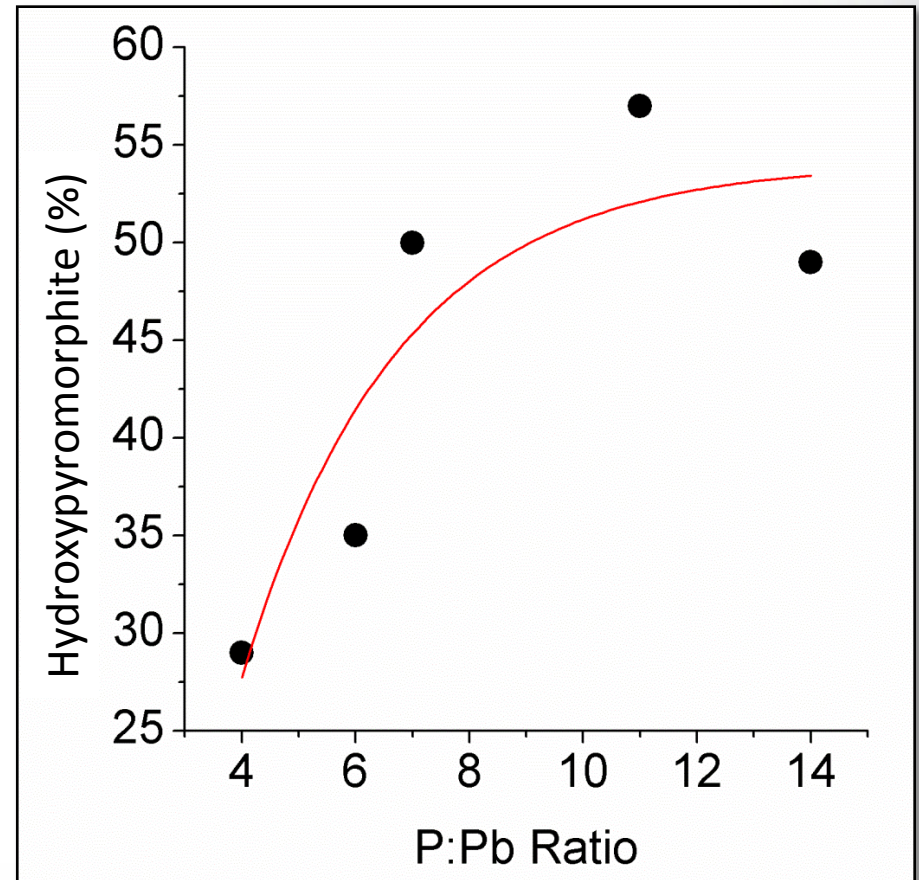
Soil Sample	Pb	P/Pb	Normalized LCF Fit				1 st Derivative LCF Fit			
			Ang	Hy-Py	Pb-Fer	Galena	Ang	Hy-Py	Pb-Fer	Galena
	mg kg ⁻¹	mol/ mol	%				%			
1A SC Pre 5	1541	4	24	29	48		24	37	42	
1C SB 2	2692	6	21	35	45		23	32	46	
2A SC Pre 6	1202	14	13	49	38		10	57	33	
3B SC Pre 6	1342	7	13	50	37		17	43	41	
6 SC Post 1	1147	11	29	39		32	24	55		21

Sample Site 6 was located in quadrant D (furthest south). All others were from quadrant B



Omaha Lead Superfund Site Lead Speciation

- Pyromorphites are not associated with the lead species emitted from lead smelting and recycling operations
- Very low bioavailability
- High levels of P in the soils has resulted in the *in-situ* formation of pyromorphite species
- Previous research has demonstrated the precipitation of pyromorphite at pH 7
- At the highest P:Pb ratios 50% of the lead is in the form of hydroxypyromorphite
- Application of P to lead contaminated soils is a remediation strategy





Chemical Speciation

- **XAS needs supporting information to be used properly**
 - **Have information on Pb extractability, solubility, or mobility in soil before using XAS**
 - **Needed to justify the study question in proposals for beam time**
- **Requires long-term planning**
 - **Time to use the facility is awarded at 4 points throughout the year**
- **Identification depends on a good selection of standards**
 - **“Need to know what’s in your soil before you can really know what’s in your soil”**
 - **No centralized database of standards**
 - **Gather general data on soil to ensure you collect standards relevant to what your site**
 - **Total concentrations of multiple elements (e.g., Ca, Mg, Fe, P, S)**
 - **Soil pH**
 - **Site history**



Conclusions

- Chemical speciation aids in understanding fate and transport, bioavailability, and remediation effectiveness.
- XAS is the best tool to directly speciate Pb in environmental samples
- Relies on supporting information
 - Depends on supporting information about the soils
 - Species identification depends on good selection of standards



Questions