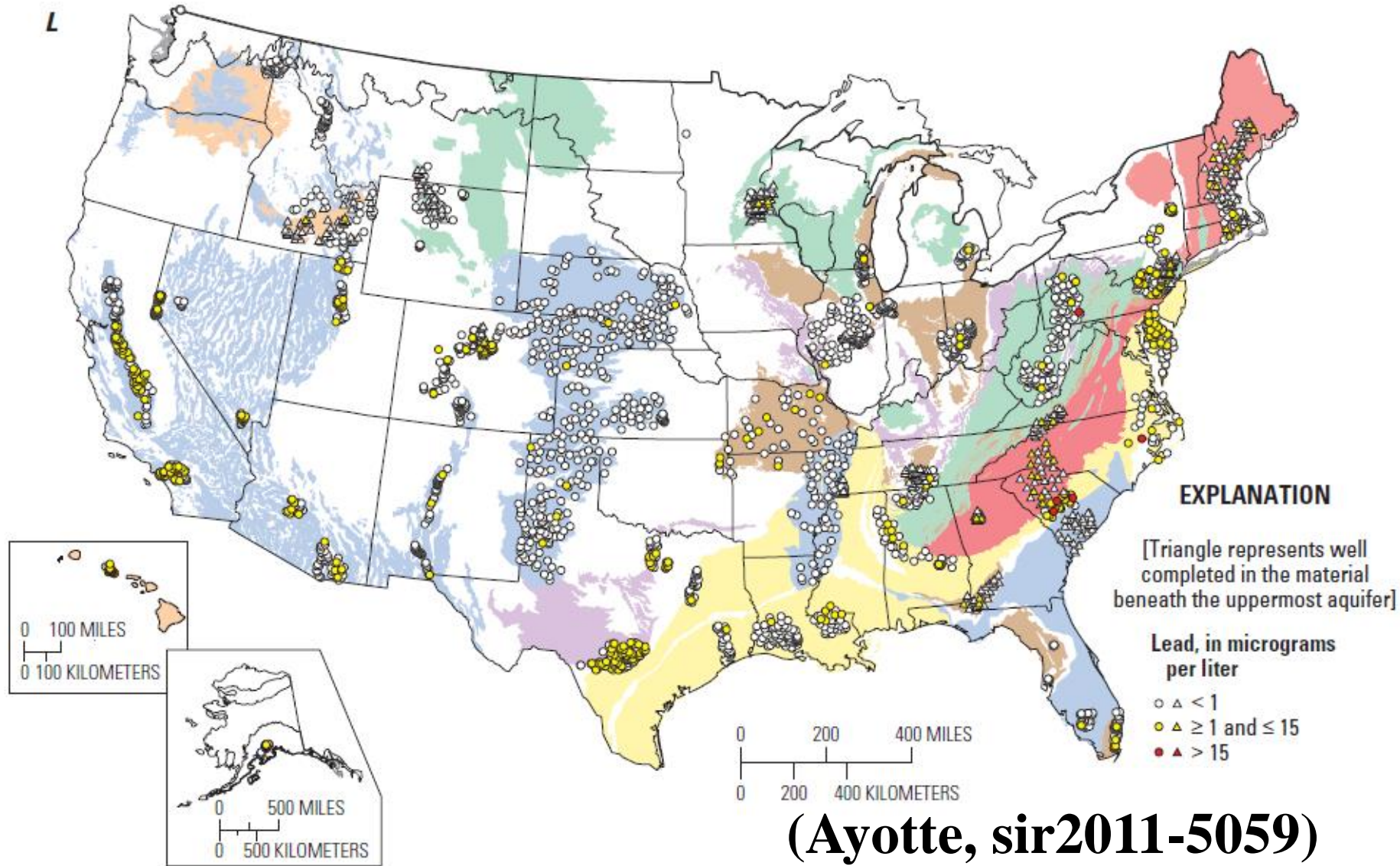


12. Lead, Pb (atomic no. 82)

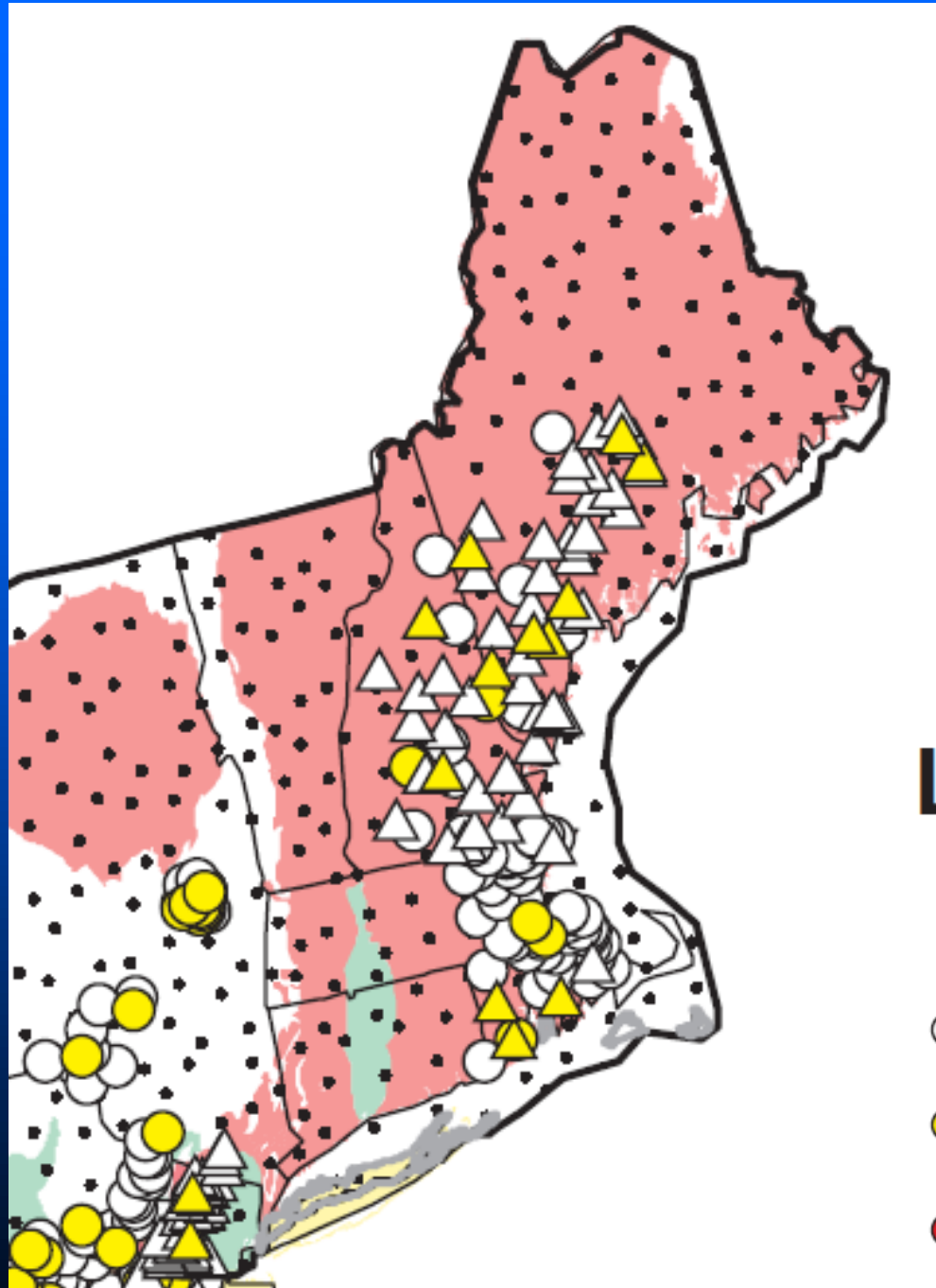
- Sources of Pb contamination include mining, metal processing, lead battery manufacturing, chemical and paint manufacturing, and lead wastes.
- USEPA drinking water action level for Pb is 15 ug/L.



Geographic distribution of Lead concentrations in groundwater collected from wells as part of the National Water-Quality Assessment Program, 1992–2003

Concentrations in Groundwater, (Ayotte, *sr2011-5059*)

[Triangle represents well
completed in the material
beneath the uppermost aquifer]



**Lead, in micrograms
per liter**

○ △ < 1

● ▲ ≥ 1 and ≤ 15

● ▲ > 15

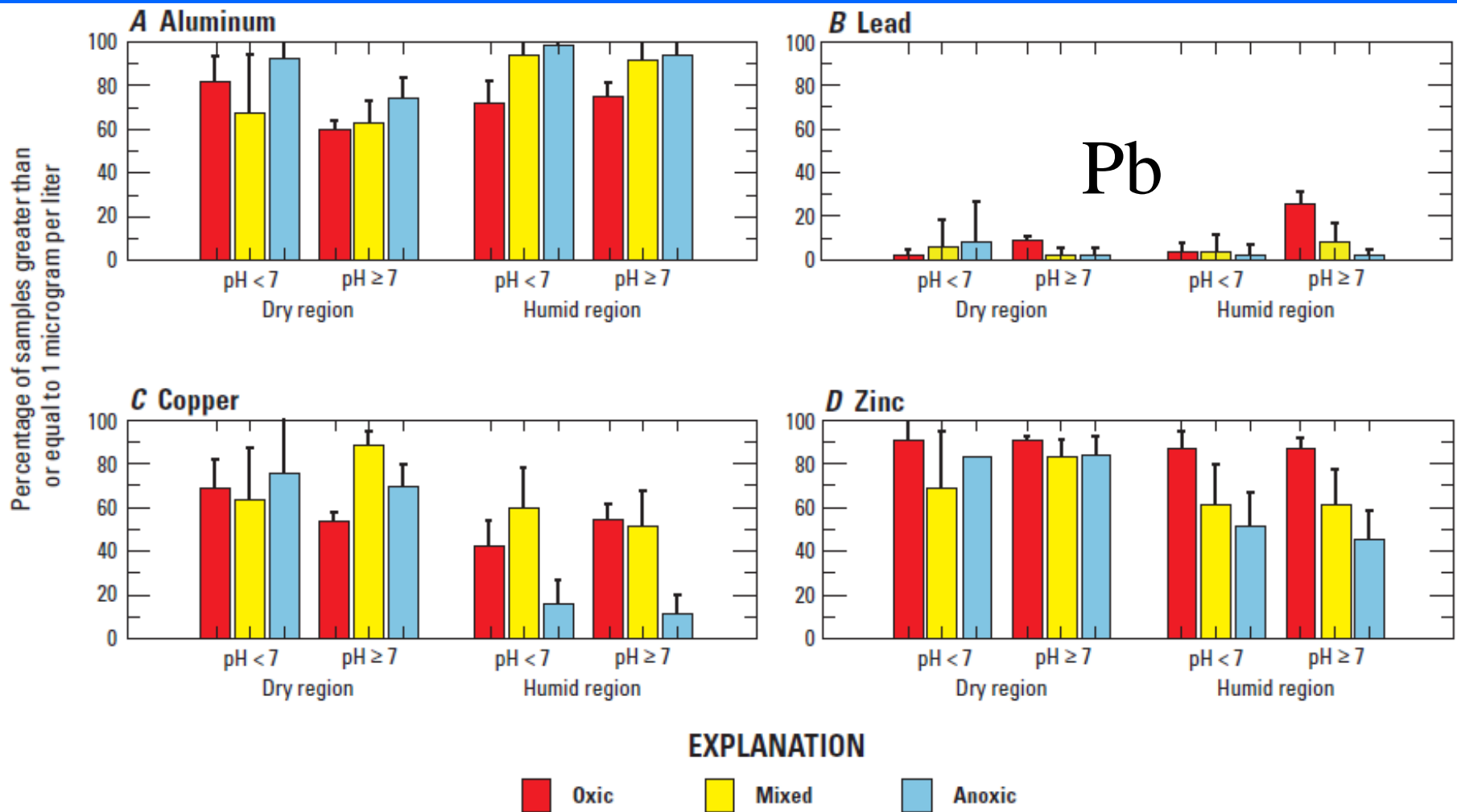
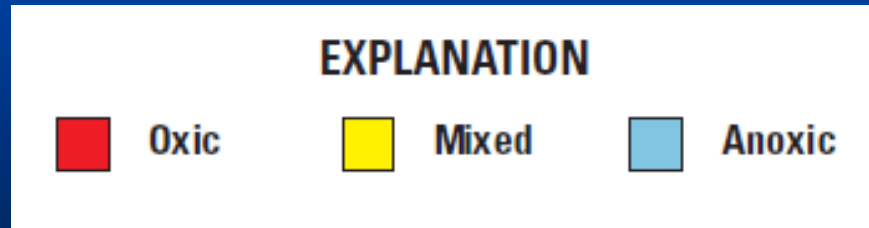
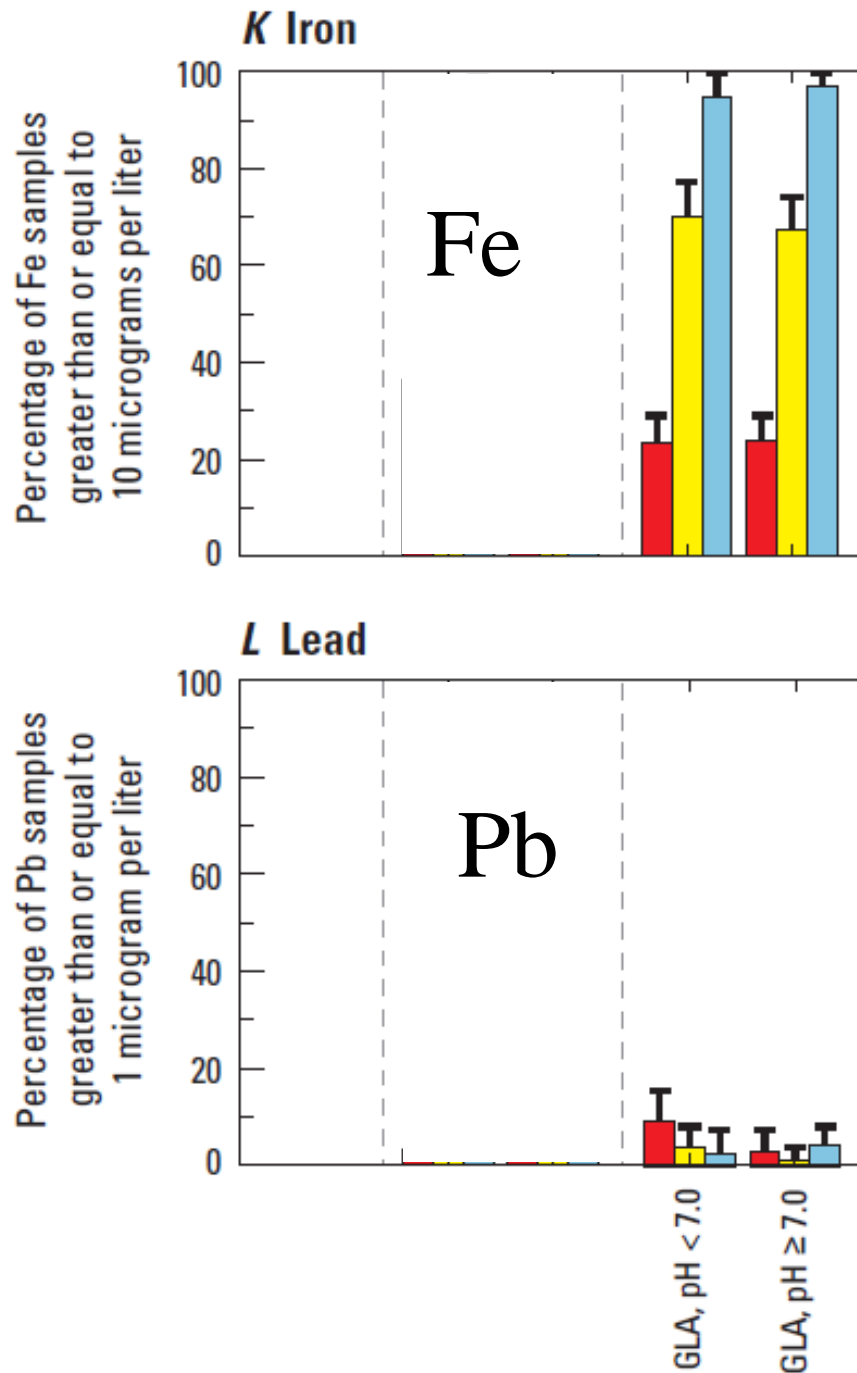


Figure 10. The percentages of groundwater samples with trace-element concentrations greater than or equal to 1 microgram per liter for (A) aluminum, (B) lead, (C) copper, and (D) zinc in dry- and humid-region unconsolidated sand and gravel aquifers. Error bars represent the 95-percent confidence interval of the mean (binomial distribution). <, less than; ≥, greater than or equal to.

Pb vs Fe



Pb Aqueous Complexes

- In pure water, Pb is mainly present as Pb^{2+} below a pH of about 7; with increasing pH, the species PbOH^+ , $\text{Pb}(\text{OH})_2$, and $\text{Pb}(\text{OH})_3^-$ are dominant over Pb^{2+} (see fig. 2.1 below).
- Low solubility compounds are formed by complexation with carbonate (PbCO_3 , $\text{Pb}(\text{CO}_3)_2^{2-}$), chloride (PbCl^+ , PbCl_2), sulfate (PbSO_4 , $\text{Pb}(\text{SO}_4)_2^{2-}$), and sulfide complexes (PbHS^+ , Pb_2S_2 (see fig. 2.2 below).

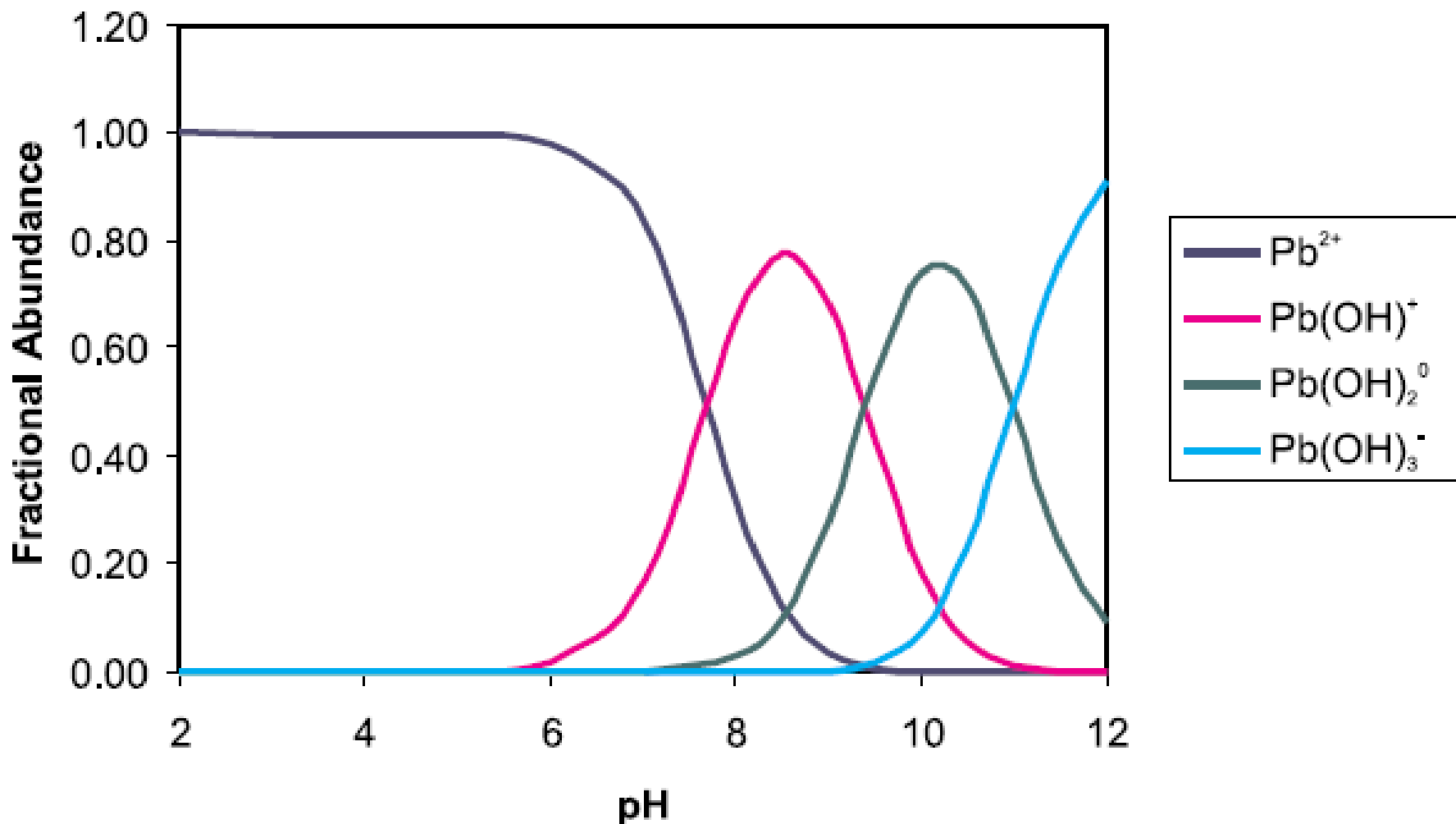


Figure 2.1 *Pb(II) species distribution in pure water at 25 °C.*

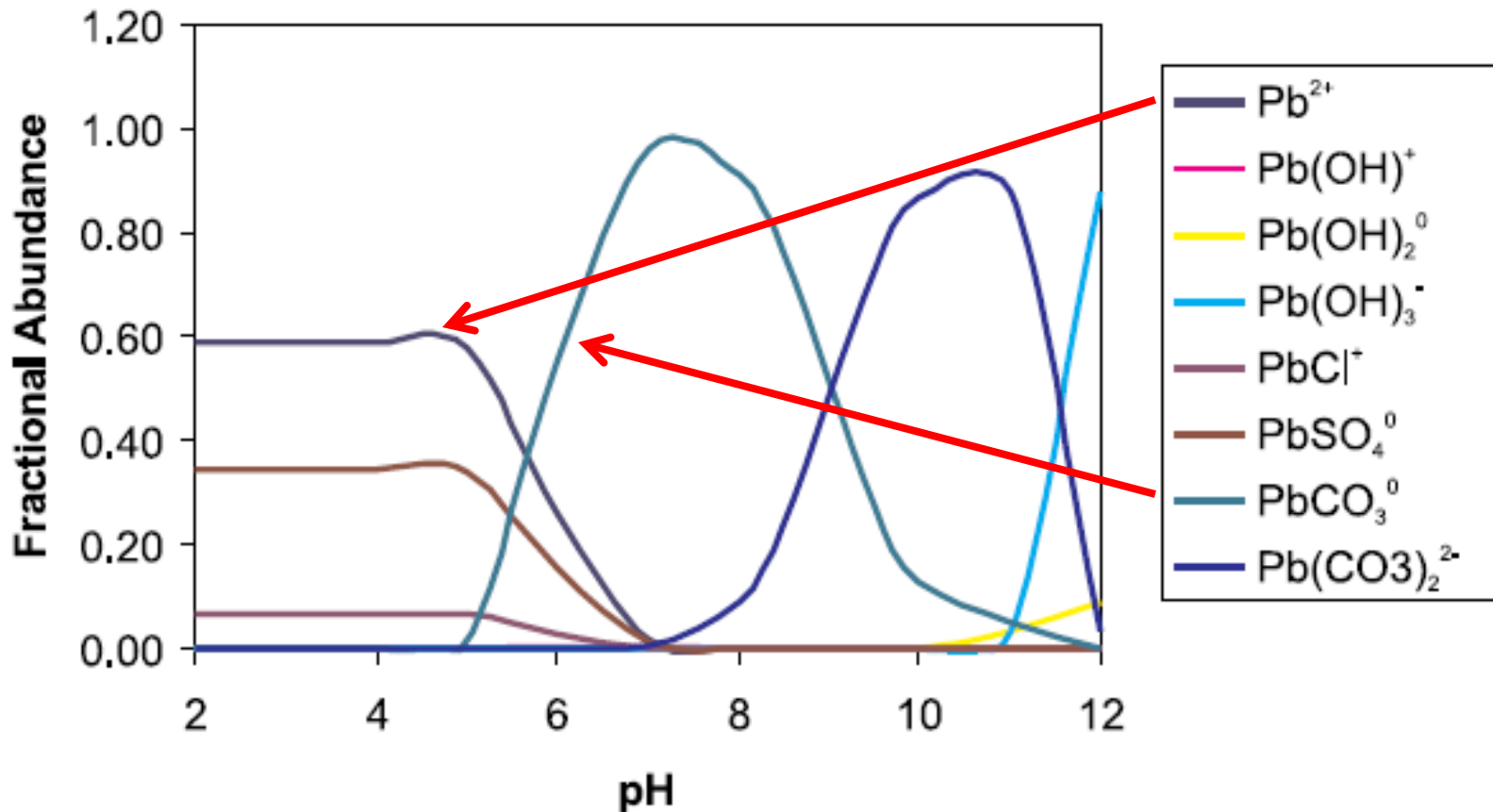
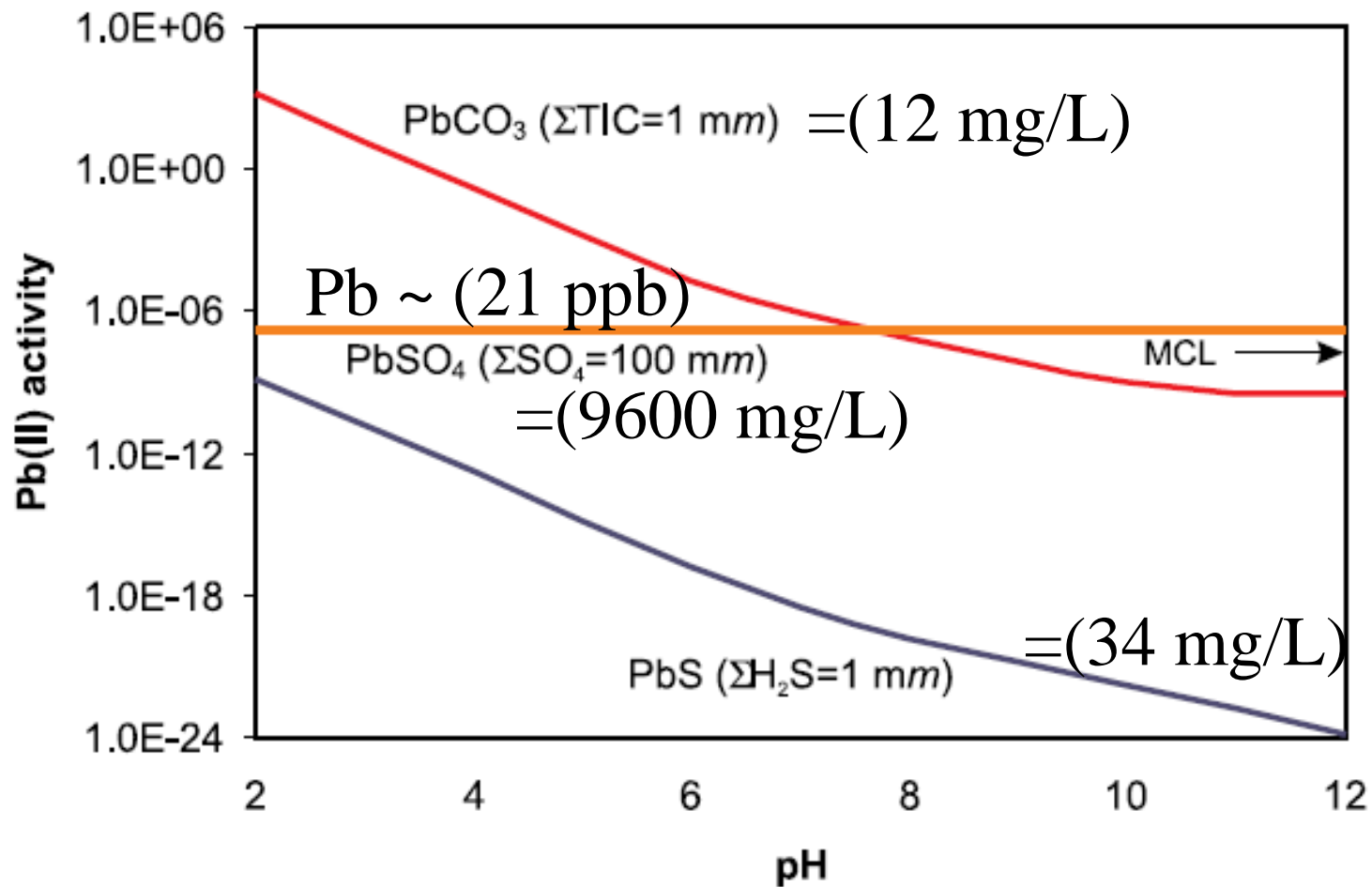


Figure 2.2 *Species distribution of lead in solution with 100 mg L⁻¹ chloride, 100 mg L⁻¹ sulfate, and 100 mg L⁻¹ total inorganic carbon, based on thermodynamic data in MINTQA2 (Allison et al., 1990).*

Pb Solubility

- In surface and ground-water systems, most Pb is undissolved and occurs as precipitates (PbCO_3 , Pb_2O , $\text{Pb}(\text{OH})_2$, PbSO_4), adsorbed ions, or coatings on minerals, or as suspended organic matter.
- Solubility calculations show Pb carbonates can keep the dissolved-lead concentration below about 50 $\mu\text{g/L}$ (10^{-12}) in water with 61 mg/L HCO_3^- and pH 7.5 - 8.5.
- **Pb is strongly retained in soils, and in most situations very little Pb is transported to surface waters or ground water. Exceptions to this behavior are low pH systems or environments with high concentrations of DOC.**

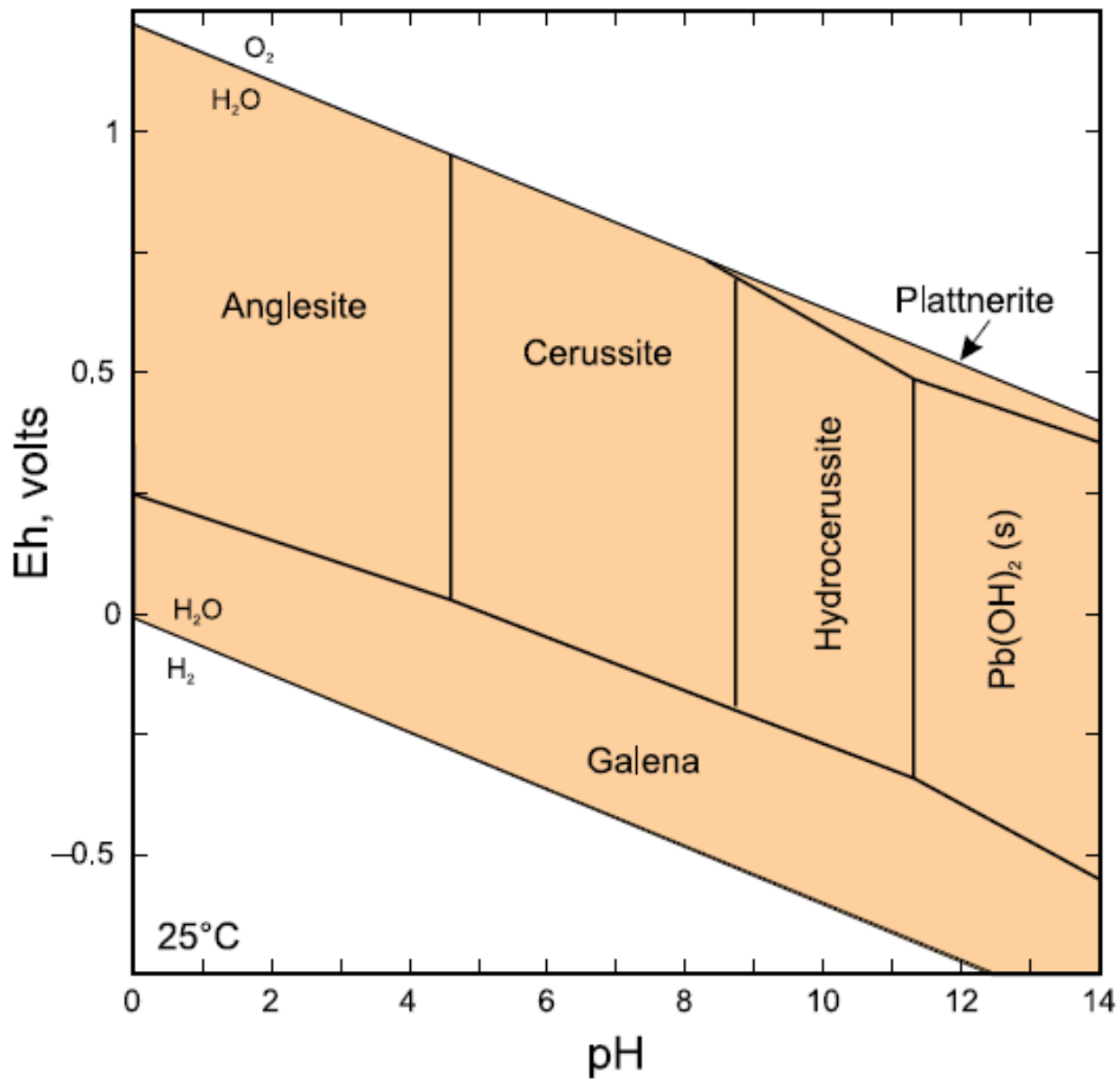


U.S. EPA, 2007b

Figure 2.4 *Pb(II) activity in equilibrium with PbCO_3 (at total inorganic carbon equal to 0.001 molal), PbSO_4 (at total sulfate equal to 0.1 molal), and PbS (at total sulfide equal to 0.001*

Pb Redox Chemistry

- Pb occurs in natural systems in the +2 oxidation state over relevant conditions of pH and oxidation-reduction potential.
- **A Eh-pH diagram for Pb indicates** that, under the specified conditions, **Pb is stable in solids** across the stability field of liquid water (fig. 2.3).
- At low pH and oxidizing conditions, Pb sulfate is stable, near-neutral to moderately alkaline pH, Pb carbonates are stable, and at $\text{pH} > 12.5$ Pb hydroxide is stable.
- In sulfidic environments, Pb sulfide (galena) is stable over a wide pH range.
- The Pb(IV) mineral phase, (plattnerite), is stable at higher pH and highly oxidizing redox potentials.



U.S. EPA, 2007b

note:
pink
indicates
solid
phase;
at these
molar
levels, the
solid
phases
dominates:
Pb = 2 mg/L
C = 12 mg/L
S = 32 mg/L

Figure 2.3 Eh-pH diagram for lead (total Pb = 10^{-5} molal, total C = 10^{-3} molal, total S = 10^{-3} molal);

Pb Redox Chemistry contd.

- In general, the geochemical transport processes of lead are not directly tied to redox conditions.
- However, because lead may form stable precipitates with redox-sensitive elements such as sulfur, lead mobility is indirectly tied to redox conditions.
- In sulfate-reducing systems, lead is expected to form insoluble PbS precipitates.
- In moderately reducing but non-sulfidic systems, however, reductive dissolution of hydrous ferric oxides that contain adsorbed lead could result in lead mobilization.

Pb Adsorption

- Adsorption of Pb on mineral surfaces results from chemical reactions that involve the release of H^+ ions, which accounts for the strong dependence of Pb adsorption on pH, increasing with increased pH.
- Pb adsorption onto the soil is fast and reversible on the time-scale of transport.
- Pb adsorbs more strongly onto ferric-hydroxide compared to most other divalent metal ions; the same is true for other ferric oxides, aluminum oxides, oxyhydroxides, and clay minerals.
- Lead adsorption onto or co-precipitation with amorphous FeS may be extensive in reducing systems.

Colloidal Transport

- Colloidal particles ($<10^{-6}$ m) can be significant forms of Pb transport in surface and ground water systems.
- For the special case of lead sorbed to colloidal hydrous ferric oxides, changes in geochemical regimes may either favor increased lead sorption or desorption.
- Increases in lead sorption may result from increases in pH or Eh; alternatively, decreases in pH or Eh may result in lead remobilization.

Cape Cod

Lead Tracer Tests: Objectives

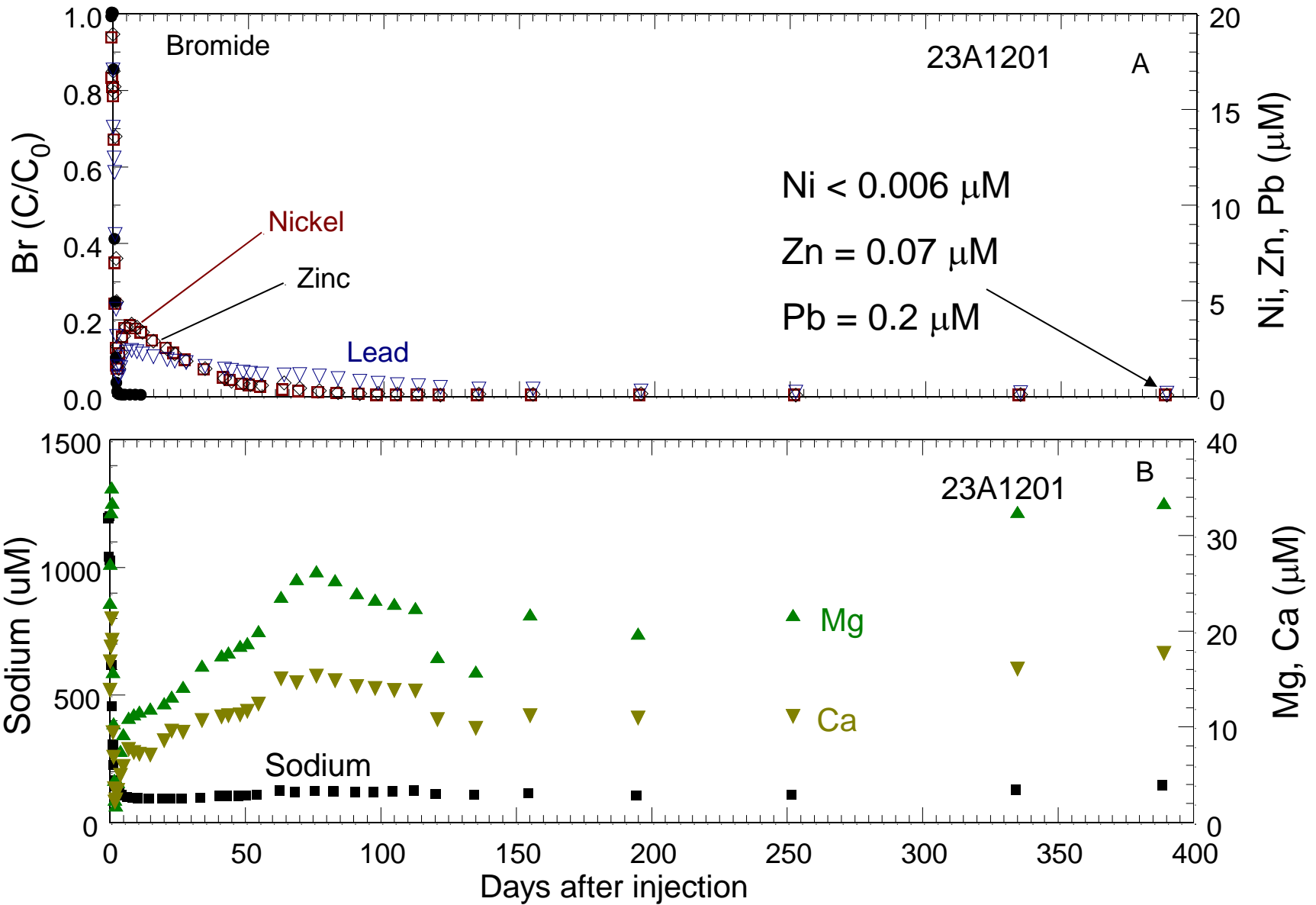
D. Kent, PC

- Examine lead mobility relative to nickel and zinc over the range of applicable chemical conditions
- Examine reversibility of lead adsorption
- Practical: lead adsorbs so strongly it is unlikely to move fast enough to detect downgradient from the injection well

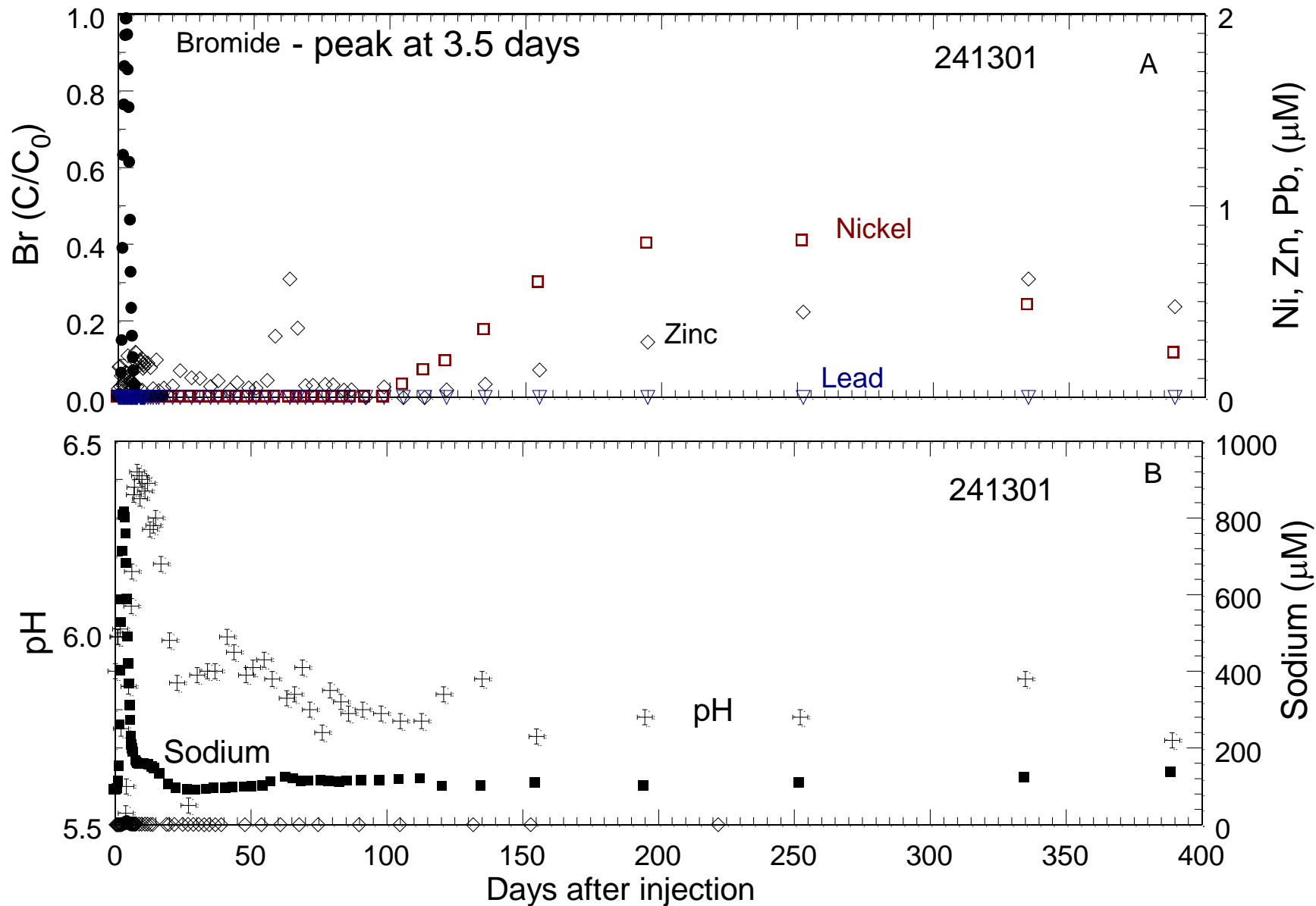
Tracer test details

- 200 liters of groundwater from injection zone
- Ni, Zn, Pb at 20 μM (4 mg/L Pb)
- Groundwater at pH 6
- Add metals as nitrate salts
- Also NaBr + $\text{B}(\text{OH})_3$ as nonreactive tracers
- Selected experiments: after about 1 year, inject EDTA to determine whether metals remaining on sediments can be desorbed

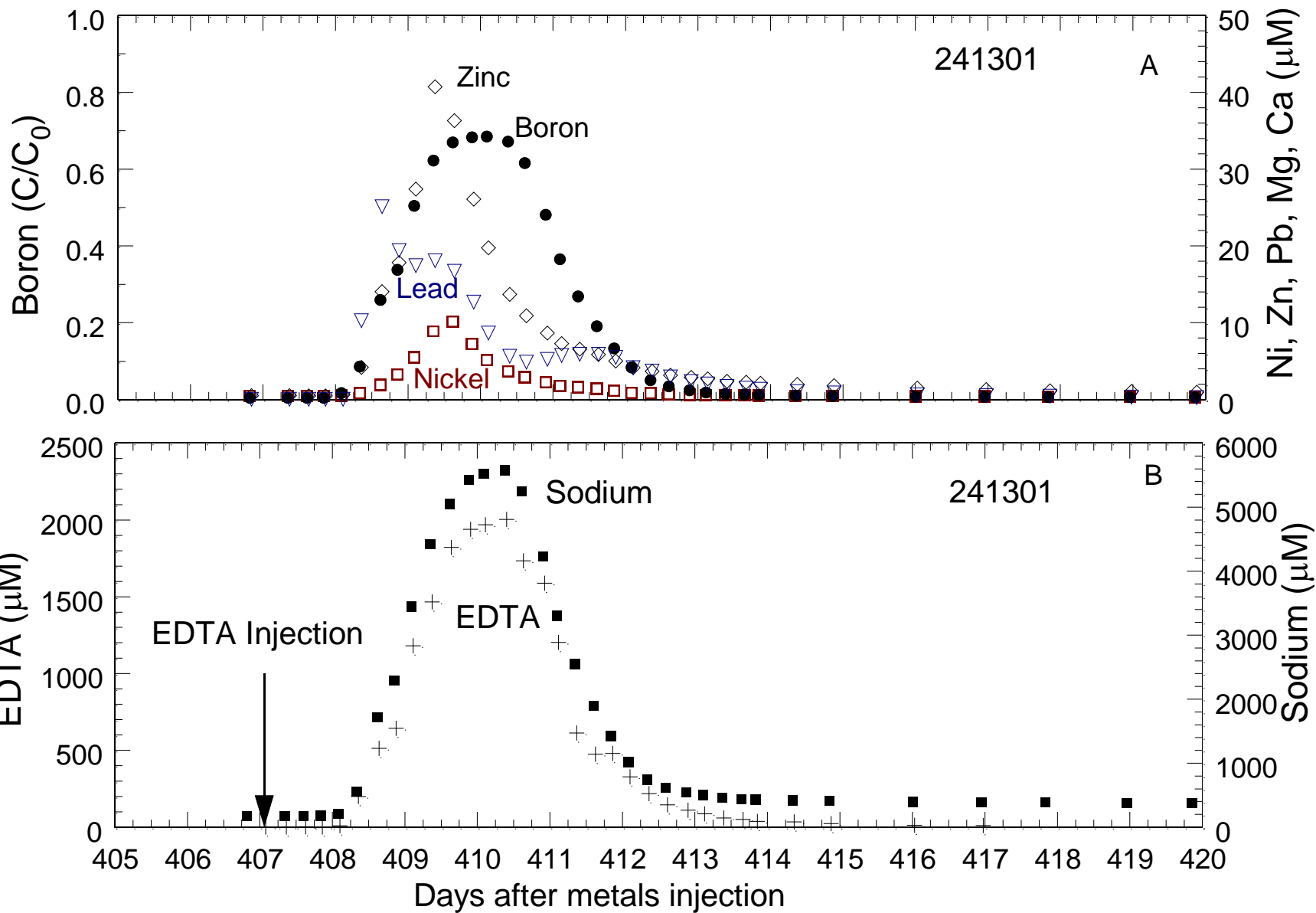
Time-series at injection port, pH 5.9 20 μM



Down-Gradient BTC 1.4 m, pH 5.9 20 μM



BTC 1.4 m, pH 5.9 20 μM



Multispecies reactive tracer test in an aquifer with spatially variable chemical conditions

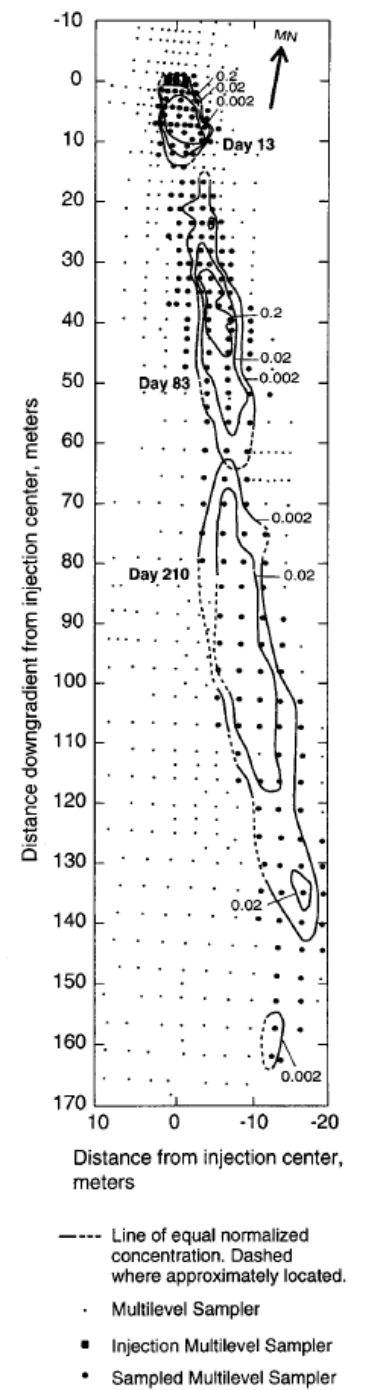
Davis, et al., 2000

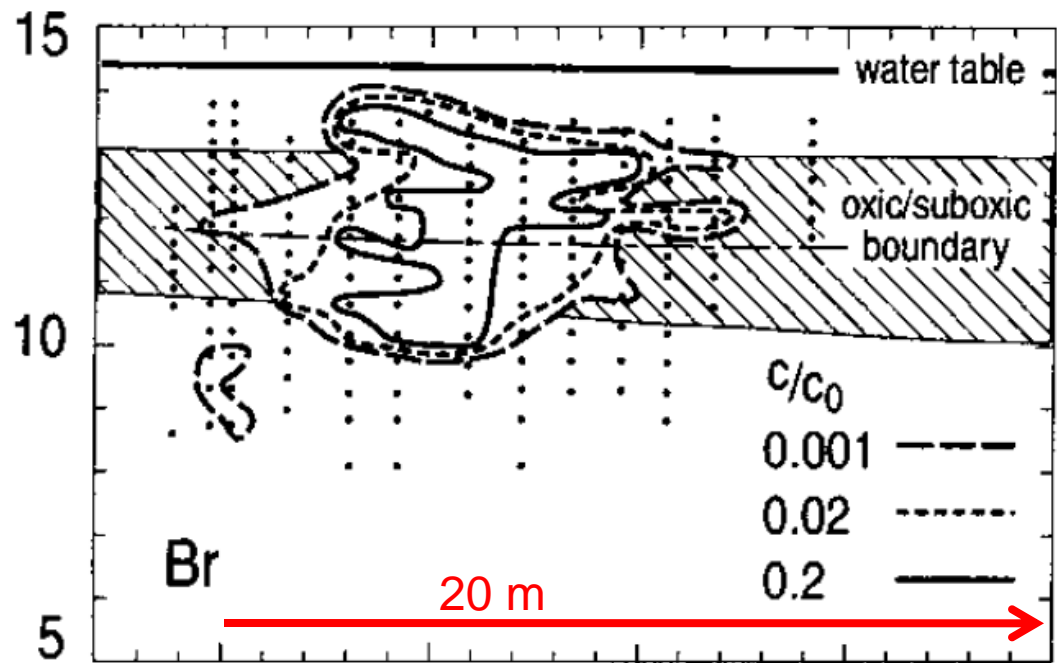
- A large-scale tracer test of multispecies reactive transport conducted in a sand and gravel aquifer on Cape Cod, MA.
- The aquifer is characterized by regions of differing chemical conditions caused by the disposal of secondary sewage effluent.
- Ten thousand liters of groundwater with added tracers (Br, Cr(VI), and EDTA complexed with **Pb**, Zn, Cu, and Ni) were injected into the aquifer and distributions of the tracers were monitored for 15 months.

Table 1. Description of Tracers and Injection

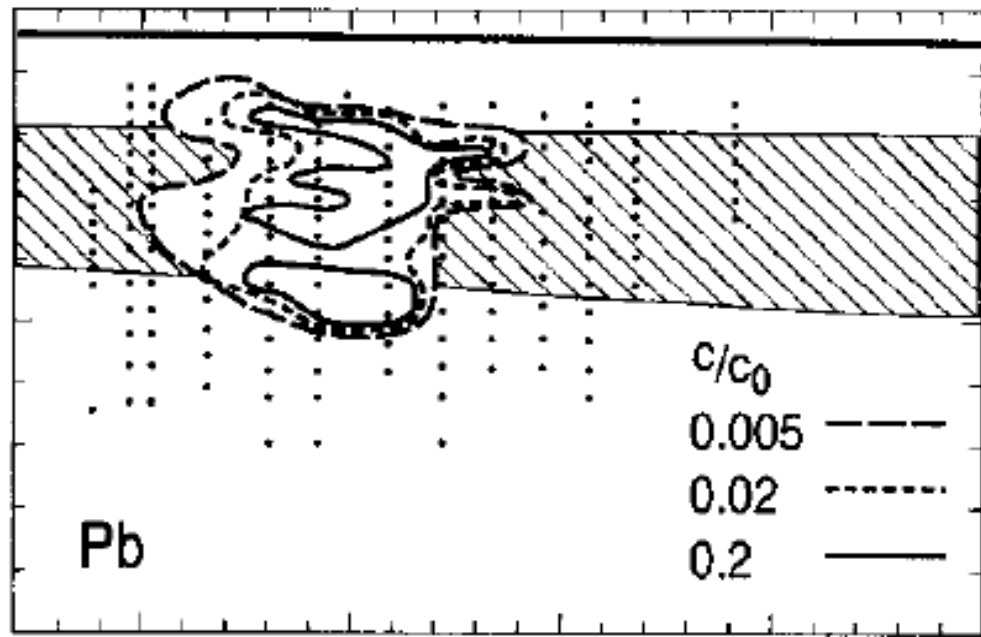
Constituent	Concentration	Reagent	Concentration/DL*
Br ⁻	3.43 mM	KBr	1140
CrO ₄ ²⁻	0.506 mM	K ₂ Cr ₂ O ₇	2660
EDTA ⁴⁻	1.112 mM	Na ₄ EDTA	140
Cu	0.266 mM	CuCl ₂ · 6H ₂ O	4220
Ni	0.256 mM	NiCl ₂ · 6H ₂ O	500
Pb	0.248 mM	Pb(NO ₃) ₂ · 6H ₂ O	520
Zn	0.266 mM	ZnCl ₂ · 6H ₂ O	1770
pH	5.6

Br distributions 13, 83, and 210 days after injection

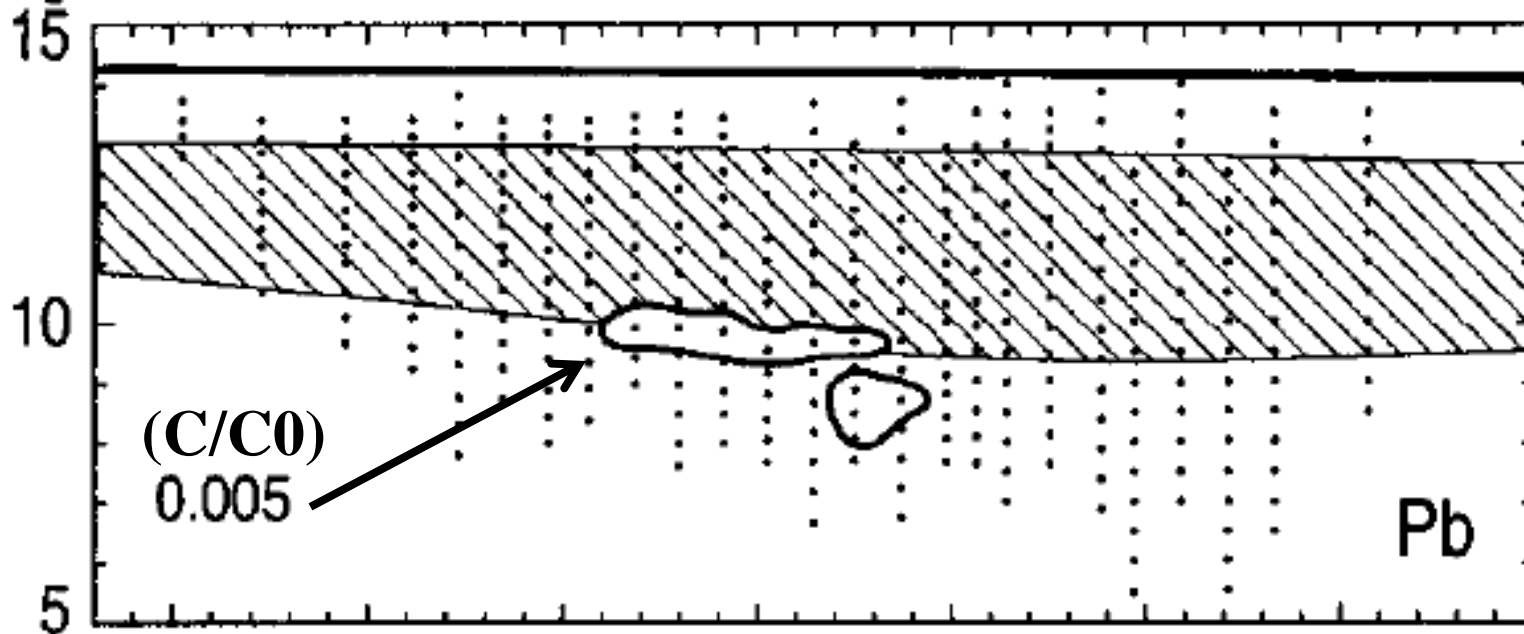
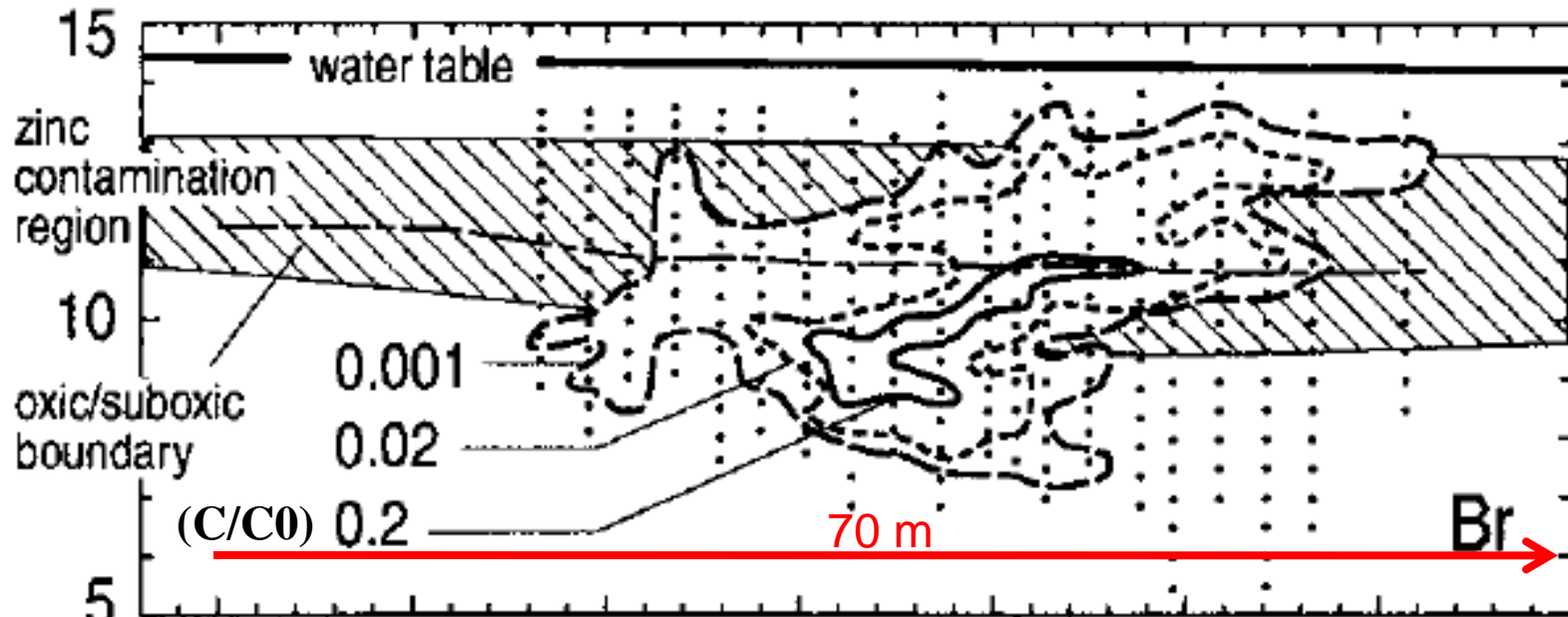


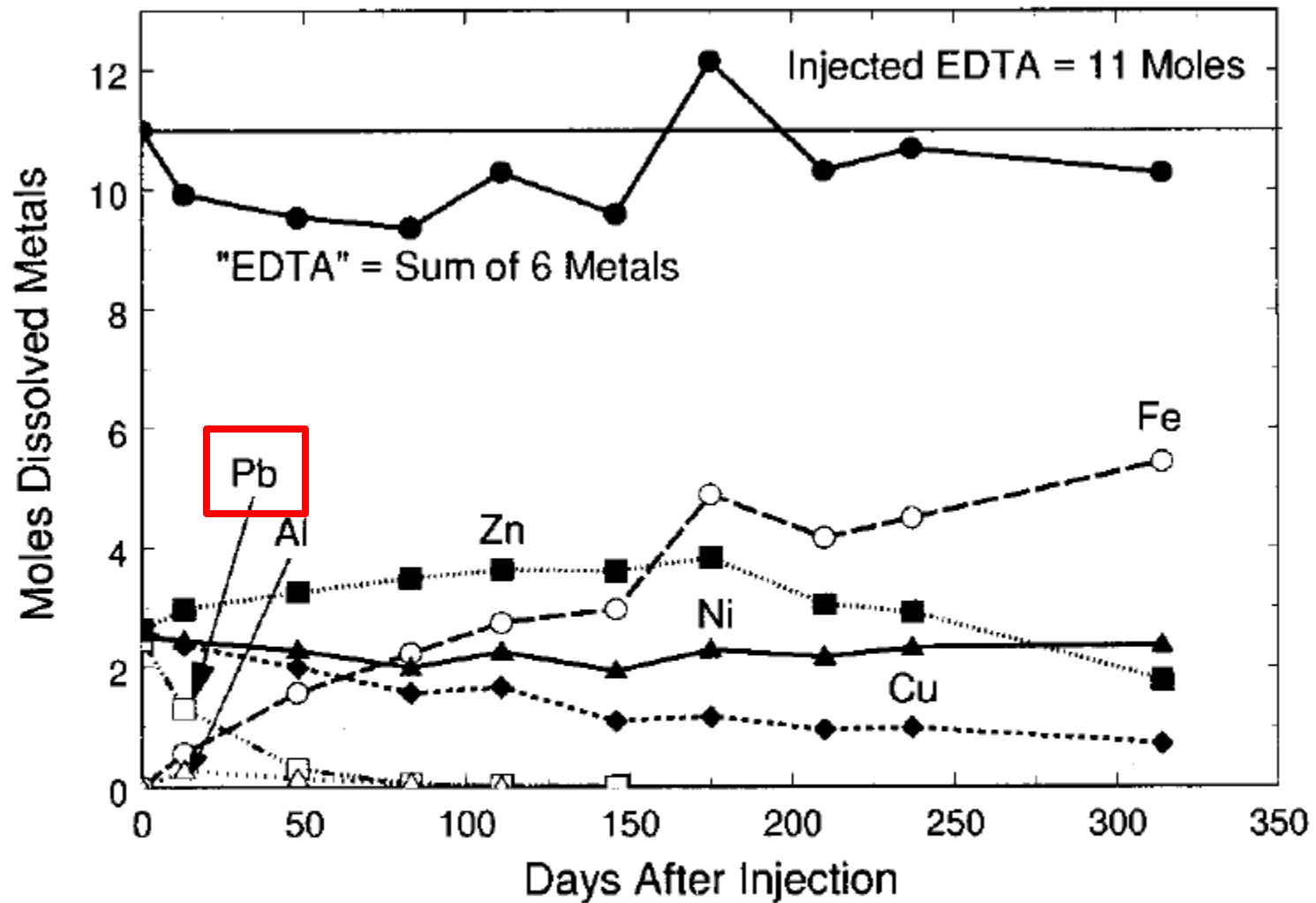


Longitudinal cross sections of Br and Pb at 13 days after injection



Longitudinal cross sections of Br and Pb, 83 days after injection





Dissolved mass of Ni, **Pb**, Cu, Zn, Fe,
and Al in the tracer cloud over time;
estimated EDTA

Conclusions

- Dissolved Pb mass significantly decreased as the tracer cloud moved down-gradient.
- Pb^{2+} formed by metal-exchange reactions would likely be strongly adsorbed onto the porous medium at the pH values present in the aquifer, resulting in the observed decreases in the dissolved mass of Pb.
- Pb was likely displaced from EDTA complexes by Zn and Fe(III) dissolved from aquifer sediments over short transport distances.
- Pb concentrations in all samples were below the detection limit beyond 40 m (130 ft) of travel.

Fate of Pb in a strongly acidic shooting-range soil: Small-scale metal distribution and its relation to preferential water flow

by Lars A. Knechtenhofer et. al.

The mobility of **Pb in a highly contaminated shooting range** soil (Losone, Ticino, Switzerland), was investigated relative to preferential water flow paths. A 2.2 m² plot located 40m behind the stop butt was irrigated with a solution containing bromide and Brilliant Blue, a slightly sorbing dye. A soil profile 50 cm in width was sampled down to 80 cm with a spatial resolution of 2.5 cm, resulting in 626 samples. **The soil is acidic (pH 3)** and organic matter-rich; maximum concentrations of **80.9 g/kg Pb** were measured in the soil.

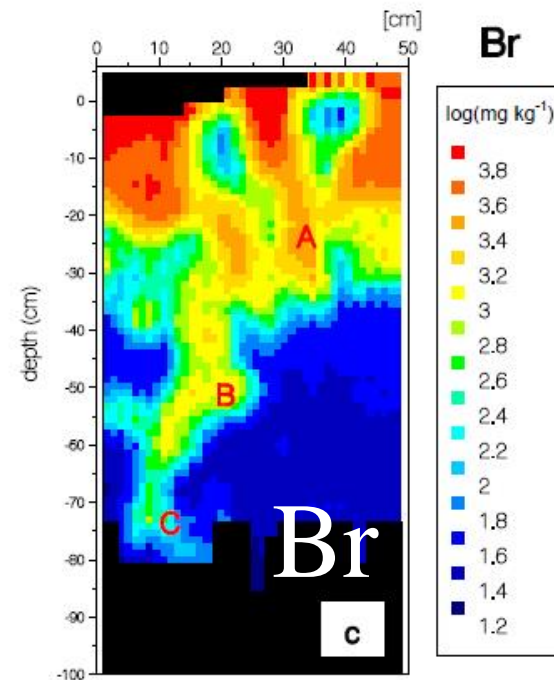
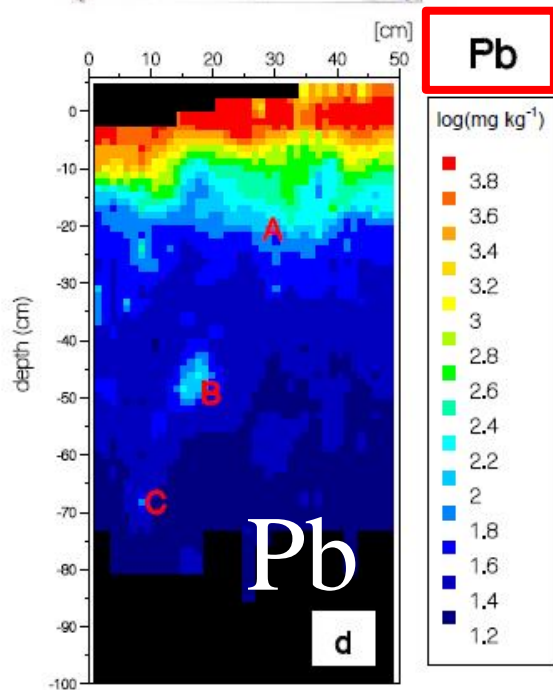
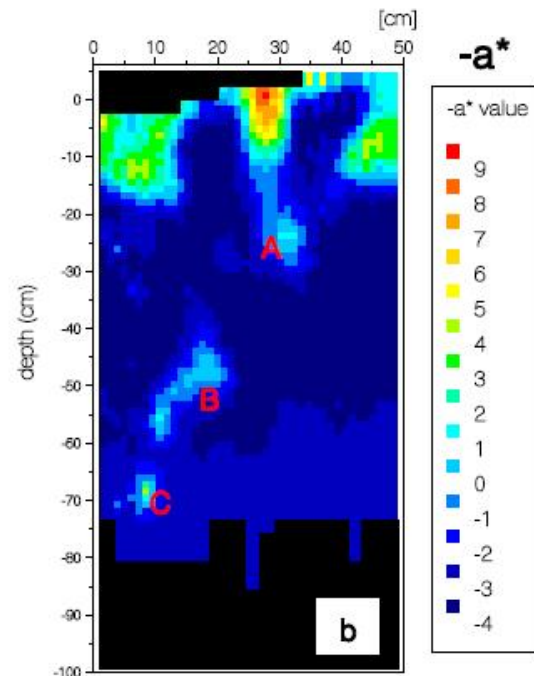
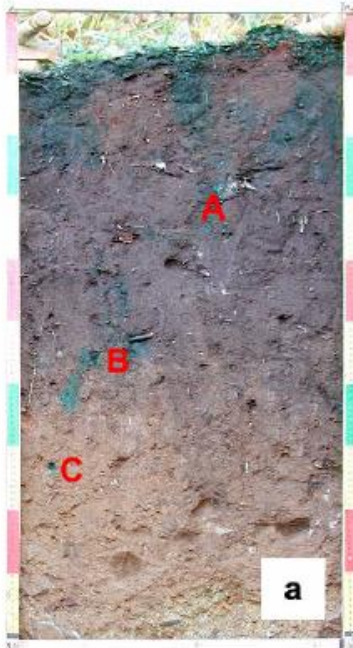


Figure 1: (a) Photograph of the sampled soil profile with water infiltration and transport paths stained with Brilliant Blue. (b) Two-dimensional distribution of Brilliant Blue (expressed as greenness color coordinate, $-a^*$), (c) Br and (d) Pb.

log c (mg/kg)

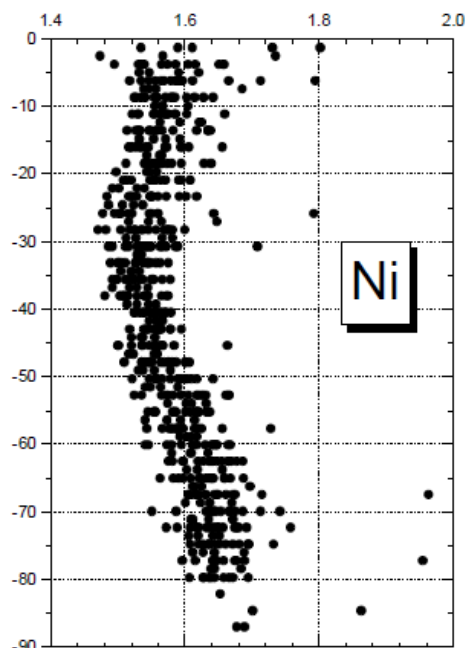
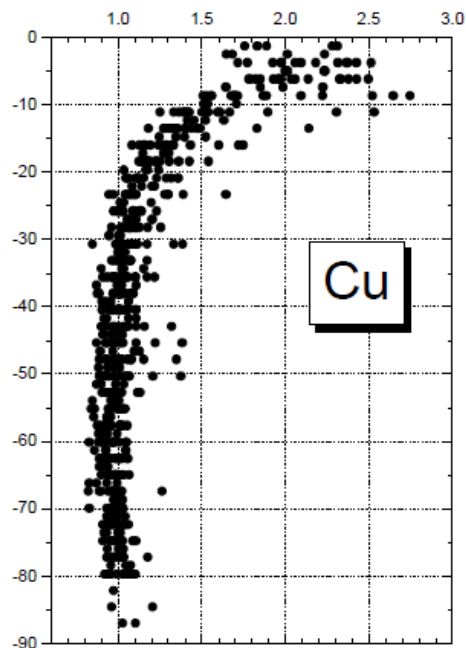
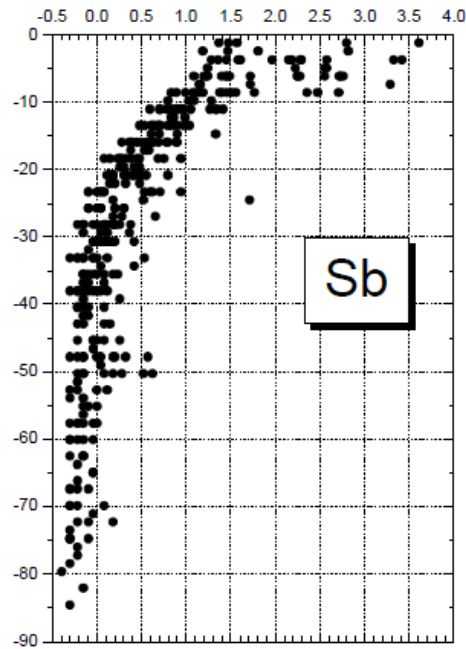
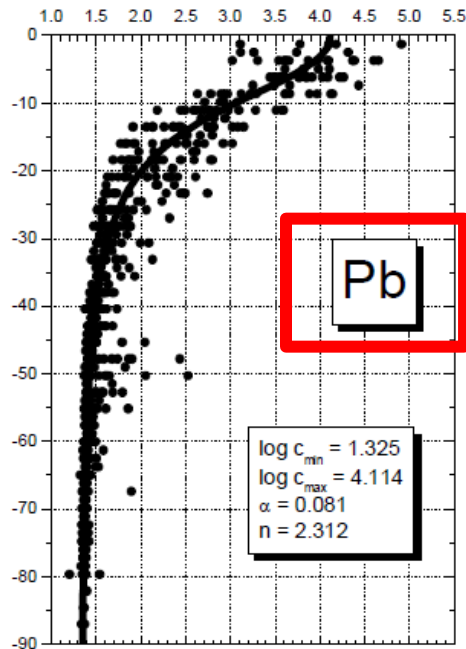


Figure 2: Depth profiles of log-transformed concentrations of **Pb**, Sb, Cu and Ni displaying all values of the grid sampling ($n = 626$).

Attenuation and Mobilization for Lead

Table 2.1 Natural attenuation and mobilization pathways for lead.

Attenuation Processes	Mobilization Processes
<p>Precipitation of insoluble carbonates, sulfides, sulfates, and phosphates. In general, $\text{pH} > 8$ will drive precipitation reactions resulting in Pb concentrations to below the MCL.</p>	<p>Dissolution of carbonates at low pH; oxidative dissolution of sulfides at low pH and high Eh; complexation/stabilization in the presence of DOC.</p>
<p>Sorption to iron hydroxides (reversible), organic matter, carbonates, sulfides ($\text{pH} > 5$).</p>	<p>Desorption at low pH; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides.</p>

USEPA, 2007b

Summary

- The fate of lead in the subsurface is controlled principally by adsorption at the solid-water interface, precipitation, and complexation with organic matter.
- These processes limit the amount of lead that can be transported into/by surface water or groundwater.
- Most Pb released to the environment is retained in the soil.

Next:

Mercury, Hg