Techniques to Understand Source Attribution and Exposure Risks at Impacted Sites

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Source Attribution vs. Exposure Risk

The source of Pb contamination and the risk of Pb contamination must be considered at two distinct issues

Source Attribution

- Pb Isotopes

Where did the Pb come from?

- Examine ratios of 4 common Pb isotopes from source material, background, and suspected impacted samples
- Isotopic ratios do not change over time

'Genetics'

Exposure Risk

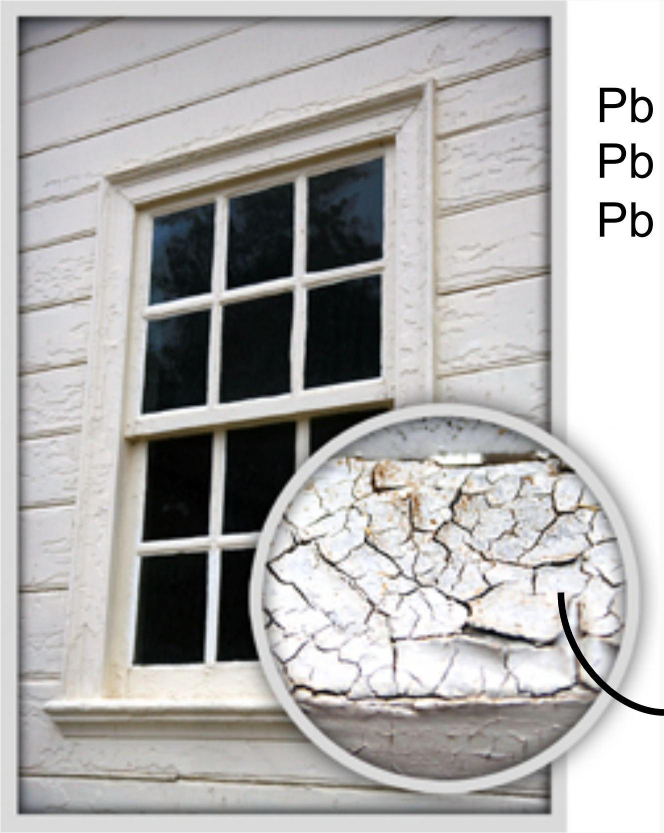
- Pb Speciation

Form of Pb drives risk. Solubility linked to speciation of Pb.

Form of Pb is environmental driven – can change over time.

'Fingerprints'

Pb Isotopes vs. Speciation



Pb oxide
Pb carbonate
Pb sulfate

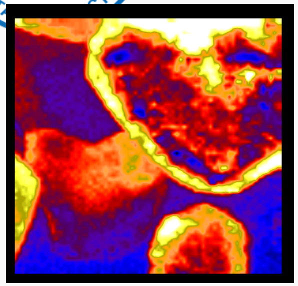
Transformation Reactions in Soil

Speciation – Synchrotron Spectroscopy

Principal Synchrotron Techniques Used in Environmental Science

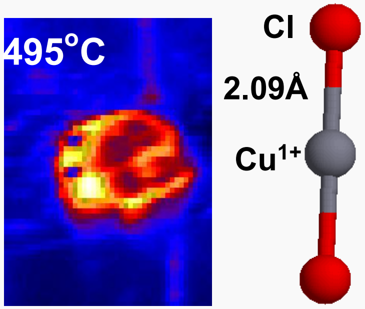
- **X-ray Fluorescence (XRF):** chemical composition (quantification, mapping)

Arsenic on Bangladesh Biotite



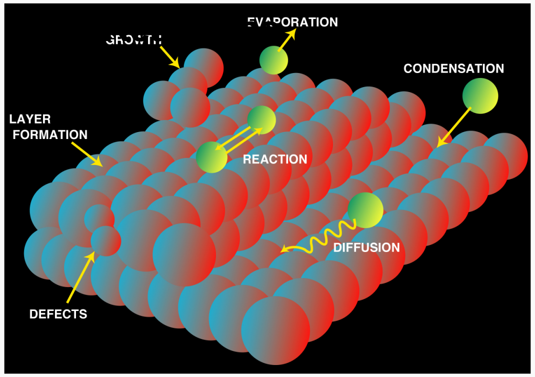
- **X-ray Absorption Fine Structure (XAFS) Spectroscopy:** chemical speciation (oxidation state, coordination, nearest neighbors)

Copper Speciation in Fluid Inclusions



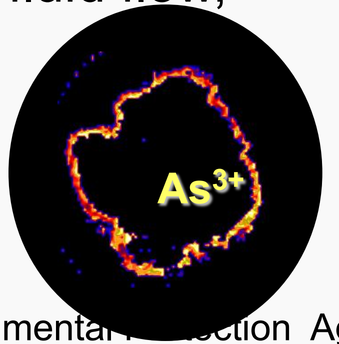
- **Surface Scattering and Diffraction:** surface structure, sorption processes

Surface



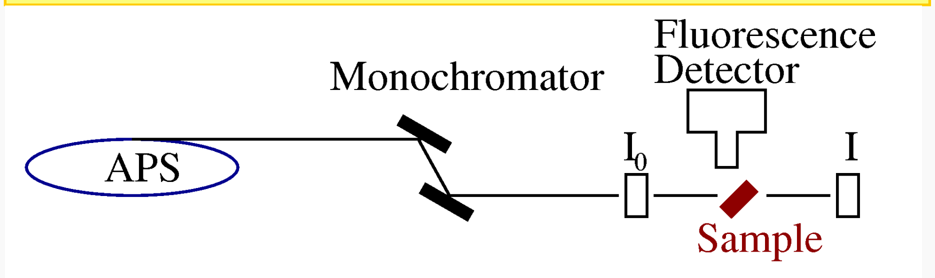
- **Microtomography:** 3D imaging of internal microstructure (porosity, fluid flow, composition)

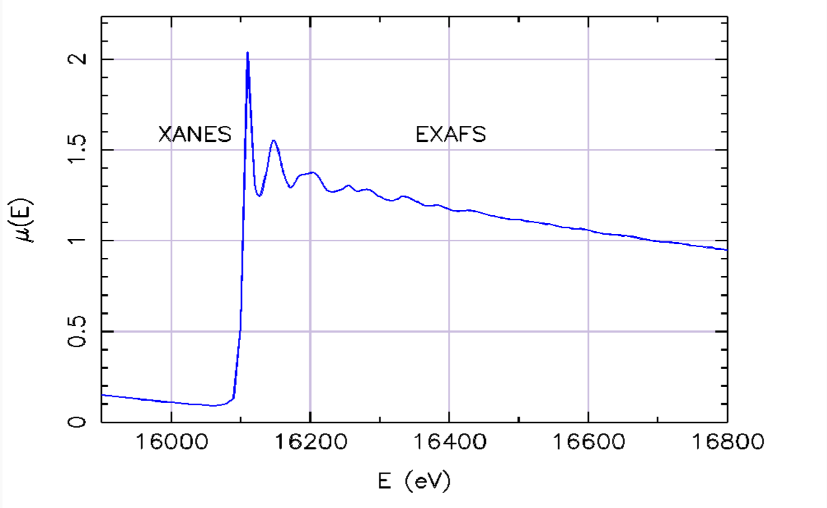
Arsenic in Cattail Root Plaque



X-ray Absorption Spectroscopy

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.

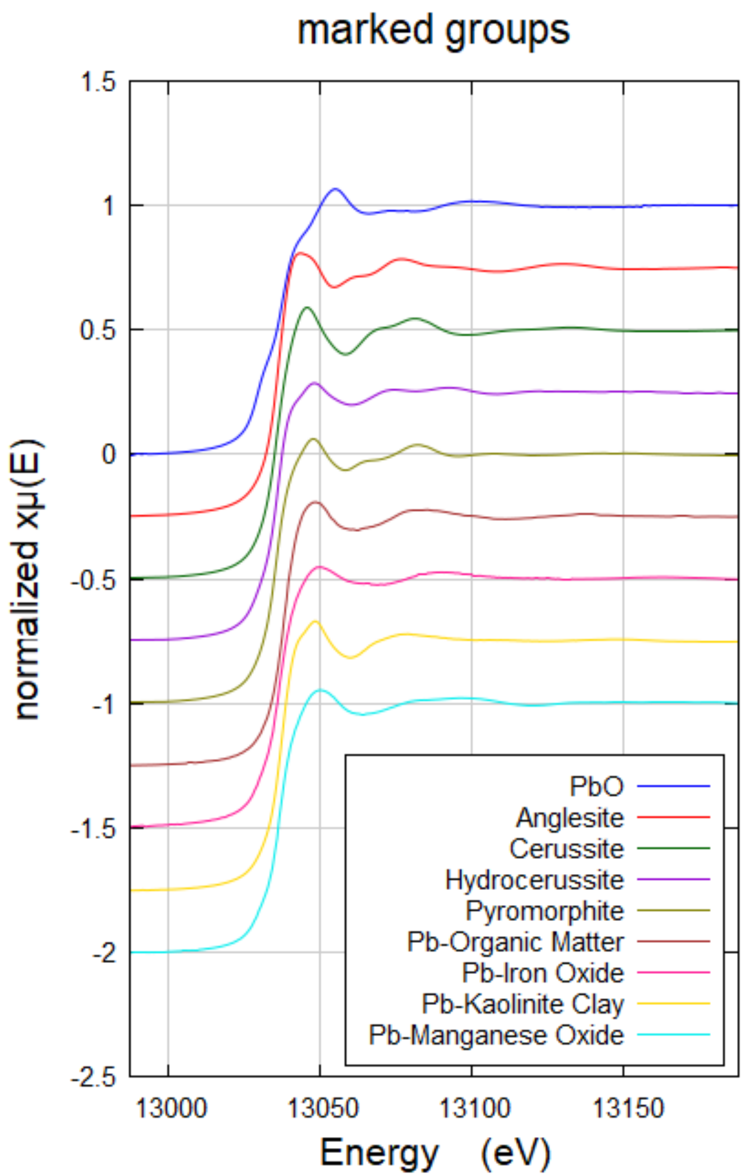
Valence Probe: XANES gives chemical state and formal valence of selected element.

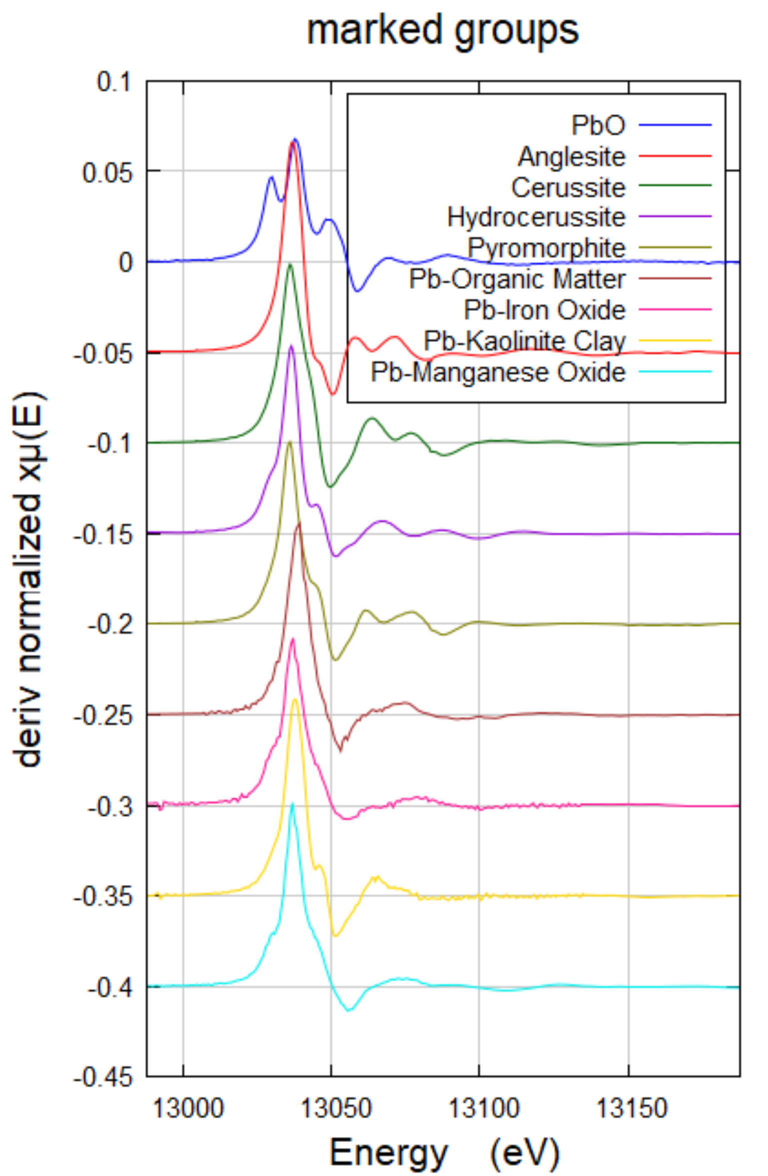
Local Structure Probe: EXAFS gives atomic species, distance, and number of near-neighbor atoms around a selected element..

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.

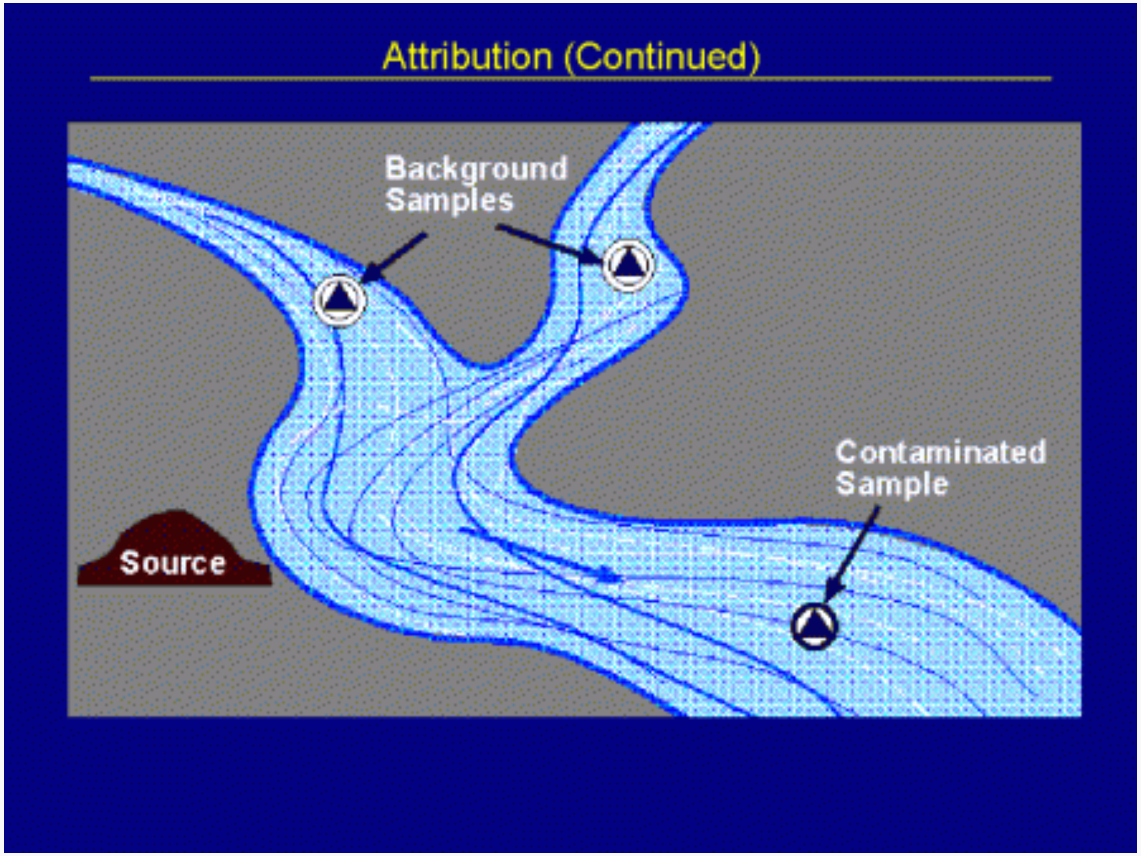
Small Spot Size: XANES and EXAFS measurements can be made on samples down to ~1 microns in size.


marked groups
normalized xμ(E)
Energy (eV)
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
13000
13050
13100
13150
PbO
Anglesite
Cerussite
Hydrocerussite
Pyromorphite
Pb-Organic Matter
Pb-Iron Oxide
Pb-Kaolinite Clay
Pb-Manganese Oxide

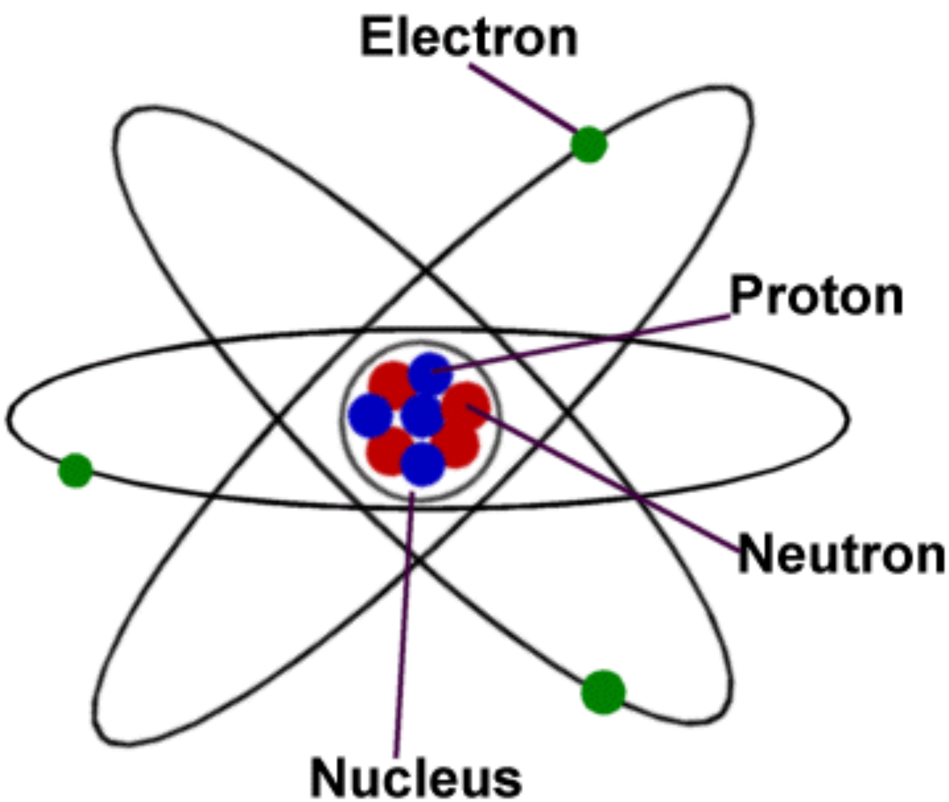

marked groups
deriv normalized xμ(E)
Energy (eV)
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
-0.4
-0.45
13000
13050
13100
13150
PbO
Anglesite
Cerussite
Hydrocerussite
Pyromorphite
Pb-Organic Matter
Pb-Iron Oxide
Pb-Kaolinite Clay
Pb-Manganese Oxide

Source Attribution

Site documentation (e.g., manifests, written statements, interviews with employees) and analytical sampling data.



Isotope Chemistry 101

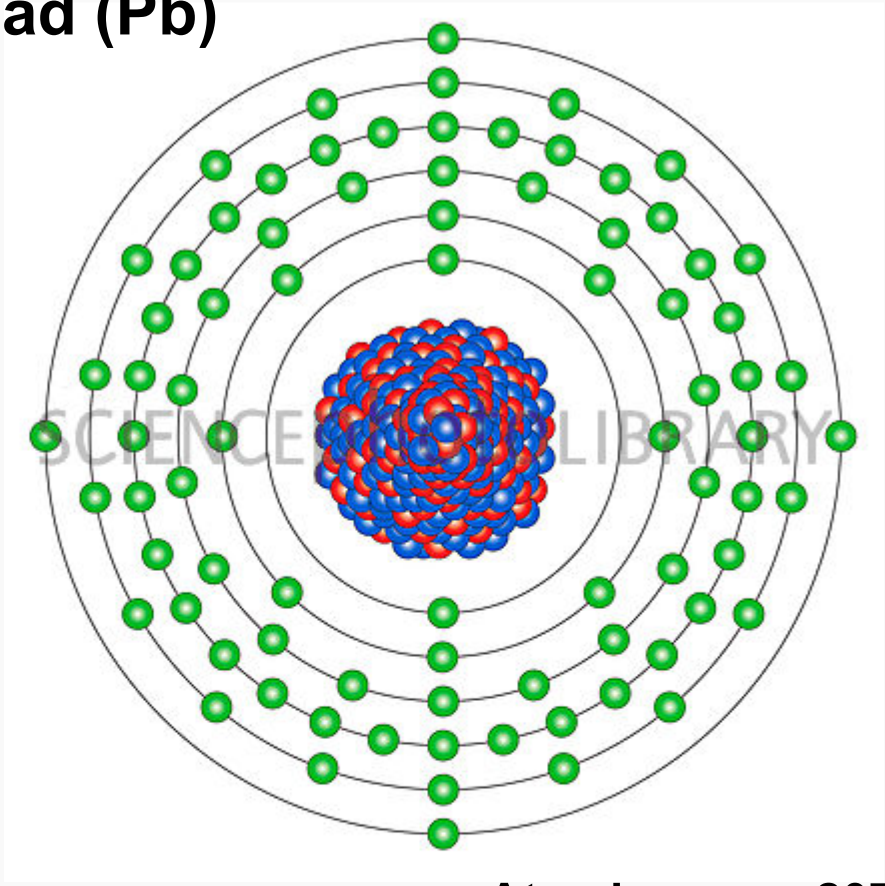


Isotopes are variants of a particular chemical element which differ in neutron number with the same number of protons.

Isotope Chemistry 101

Lead (Pb)

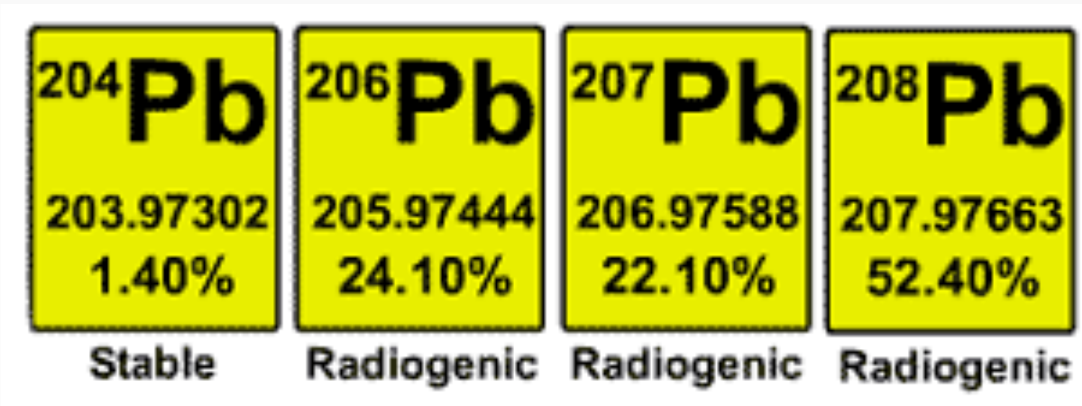
Atomic number: 82

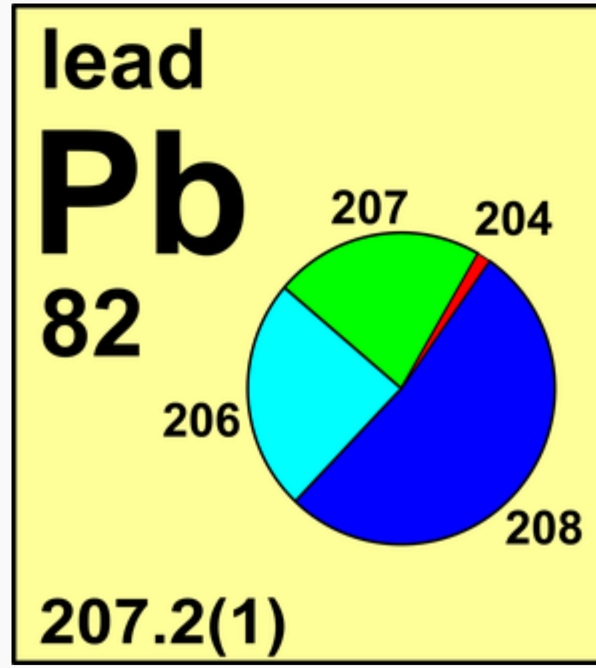


Atomic mass: 207.2

Neutrons serve the purpose of keeping atoms stable; offsetting repulsive positive charges in the nucleus and balancing negative charges of electrons on the nucleus.

Pb Isotopes





Isotopic measurements are concentration based; for ‘genetic’ ratios are utilized to determine compositional relationships:

$^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$

Pb Isotopes

Decay processes of ^{238}U, ^{235}U, and ^{232}Th and their half-lives.

Reaction	Decay constant (year^{-1})	Half-life (years)
$^{238}_{92}U \rightarrow ^{206}_{82}Pb + 8^{4}_{2}He + 6\beta^-$	1.55125×10^{-10}	4.468×10^{9}
$^{235}_{92}U \rightarrow ^{207}_{82}Pb + 7^{4}_{2}He + 4\beta^-$	9.8485×10^{-10}	7.038×10^{8}
$^{232}_{90}Th \rightarrow ^{208}_{82}Pb + 6^{4}_{2}He + 4\beta^-$	4.9475×10^{-11}	1.4008×10^{10}

Pb Isotopes

Examples of Pb isotopic compositions ($^{206}Pb/^{207}Pb$) of different anthropogenic Pb sources in the environment

Sample	Country (location)	$^{206}Pb/^{207}Pb$	
		Range	Mean ± SD
Gasoline and vehicular Pb			
Leaded gasoline	United Kingdom	1.059–1.079	1.067±0.007
Leaded gasoline	France (NW)	1.060–1.100	1.083±0.015
Leaded gasoline	France	1.069–1.094	1.084±0.009
Leaded gasoline	Switzerland (Geneva)	1.081–1.132	1.113±0.015
Road tunnel dust	Switzerland (Milchbuck)	1.109–1.118	1.114±0.004
Vehicle exhaust	Switzerland (Milchbuck)	1.086–1.125	1.107±0.012
Leaded gasoline	Czech Republic		1.110±0.016
Road tunnel dust	Czech Republic (Prague)		1.135±0.001
Leaded gasoline	Israel (Jerusalem)	1.094–1.119	1.109±0.007
Unleaded gasoline	Israel (Jerusalem)	1.108–1.146	1.126±0.015
Leaded gasoline	Mexico	1.202–1.204	1.203±0.001
Leaded gasoline	Canada	0.920–1.190	1.105±0.086
Leaded gasoline	USA	1.040–1.390	1.183±0.103
Leaded gasoline	Russia	1.134–1.149	1.142±0.008
Vehicle exhaust (leaded)	China (Shanghai)	1.098–1.116	1.110±0.005
Vehicle exhaust (unleaded)	China (Shanghai)	1.138–1.160	1.147±0.004

Pb Isotopes

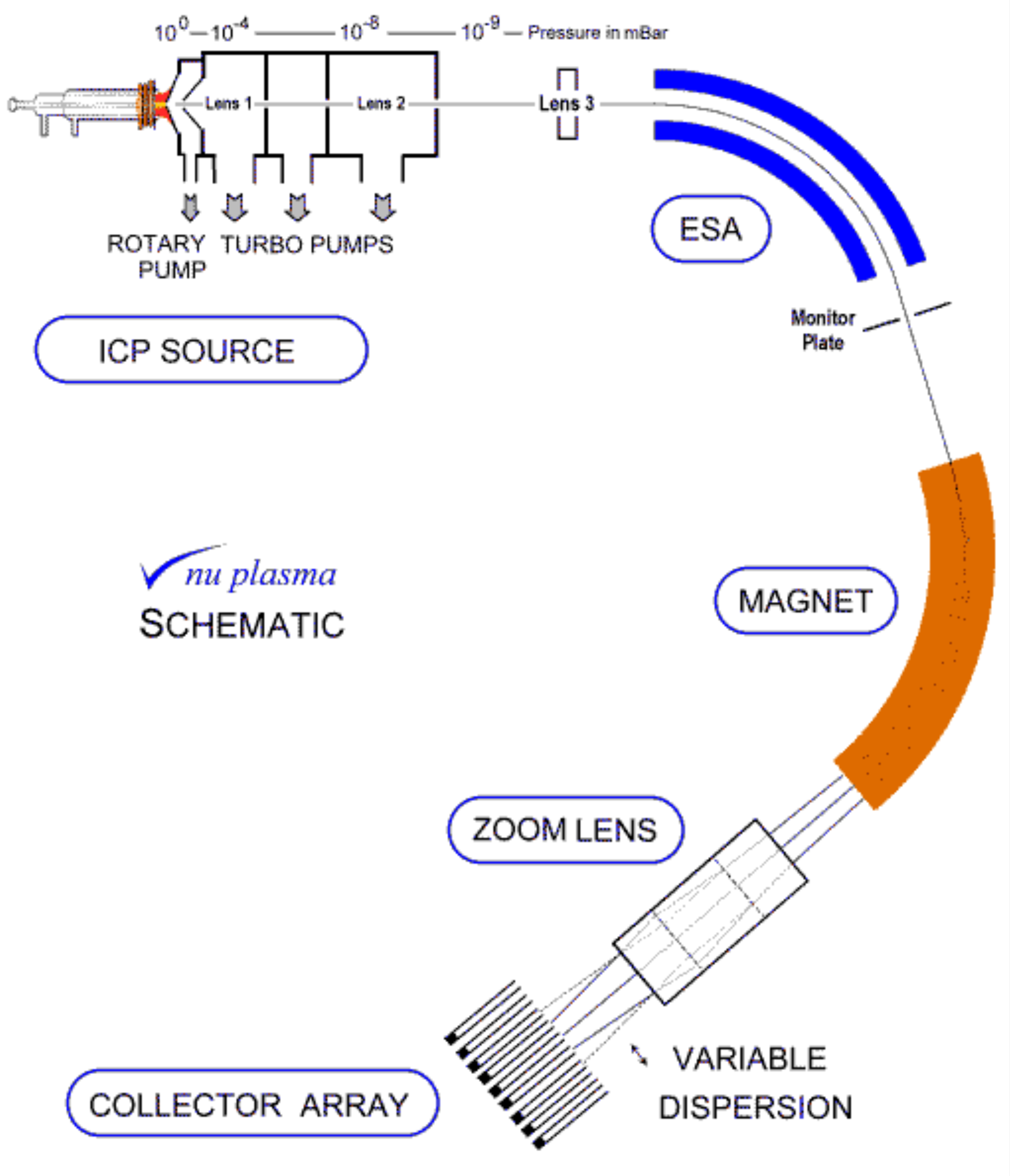
Examples of Pb isotopic compositions ($^{206}Pb/^{207}Pb$) of different anthropogenic Pb sources in the environment

Sample	Country (location)	$^{206}Pb/^{207}Pb$	
		Range	Mean ± SD
Slag — Pb smelter (ore processing)	Czech Republic (Příbram)		1.165±0.004
Slag — Pb smelter (battery processing)	Czech Republic (Příbram)		1.168±0.004
Fly ash — Pb smelter (ore processing)	Czech Republic (Příbram)		1.167±0.003
Ingots — Pb smelter	USA (Bunker Hill/Idaho)	1.070–1.140	1.095±0.029
Ingots — Pb smelter	USA (Doe Run/Missouri)	1.310–1.340	1.330±0.014
Slags and ingots — Pb smelter	USA (Eagle-Picher/Kansas–Okl.–Missouri)	1.210–1.360	1.282±0.058
Slag — Pb smelter	USA (ILP/Utah)		1.150
Electric-arc furnace dust — Zn smelter	USA (Palmerton, Pennsylvania)	1.206–1.224	1.213±0.055
Cu smelter emissions	Canada (Rouyn-Noranda)	0.920–1.030	

Attribution: Pb Isotopic Analysis via MC-ICP-MS

- USGS (Denver, CO) Multicollector-Inductively Coupled Plasma Mass Spectrometer Lab.
- Abundance of Pb isotopes in a sample depends strictly on the concentrations of primordial Pb, U and Th and the lengths of the decay processes, i.e., half-lives
- Lead is present in the environment as four main isotopes: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{204}Pb (1%)
- Lead isotopic studies therefore provide a convenient approach for studying and tracing lead source pollution in different environmental compartments

Pb Isotopes - Environmental Forensics



Pb Isotopes - Environmental Forensics

The Big River Mine Tailings/St. Joe Minerals Corp. Site is located in a former mining region known as the "Old Lead Belt," which is 70 miles south of St. Louis (St. Francois County). This site is composed of eight large areas of mine waste in this rural region, approximately 110 square miles in size.

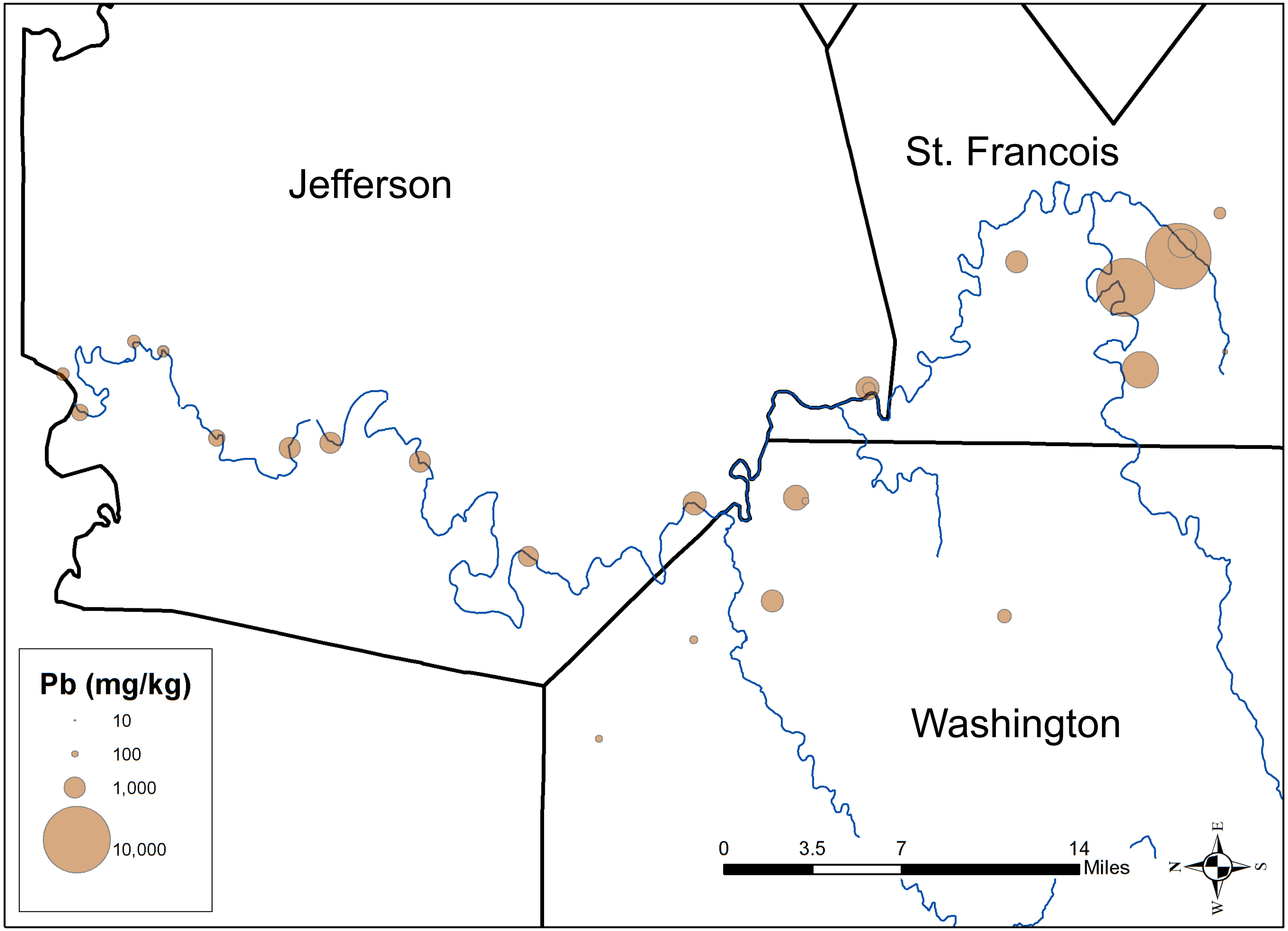
In 1977, heavy rains caused an estimated 50,000 cubic yards of tailings to slough into the Big River. Flooding events are common.

A barite mine area in Washington County is a suspected second source of Pb contamination in the Big River.

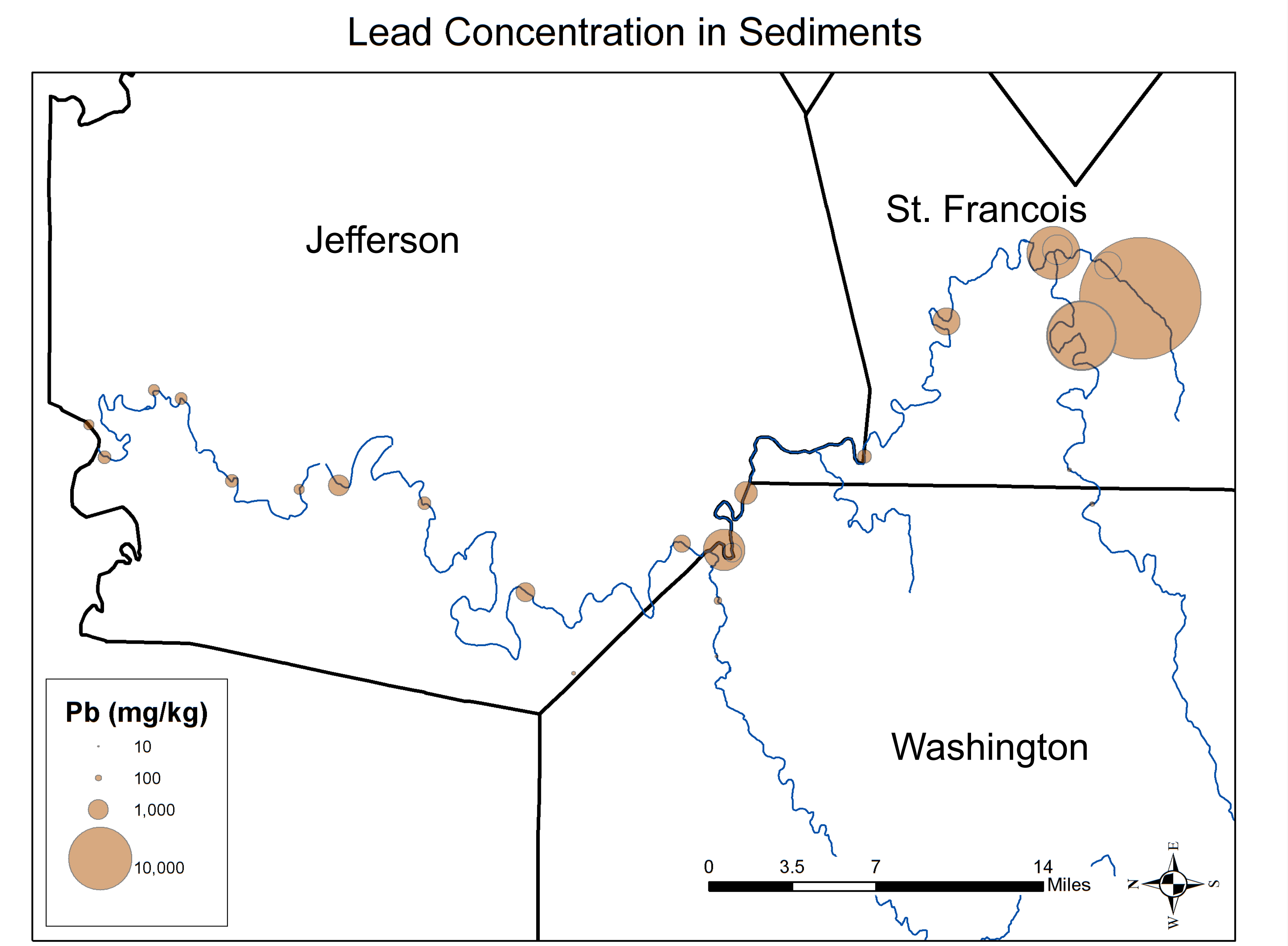
The Big River also flows through Jefferson County, depositing into the Meramec River and finally the Mississippi.

Pb Isotopes - Environmental Forensics

Lead Concentration in Soils



Pb Isotopes - Environmental Forensics



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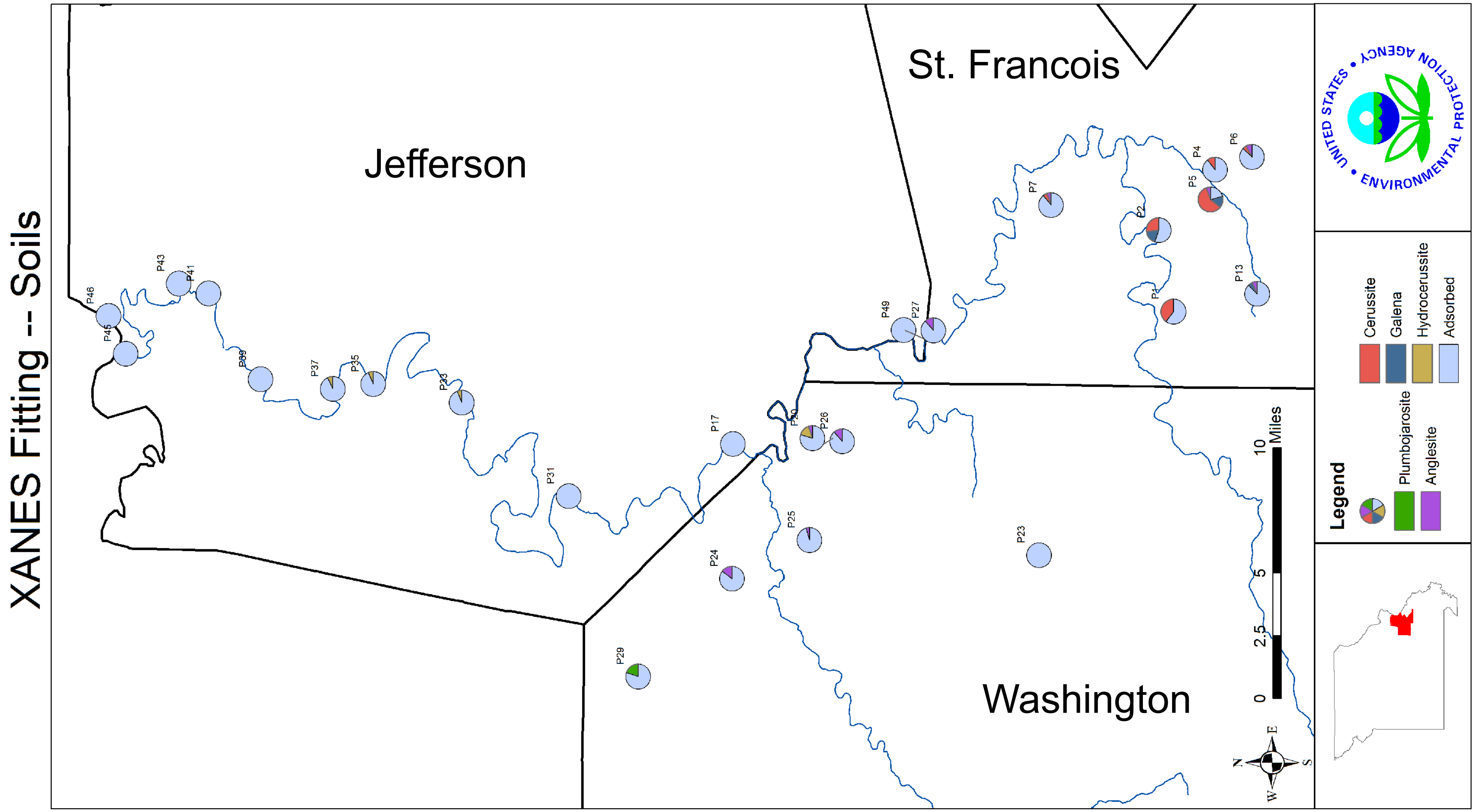
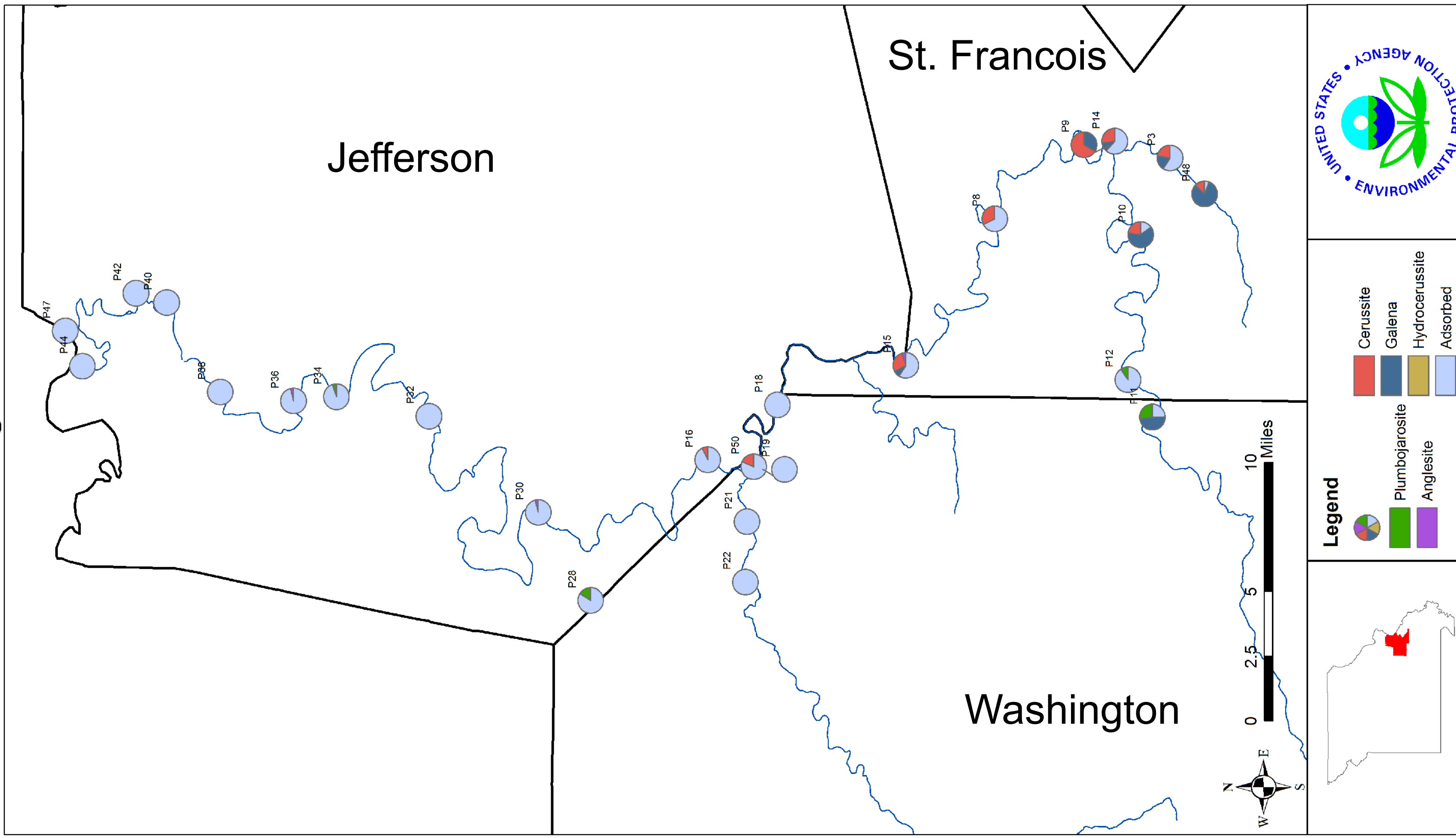
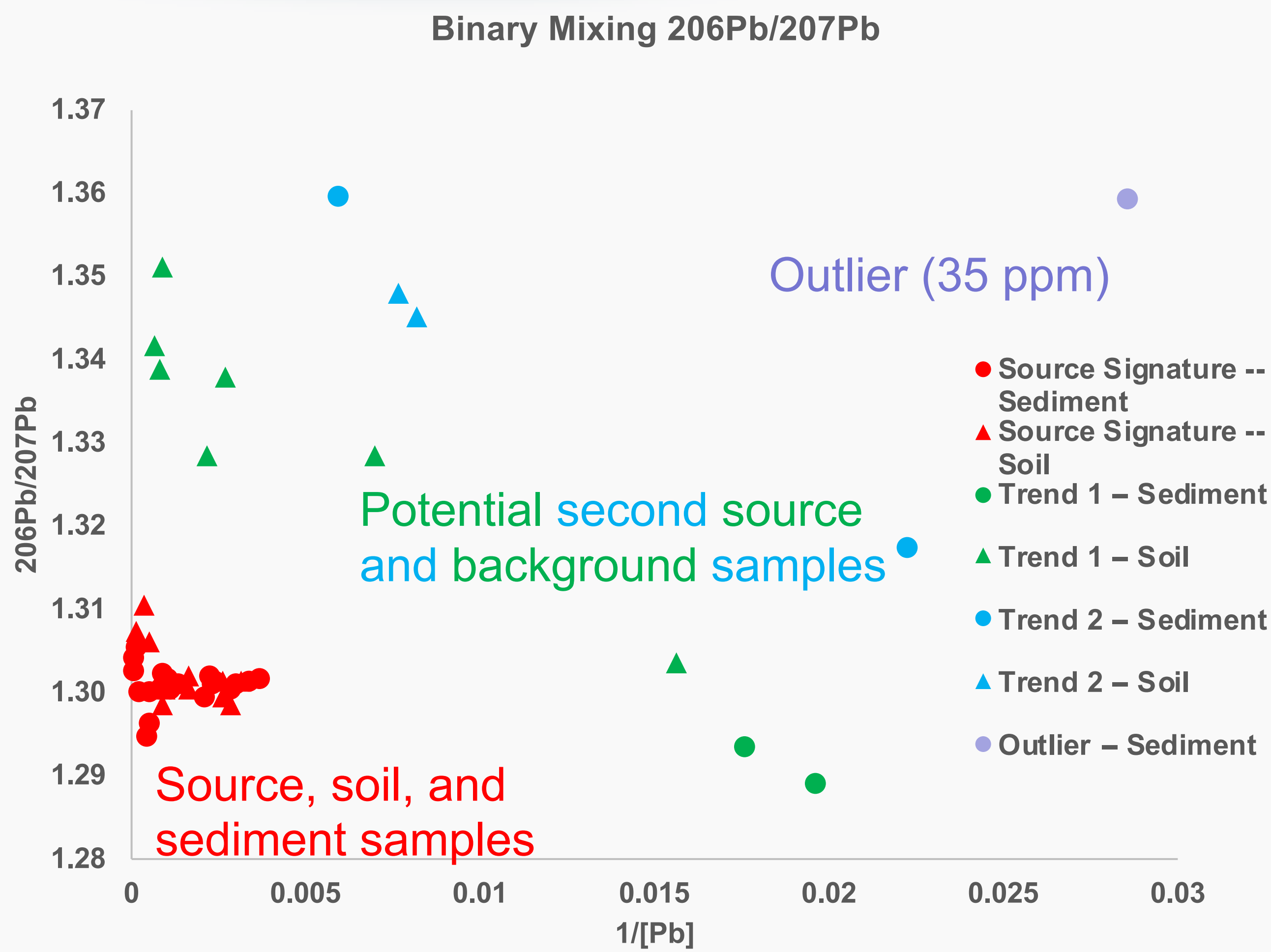


Pb Isotopes - Environmental Forensics

XANES Fitting -- Sediments

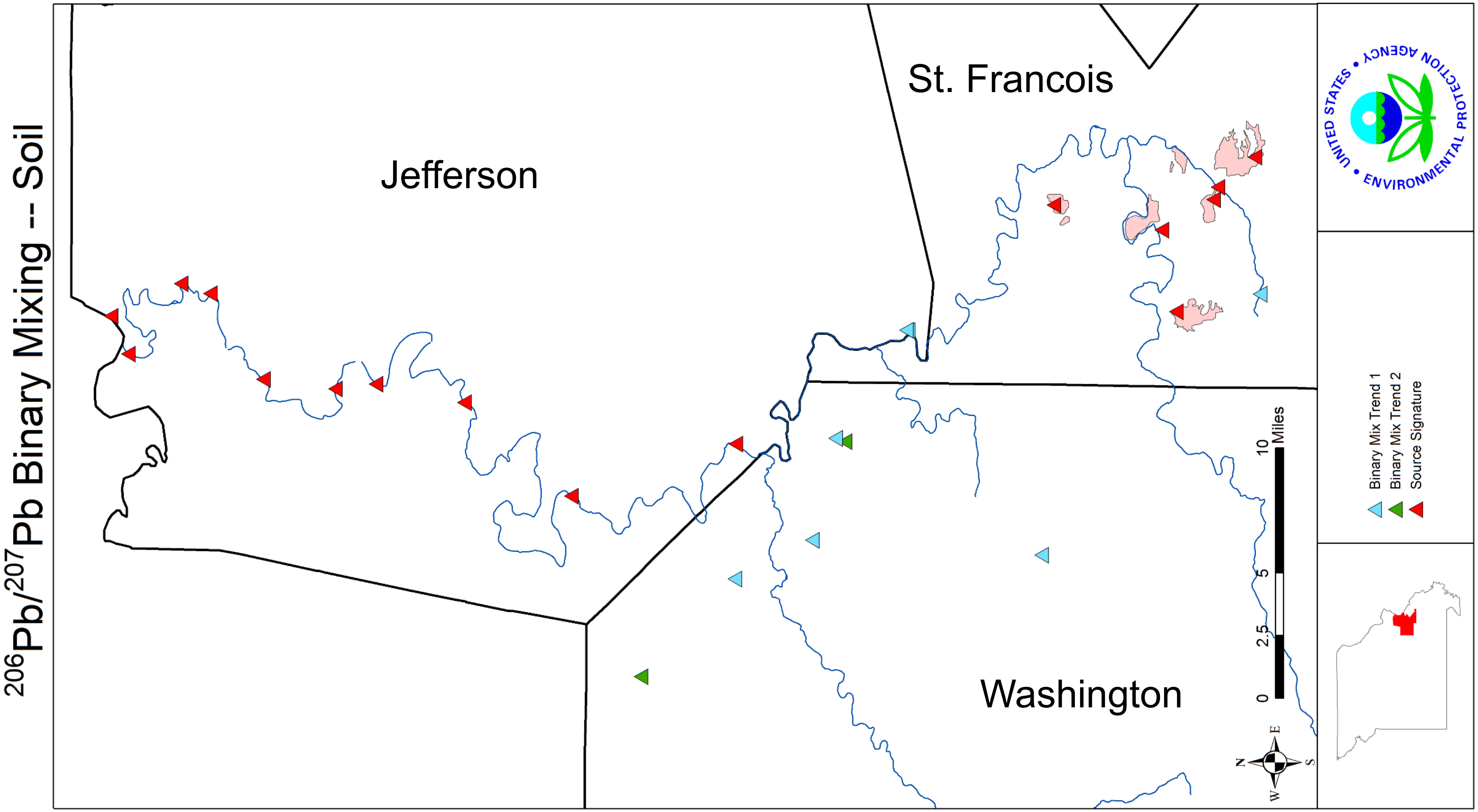


Pb Isotopes - Environmental Forensics



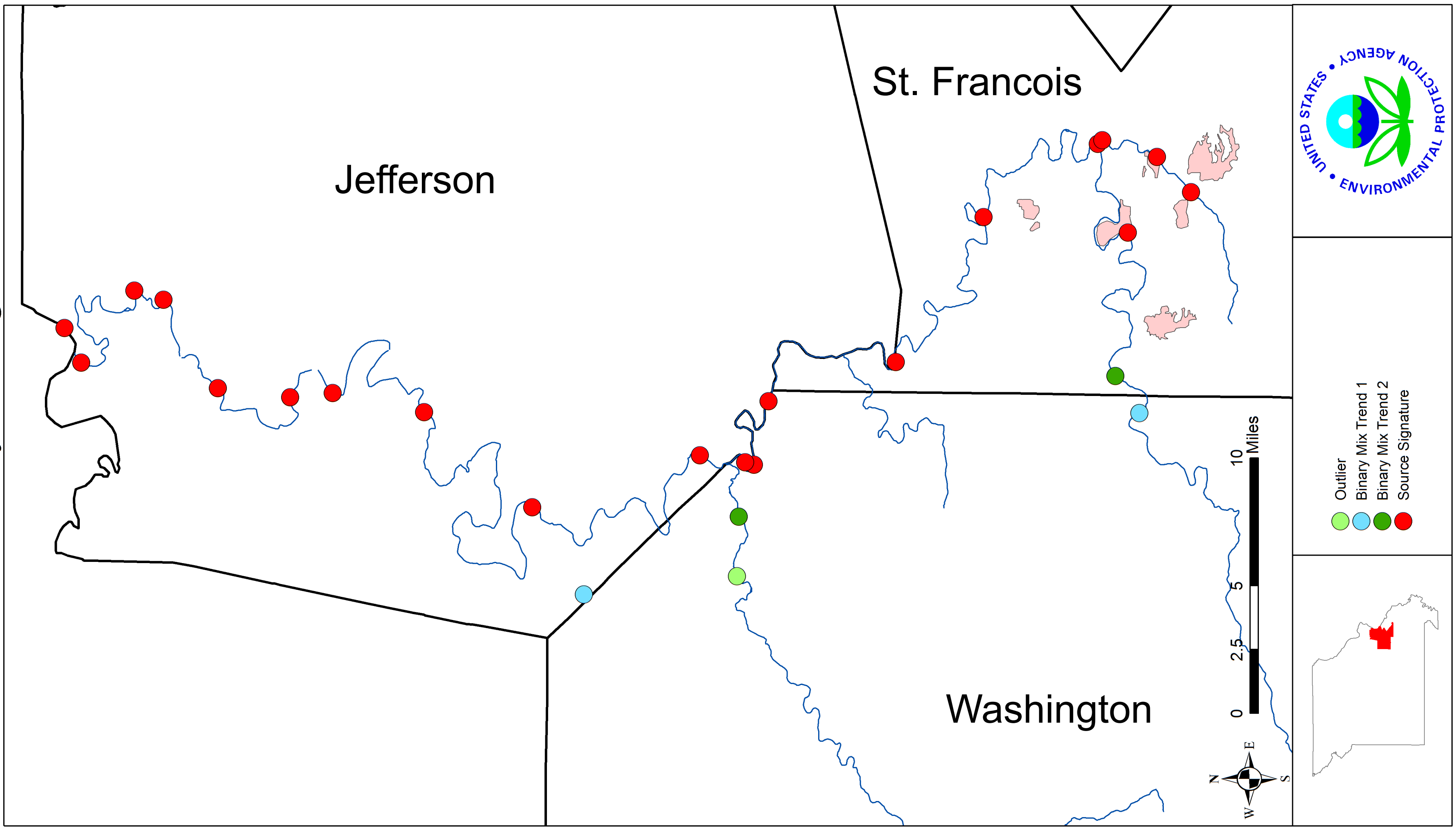
Collected sediment and soil samples were subjected to Pb isotopic analysis and shown here via binary mixing of $^{206}Pb/^{207}Pb$ vs 1/[Pb] concentration. Four groups are identified as 1) source, soil and sediment samples, 2&3) potential second source and background samples (indistinguishable), and 4) one outlier.

Pb Isotopes - Environmental Forensics



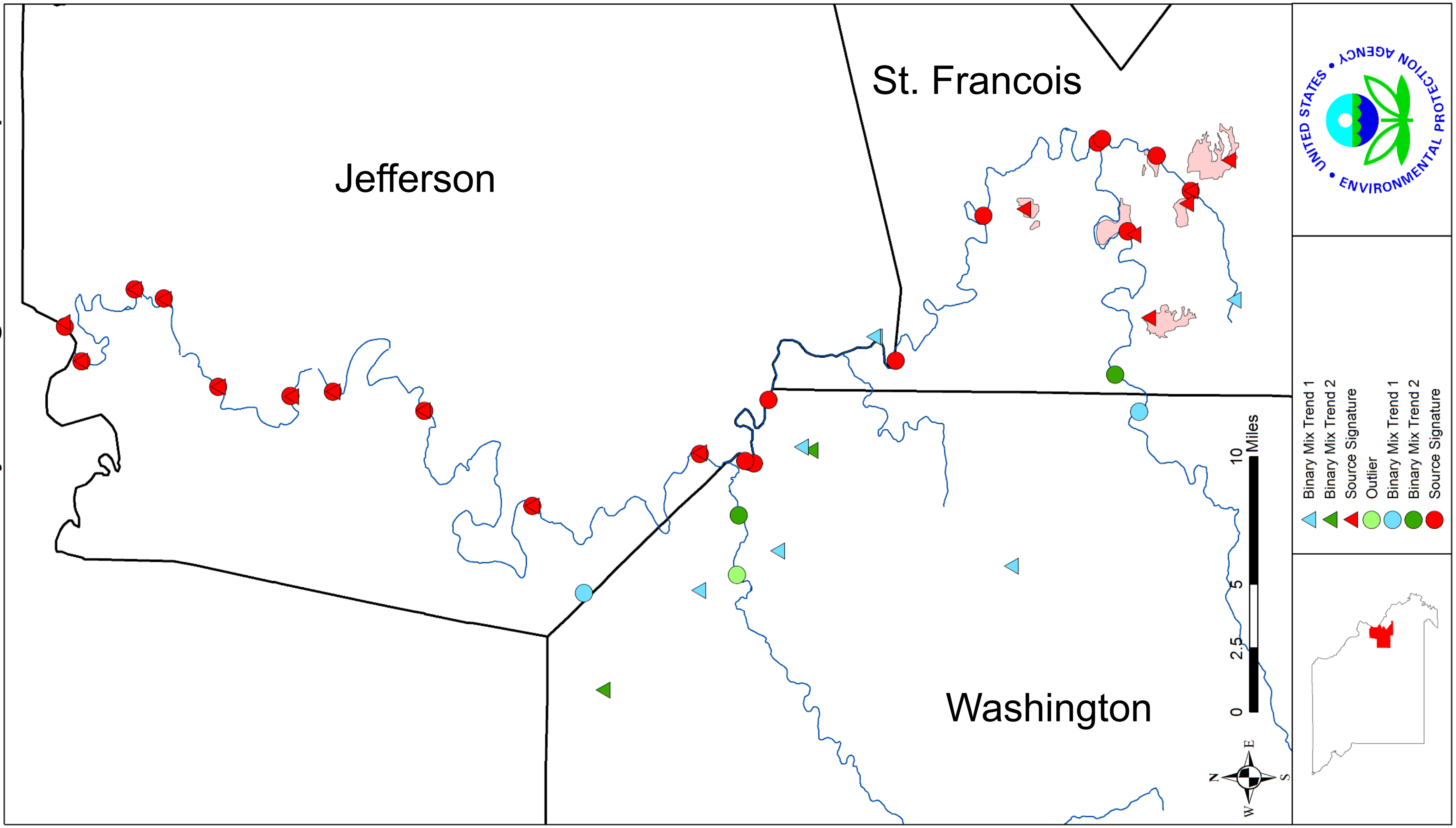
Pb Isotopes - Environmental Forensics

$^{206}Pb/^{207}Pb$ Binary Mixing -- Sediment



Pb Isotopes - Environmental Forensics

$^{206}Pb/^{207}Pb$ Binary Mixing -- All Samples



Conclusions

The source of Pb contamination and the risk of Pb contamination must be considered at two distinct issues

Source Attribution

- Pb Isotopes

Where did the Pb come from?

- Examine ratios of 4 common Pb isotopes from source material, background, and suspected impacted samples
- Isotopic ratios do not change over time

‘Genetics’

Exposure Risk

- Pb Speciation

Form of Pb drives risk. Solubility linked to speciation of Pb.

Form of Pb is environmental driven – can change over time. A snapshot of current conditions.

‘Fingerprints’

Questions?

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