

# Geochemical Landscapes - Continental-Scale Pilot Study

# Background

- GSC senior management approached at Tri-National Geological Surveys meeting, November 1999, to collaborate in a continental-scale project to provide geochemical data to support risk assessment and management activities concerning soils
- Planning workshop, Denver, October 2002
- Stakeholder Workshop to further discuss concept, Denver, March 2003, 112 attendees from 40 government agencies, academia, consultancies and the medical community from all three countries
- Fieldwork planning workshop, UC-Davis, March 2004  
– continental transects and a detailed regional-scale Sierras-to-Pacific study (USGS only)
- US and Canadian pilot study transects sampled summer-fall 2004

# Purposes of continental-scale transects pilot study

- Optimize field logistics
- Test/refine sampling protocols across large gradients of climate and topography
- Test/refine analytical techniques
- Estimate geochemical and microbiological variations at continental scale
- Develop short-term products to aid in advancement of full North American survey

# Sample types collected at each site

- 0-5 cm (265 samples)
  - Separate sample for organic compounds
- O-horizon (38 samples)
- A-horizon (244 samples)
  - Separate samples (2) for microbial characterization
- C-horizon or closest approximation (258 samples)
- Forest litter (17 samples—not analyzed)
- Total of 1558 samples collected from 265 sites

# Sample Analyses

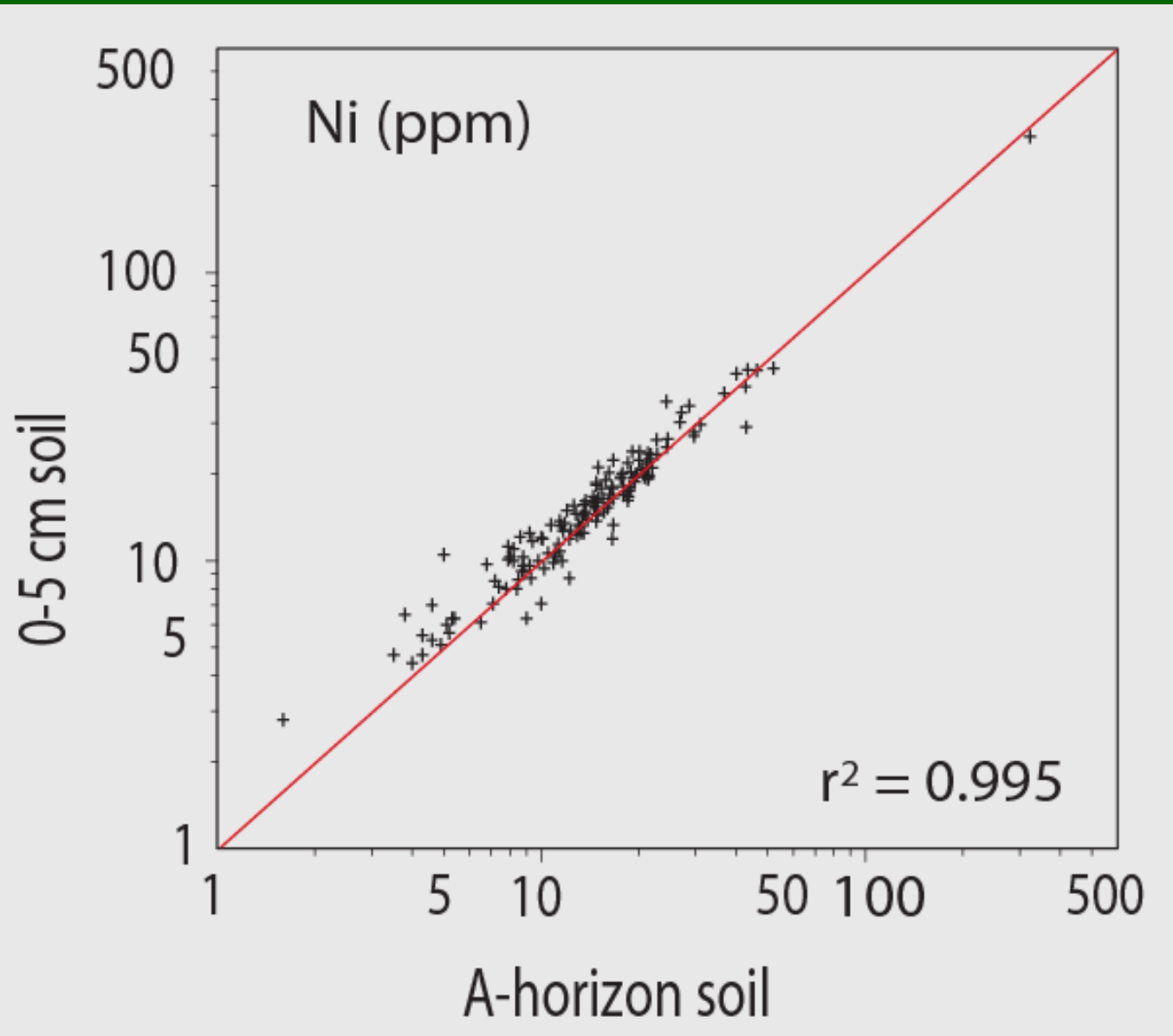
- Near-total extraction for 42 major and trace elements (ICP-MS/ICP-AES) – USGS
- Forms of carbon, total sulfur – USGS
- Water extraction (A-horizon) – GSC
- Gastric fluid extraction (0-5 cm) – USGS
- Gamma-ray spectrometry – GSC
- Phospholipid fatty acid analysis – University of California at Davis
- Enzyme assays – Oregon State /Ohio State



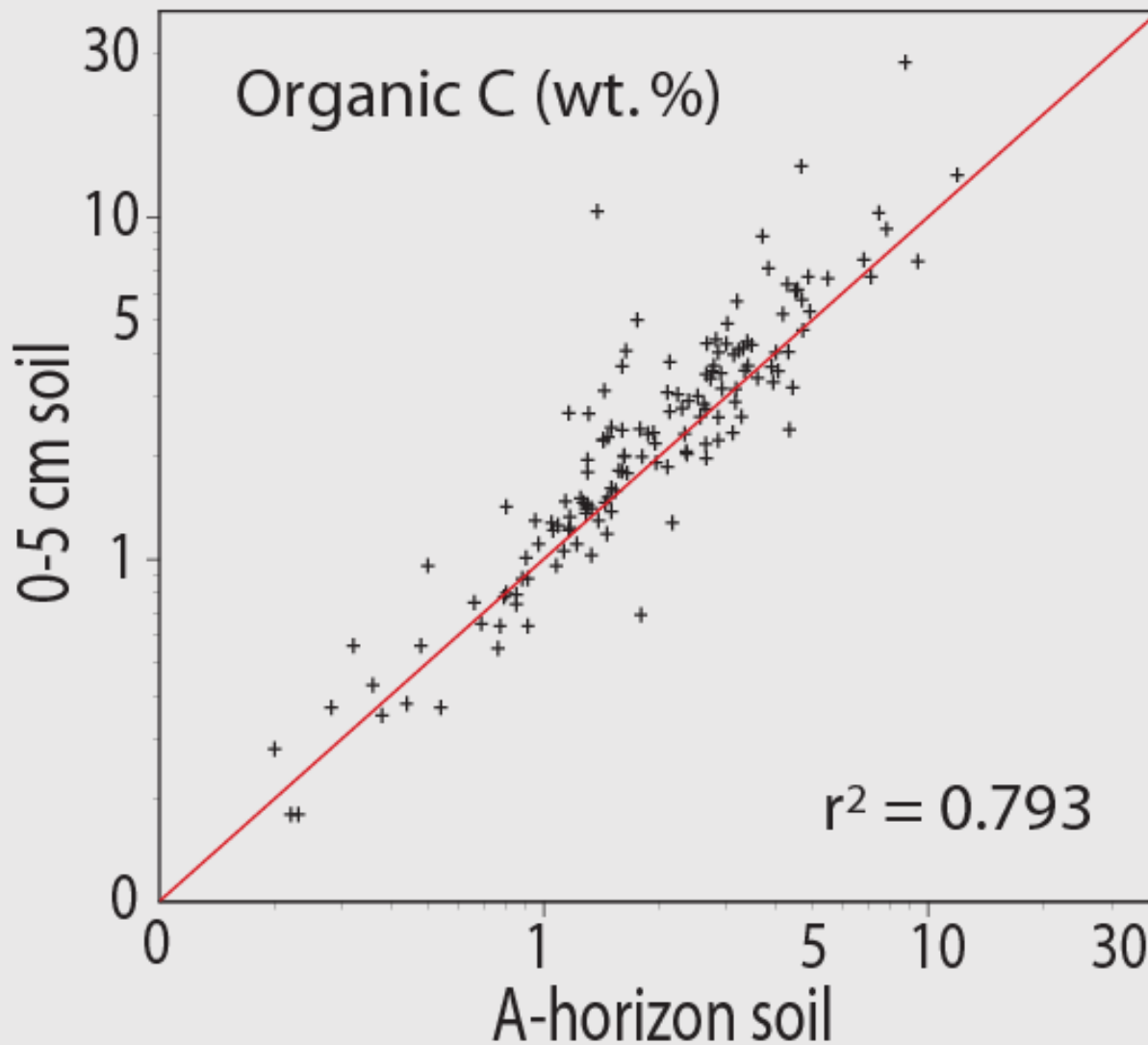
# **Sample Analyses (continued)**

- **BioLog community profiling – USGS**
- **Human and agricultural pathogen screening – USGS**
- **Near- and mid-IR diffuse reflectance spectrometry – USDA/ARS**
- **Screen for 22 organochlorine pesticides – contract laboratory**
- **ELISA screen for selected pesticides and carcinogenic PAHs – USGS**

# 0-5 cm vs. A-horizon soils



# 0-5 cm vs. A-horizon soils



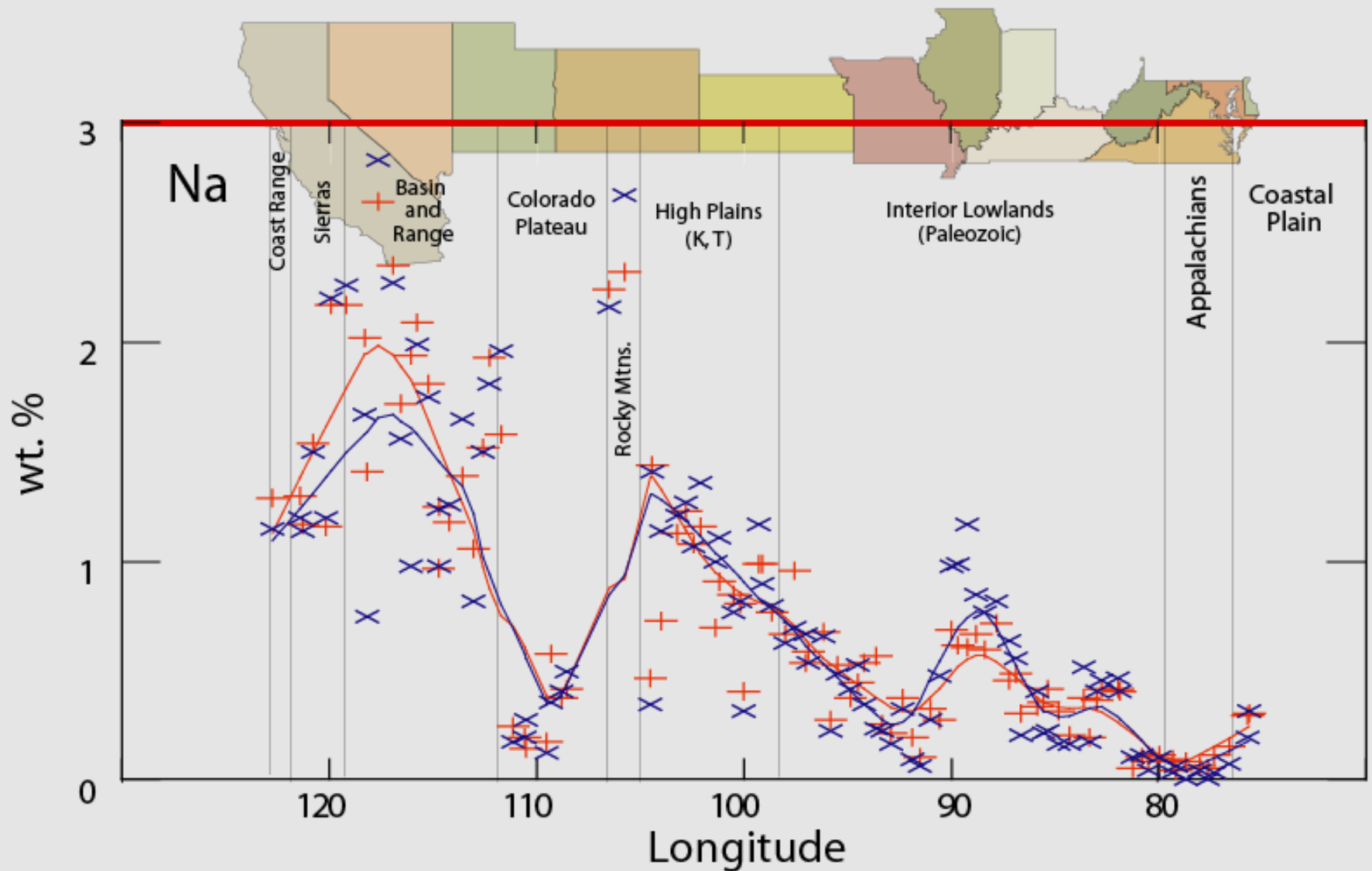


# 0-5 cm vs. A-horizon soils

relative % difference (RPD)

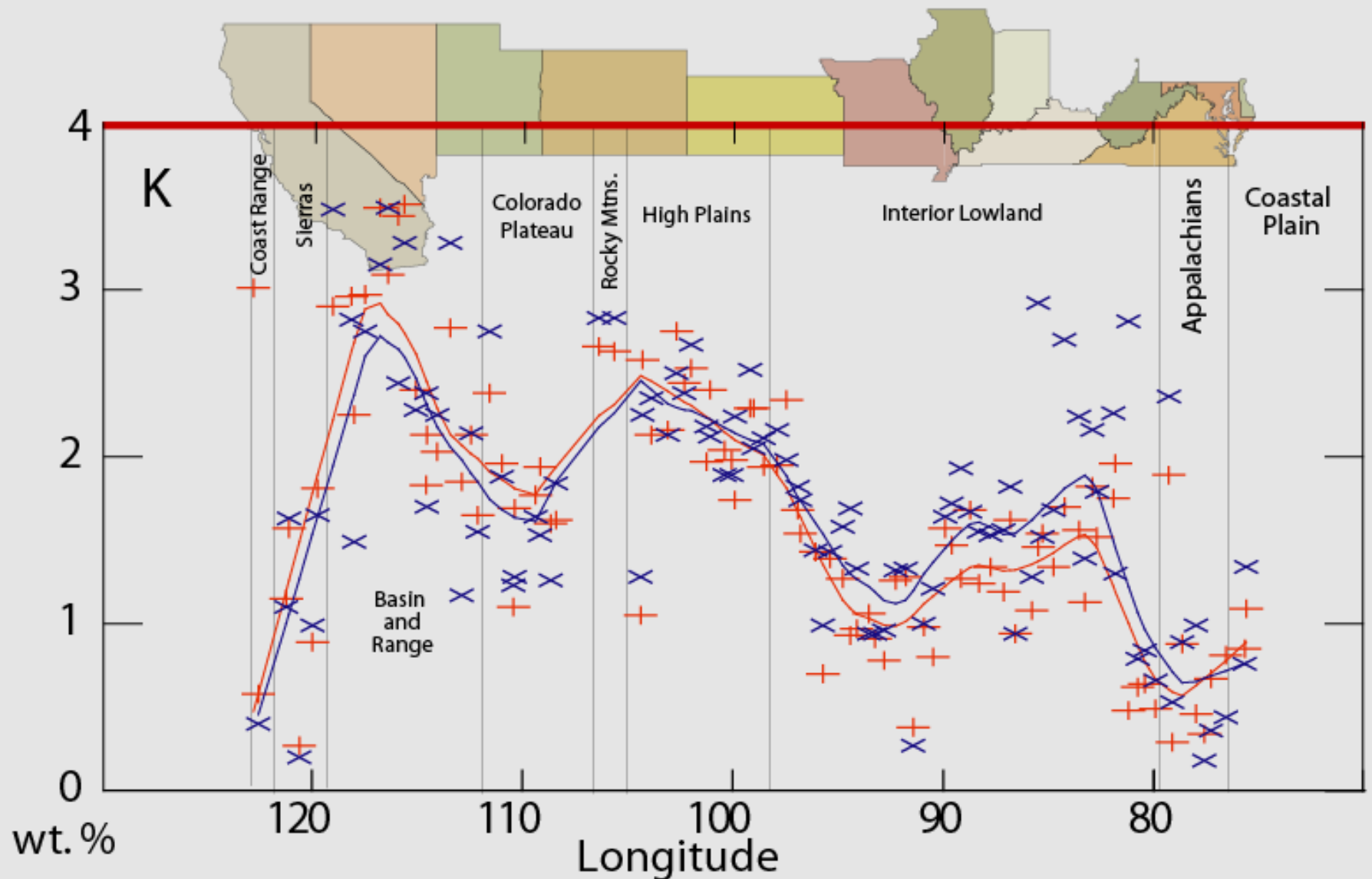
| Element | RPD   | Element     | RPD   |
|---------|-------|-------------|-------|
| Al      | 7.17  | Zn          | 10.77 |
| K       | 7.26  | Sr          | 11.03 |
| U       | 7.64  | Ti          | 11.84 |
| V       | 8.36  | Mn          | 12.53 |
| Pb      | 8.43  | Mg          | 12.54 |
| Tl      | 8.95  | Ni          | 12.79 |
| Co      | 9.30  | Cr          | 12.18 |
| Sc      | 9.42  | P           | 13.71 |
| Fe      | 9.47  | Cd          | 15.99 |
| La      | 9.54  | Ca          | 16.73 |
| Sb      | 9.61  | W           | 18.13 |
| Th      | 10.20 | As          | 18.14 |
| Na      | 10.23 | Cu          | 20.84 |
| Mo      | 10.34 | Hg          | 26.22 |
| Zn      | 10.77 | Organic C   | 28.42 |
| Mo      | 10.34 | Carbonate C | 31.13 |

# A- and C-horizon soils: E-W transect



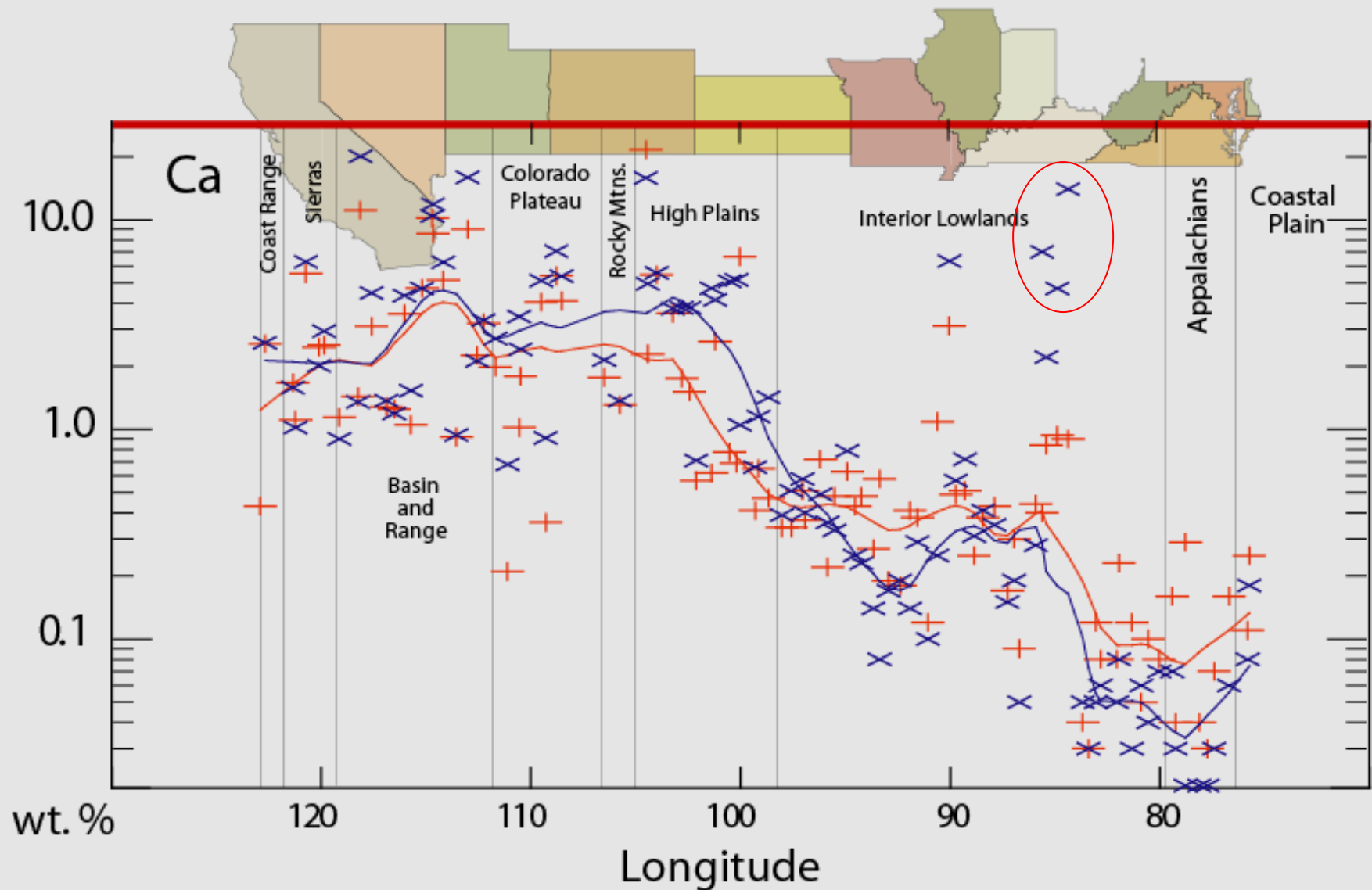
— A-horizon  
— C-horizon

# A- and C-horizon soils: E-W transect

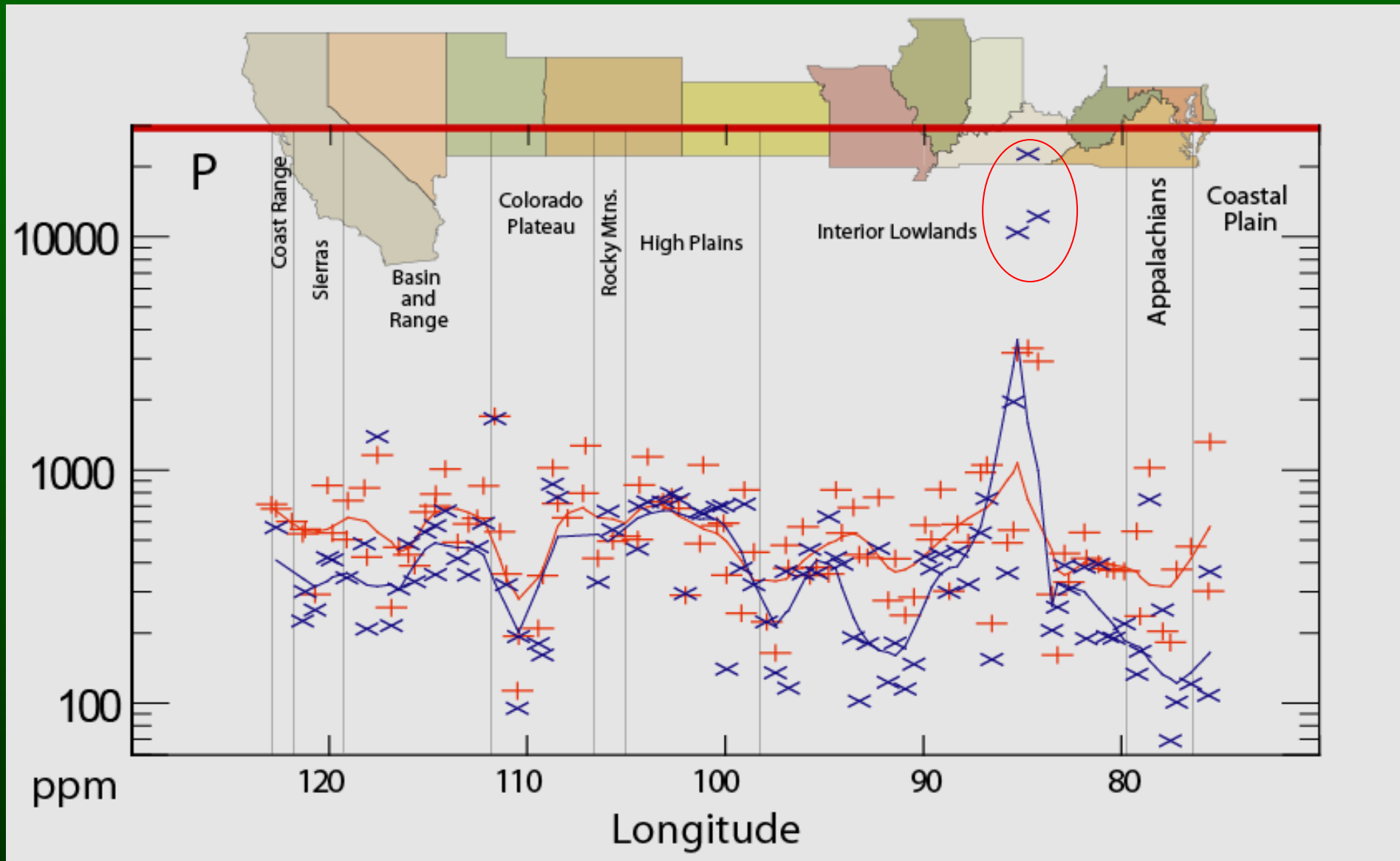


— A-horizon  
— C-horizon

# A- and C-horizon soils: E-W transect

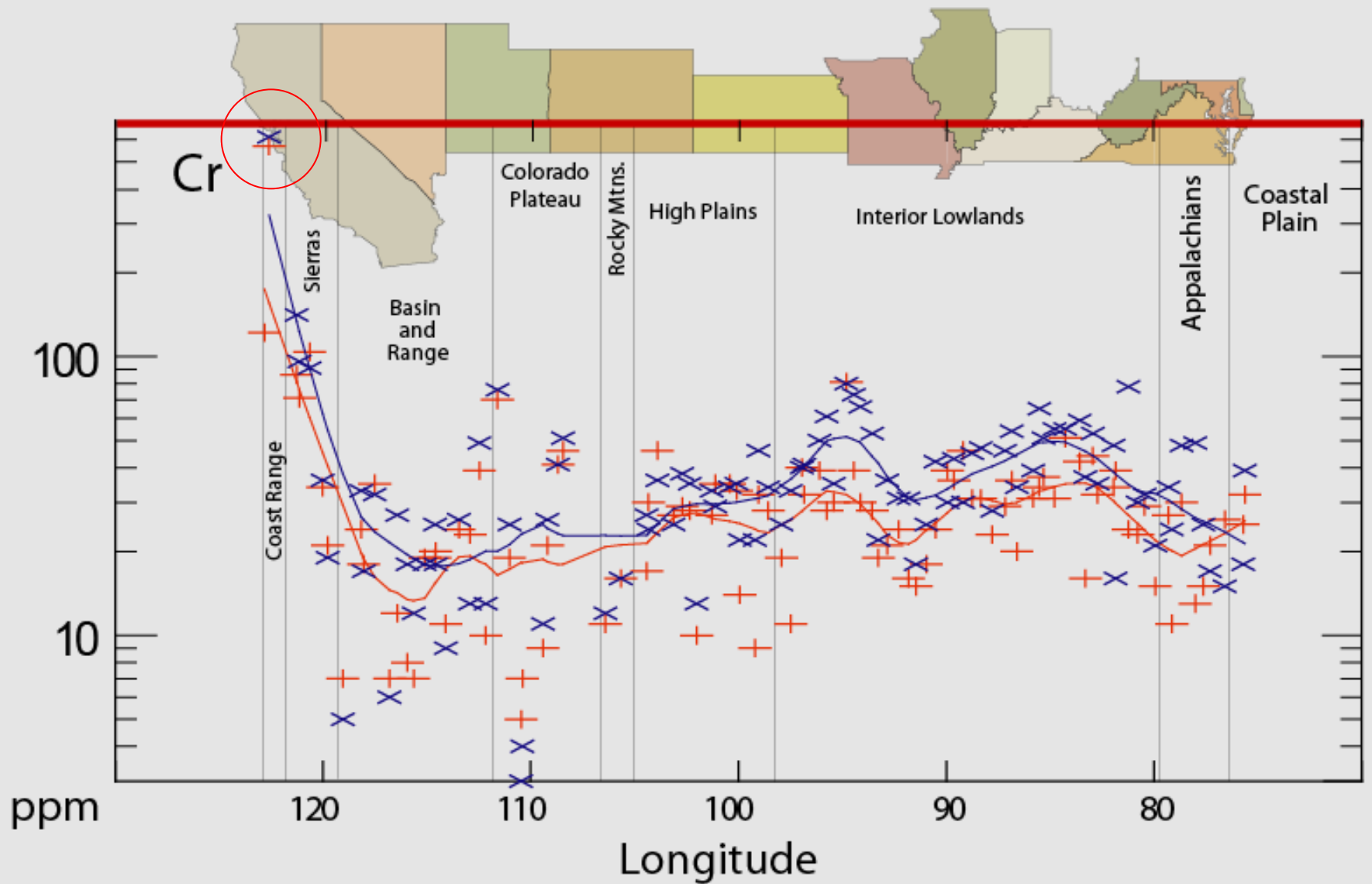


# A- and C-horizon soils: E-W transect



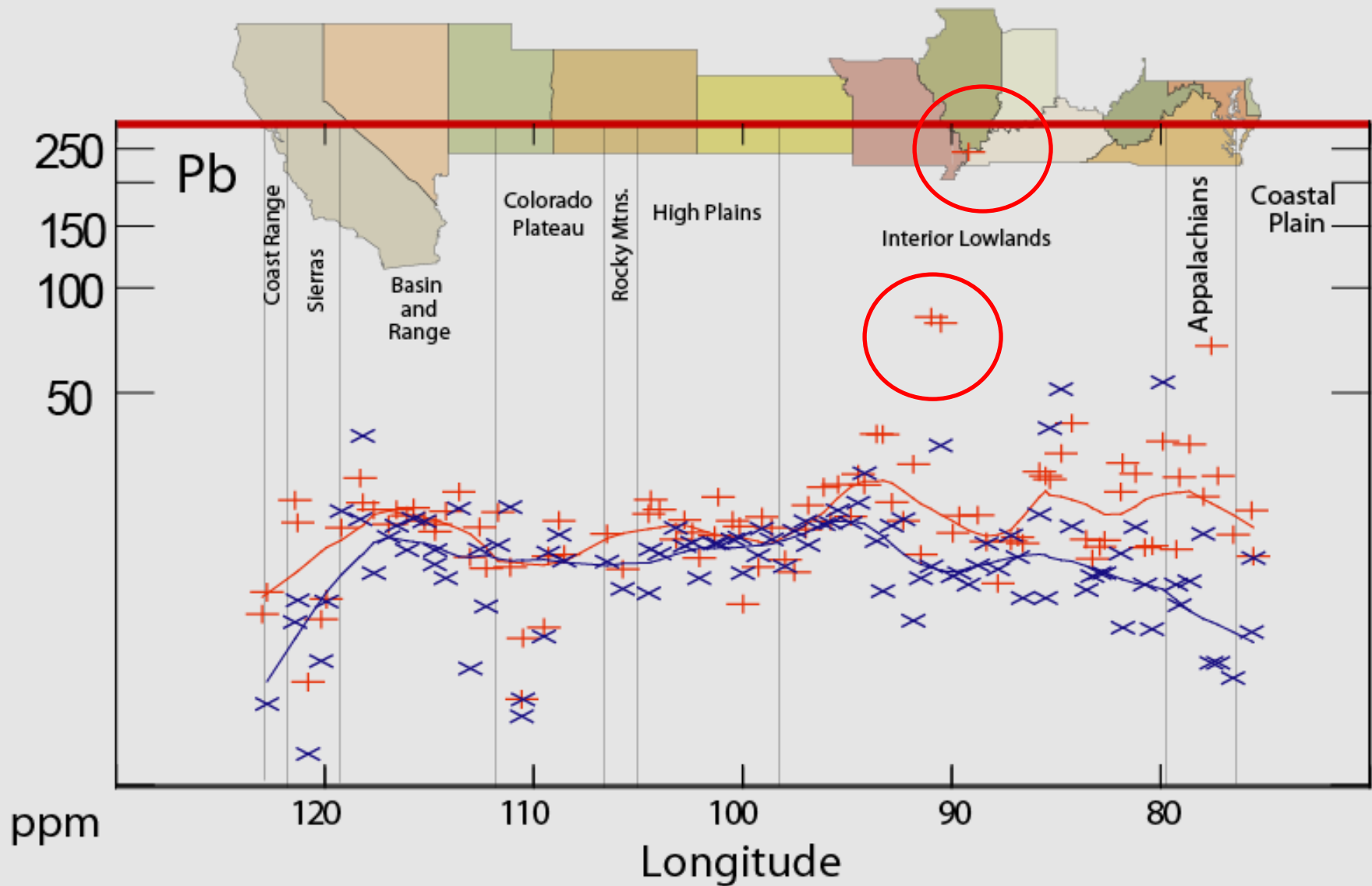
— A-horizon  
— C-horizon

# A- and C-horizon soils: E-W transect



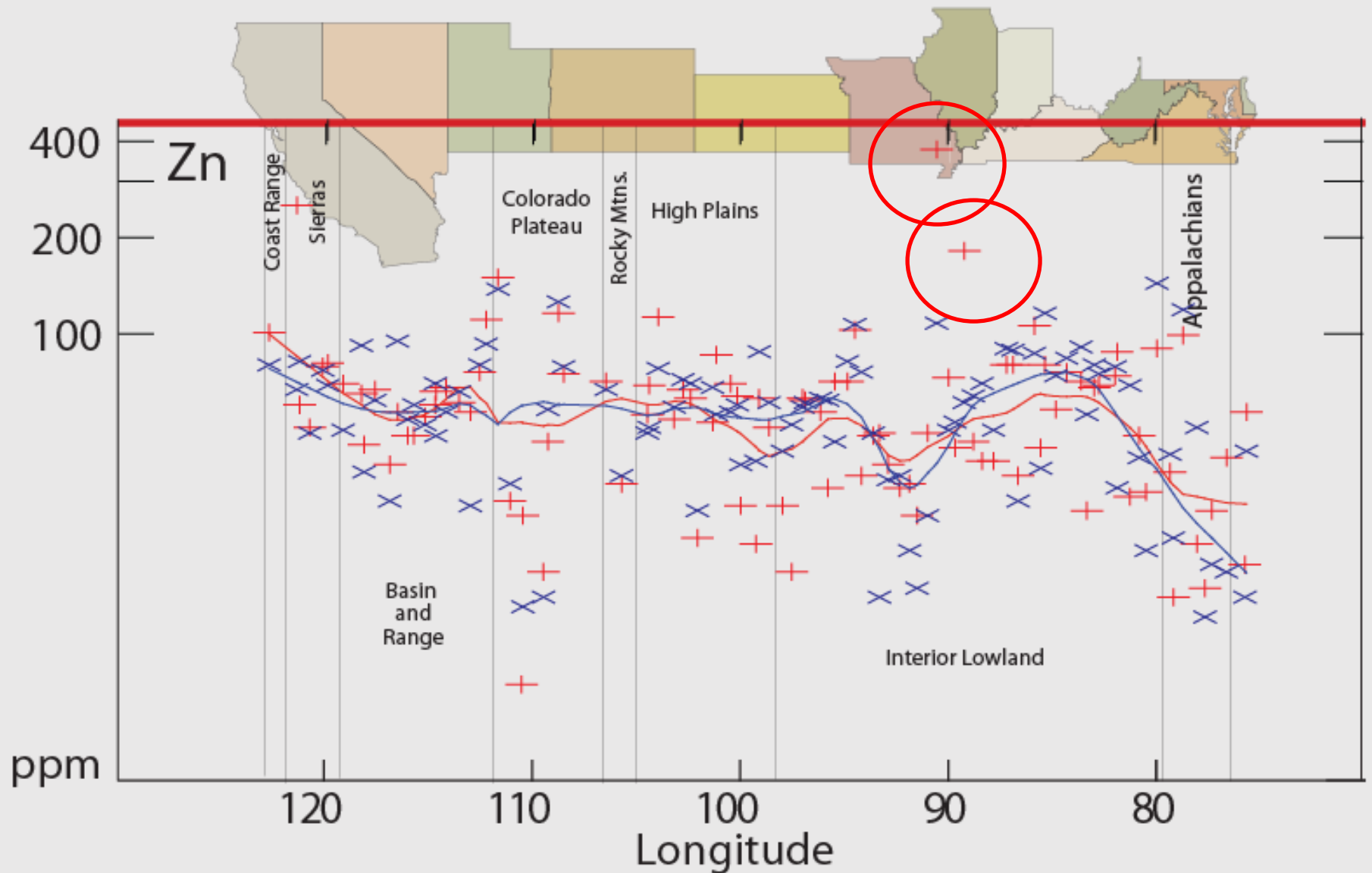
— A-horizon  
— C-horizon

# A- and C-horizon soils: E-W transect

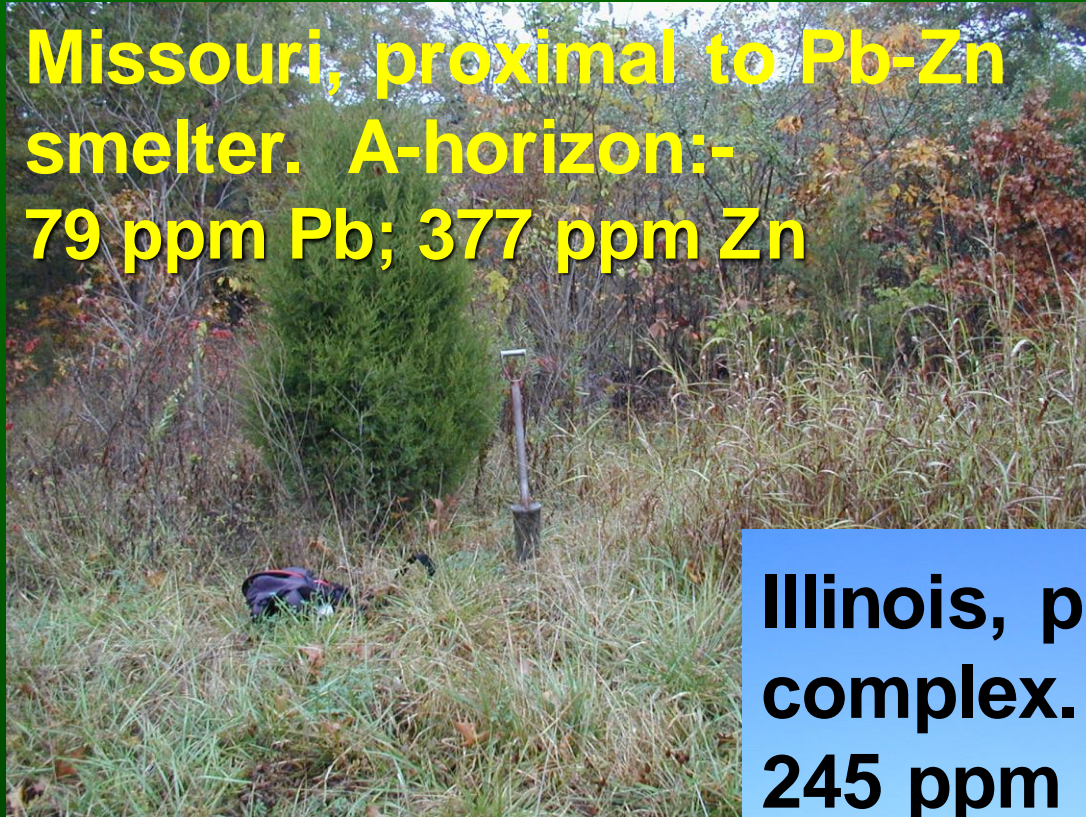




# A- and C-horizon soils: E-W transect



**Missouri, proximal to Pb-Zn  
smelter. A-horizon:-  
79 ppm Pb; 377 ppm Zn**

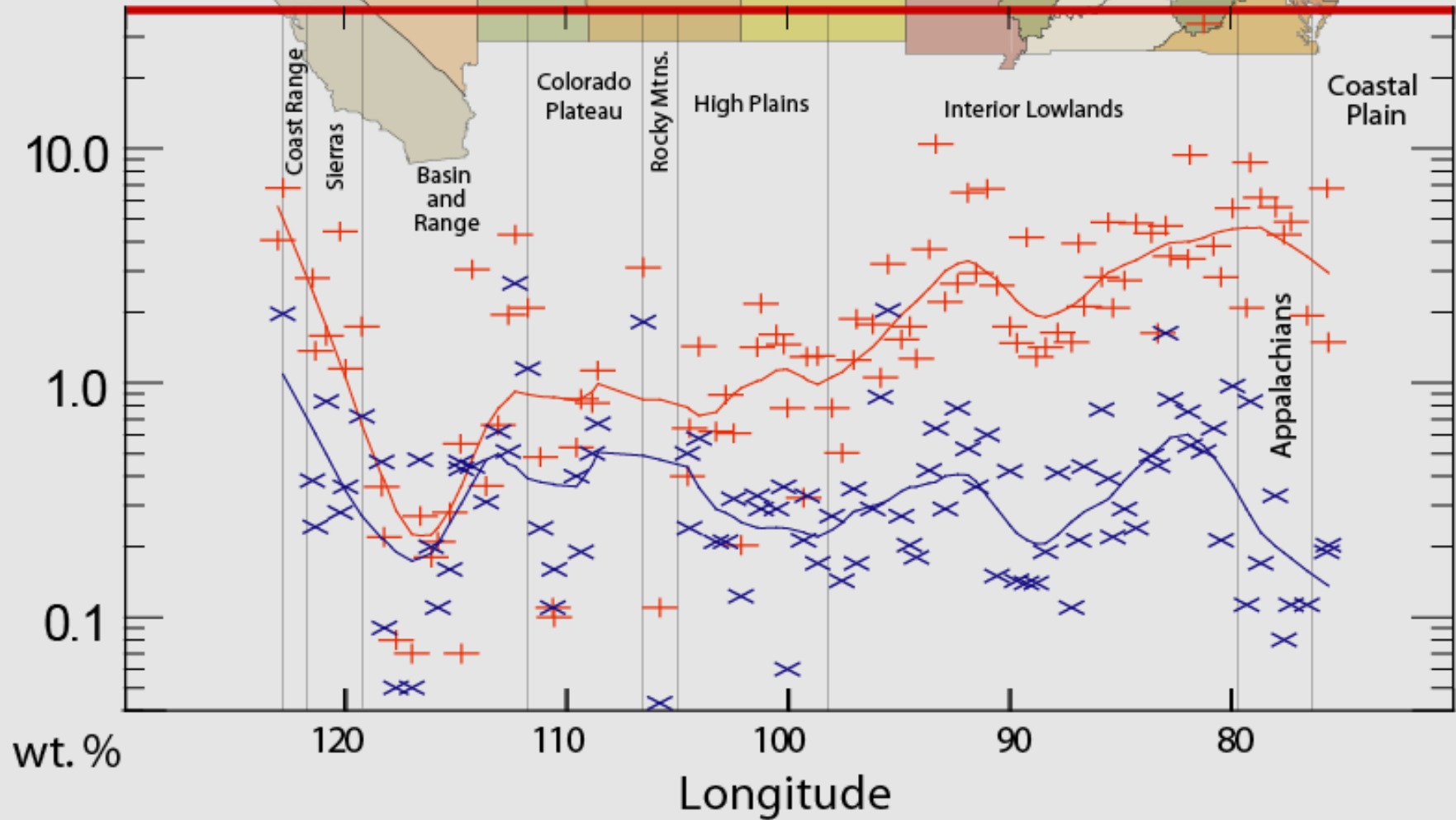


**Illinois, proximal to industrial  
complex. A-horizon:-  
245 ppm Pb; 182 ppm Zn**

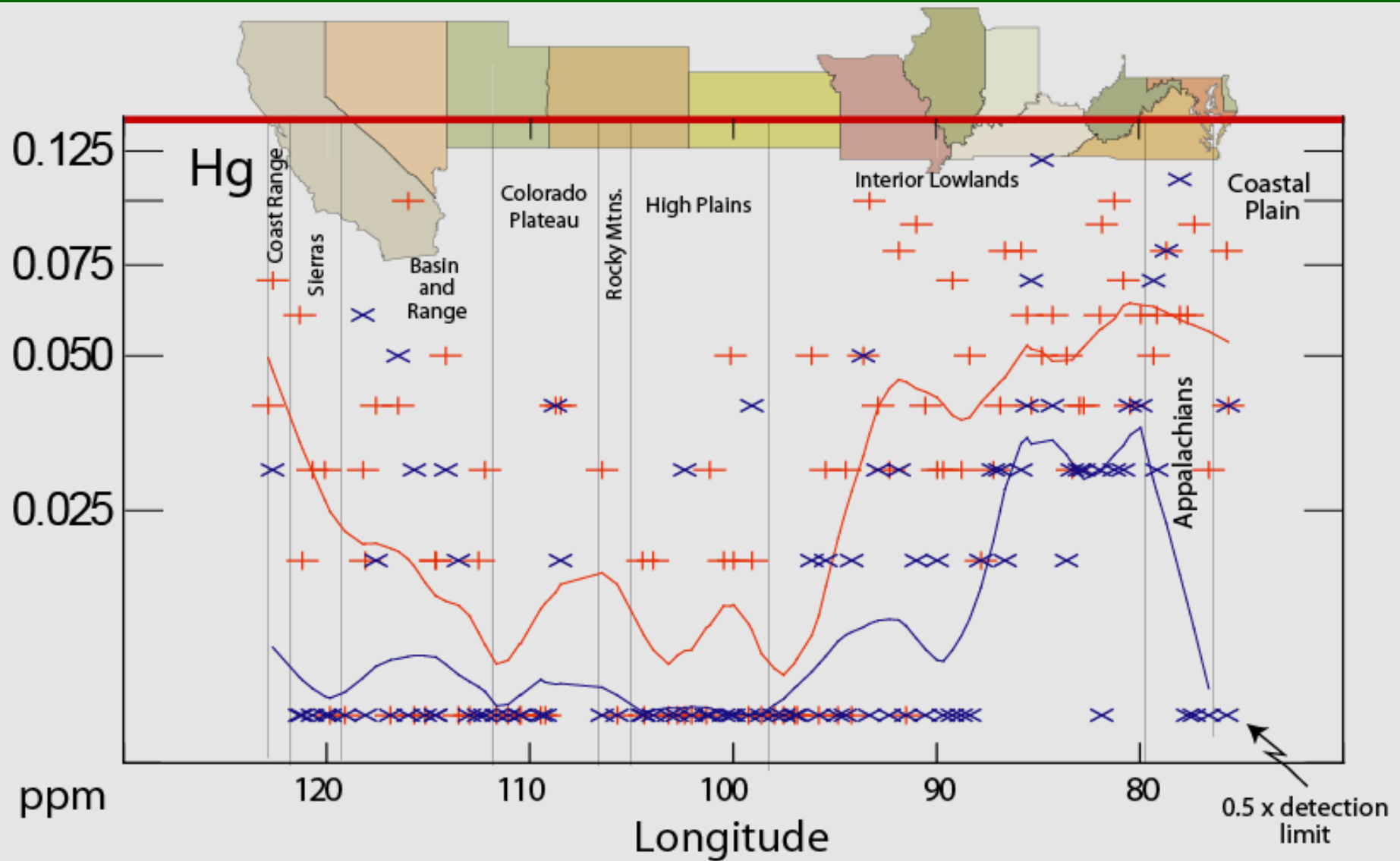


# A- and C-horizon soils: E-W transect

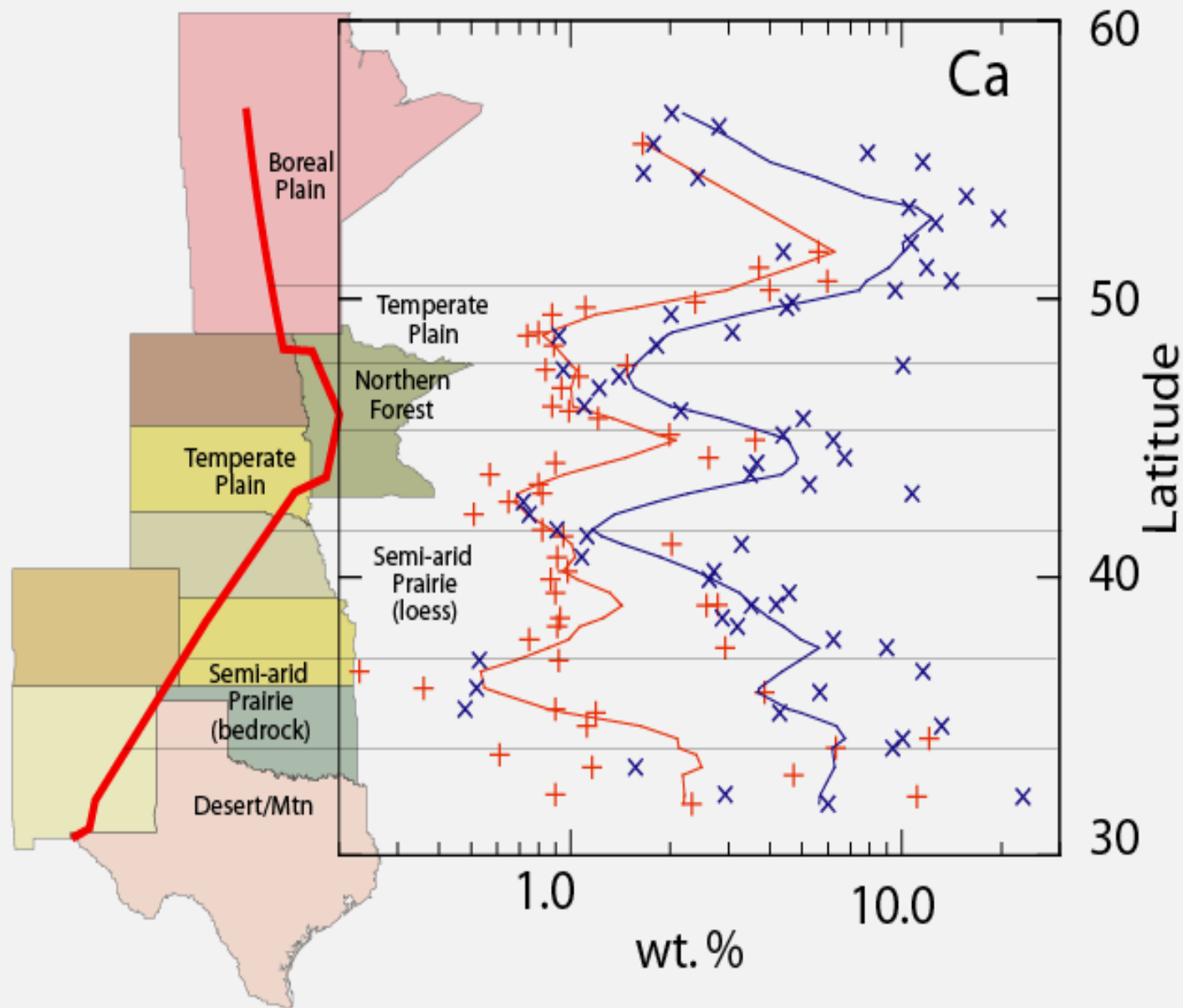
organic C



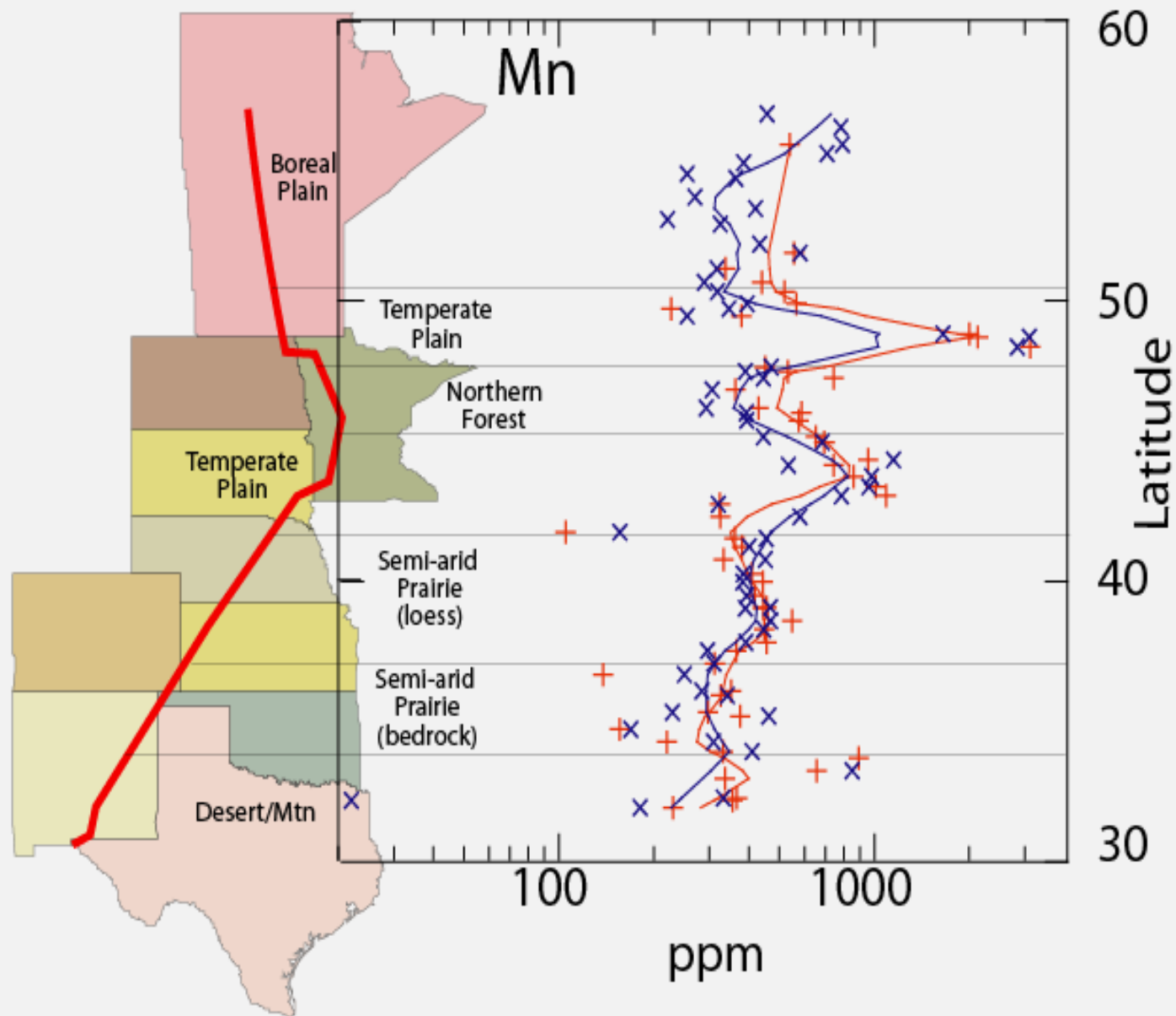
# A- and C-horizon soils: E-W transect







**A- & C-  
horizon  
soils:  
N-S  
transect**



**A- & C-horizon  
soils:  
N-S  
transect**

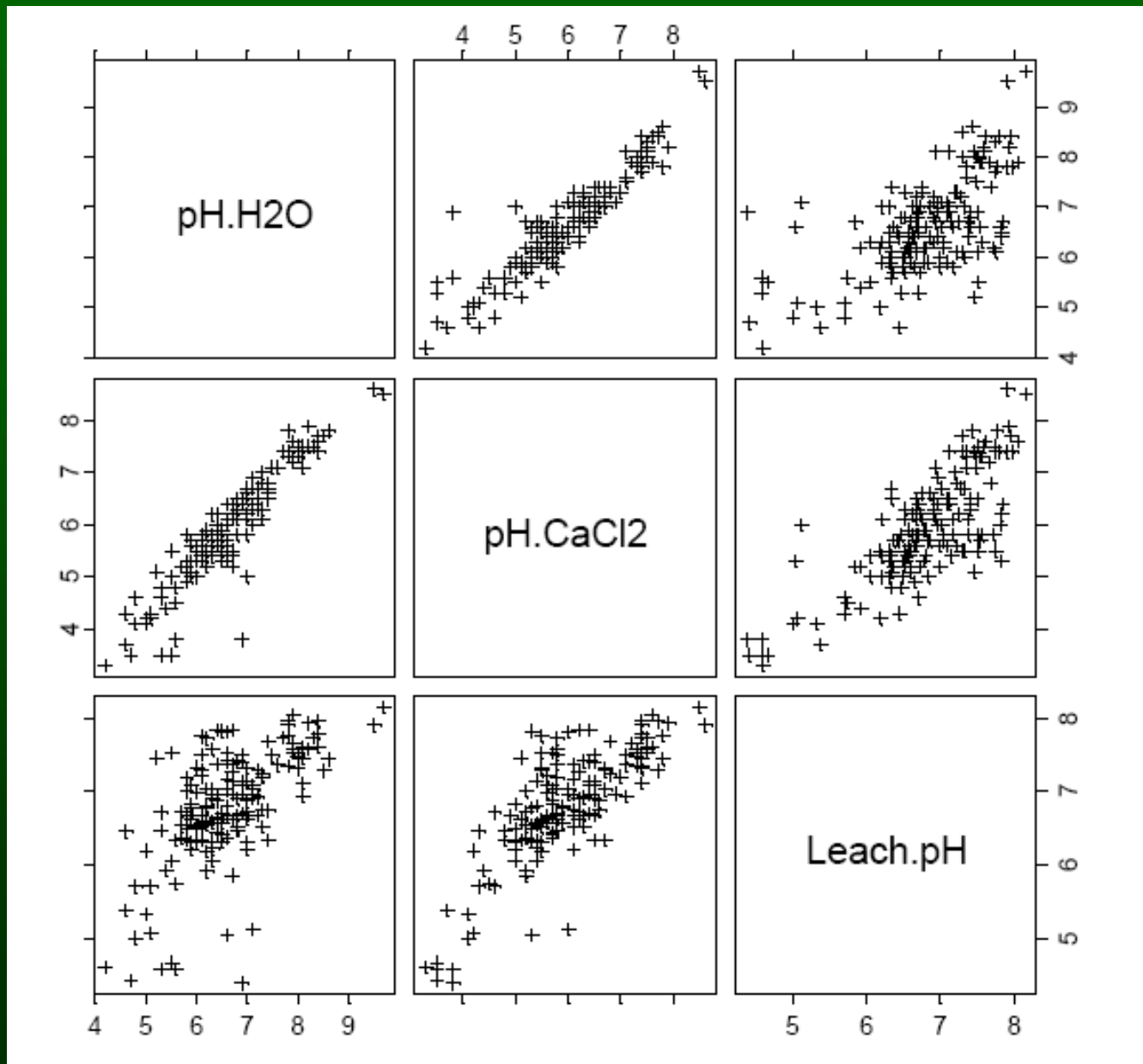
— A-horizon  
— C-horizon

# pH determinations for A-horizon soils

- Determined by 3 methods:
  - Standard water method (10 g soil diluted with 20 ml DI water)
  - $\text{CaCl}_2$  slurry method (add 20 ml 0.02M  $\text{CaCl}_2$ )
  - Following 20 hour DI-water leach (1 g sample in 40 ml RO-DI-water)



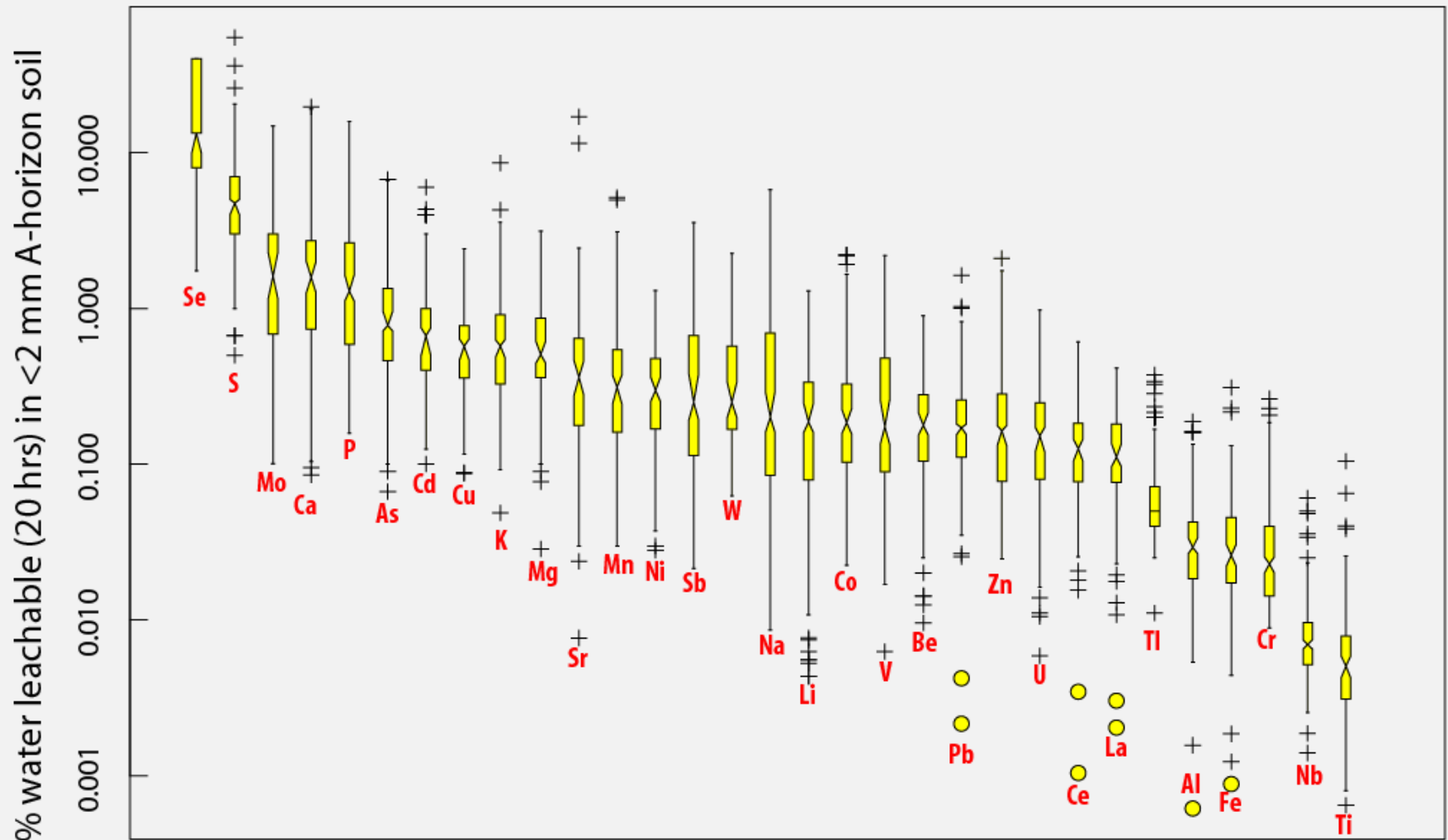
# Comparison of 3 pH determinations



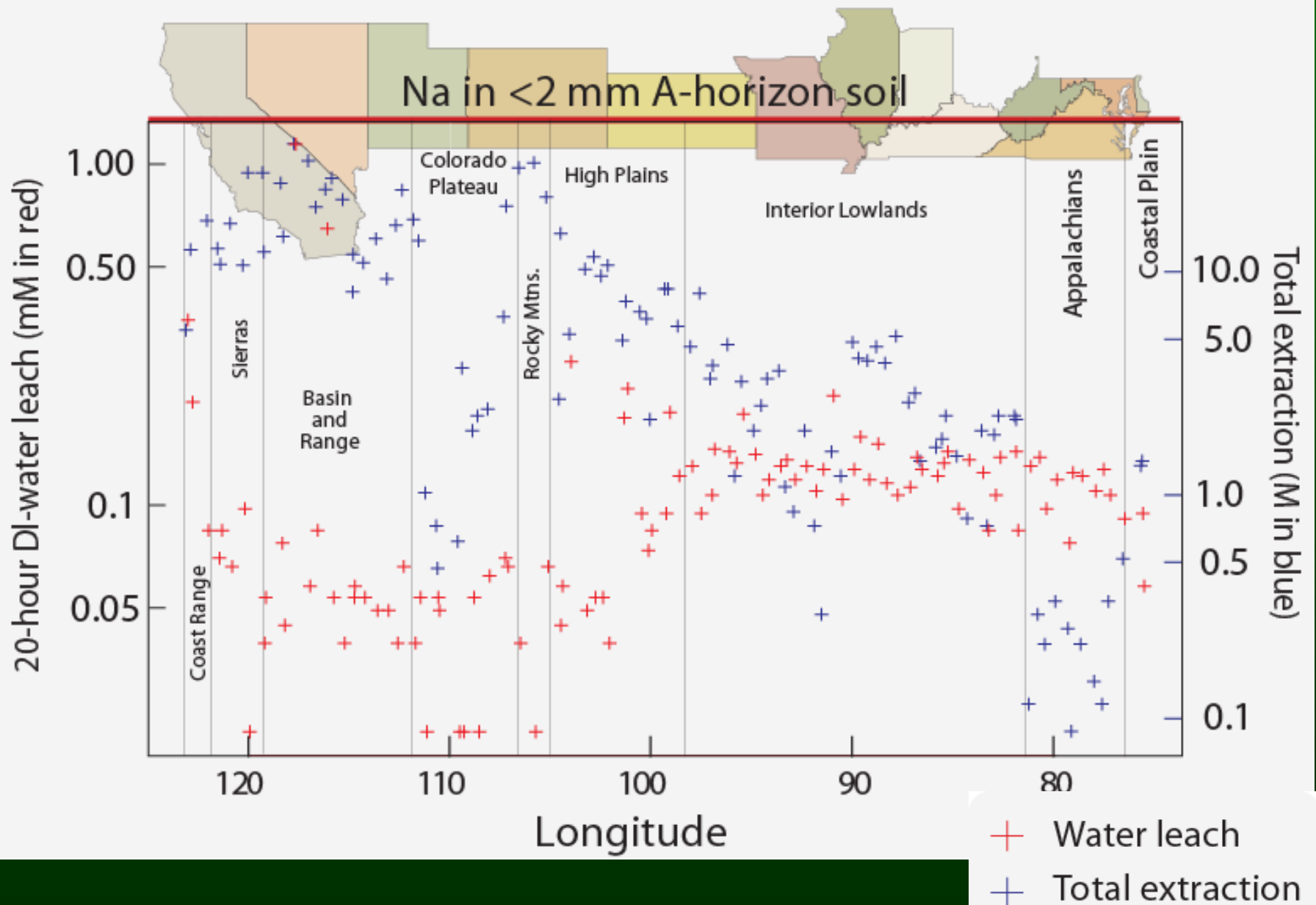
# **Water extractions in < 2mm A-horizon soil**

- 1 g soil to 40 mL deionized water
- Shake horizontally for 20 hours
- Centrifuge for 10 min at 3800 RPM
- Decant supernatant
- Dilute samples 2x with 2% HNO<sub>3</sub> and mix
- Centrifuge for 20 min at 4200 RPM
- Analyze same day

# Bioaccessability – A-horizon soils

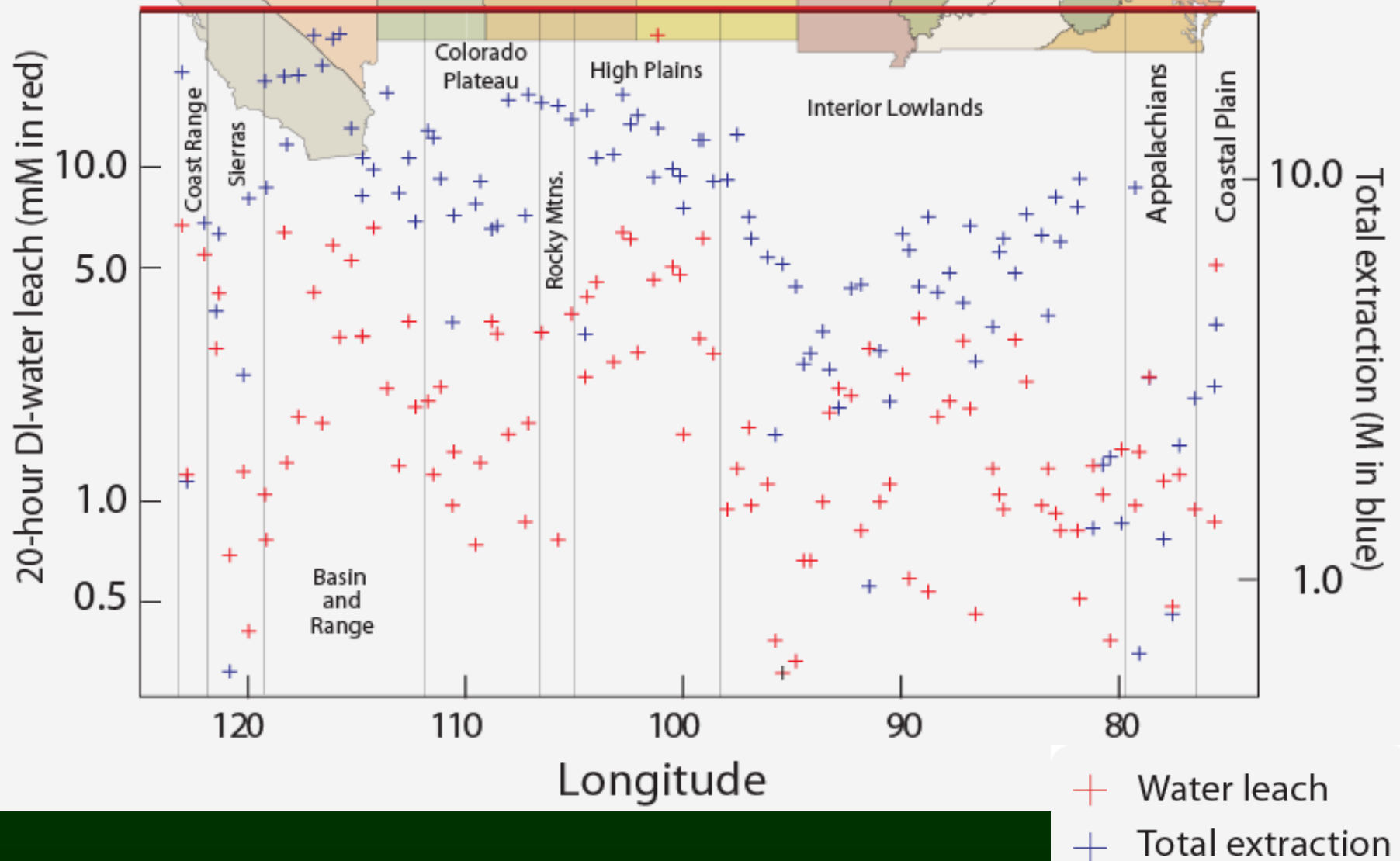


# Na total vs. water extraction: E-W transect



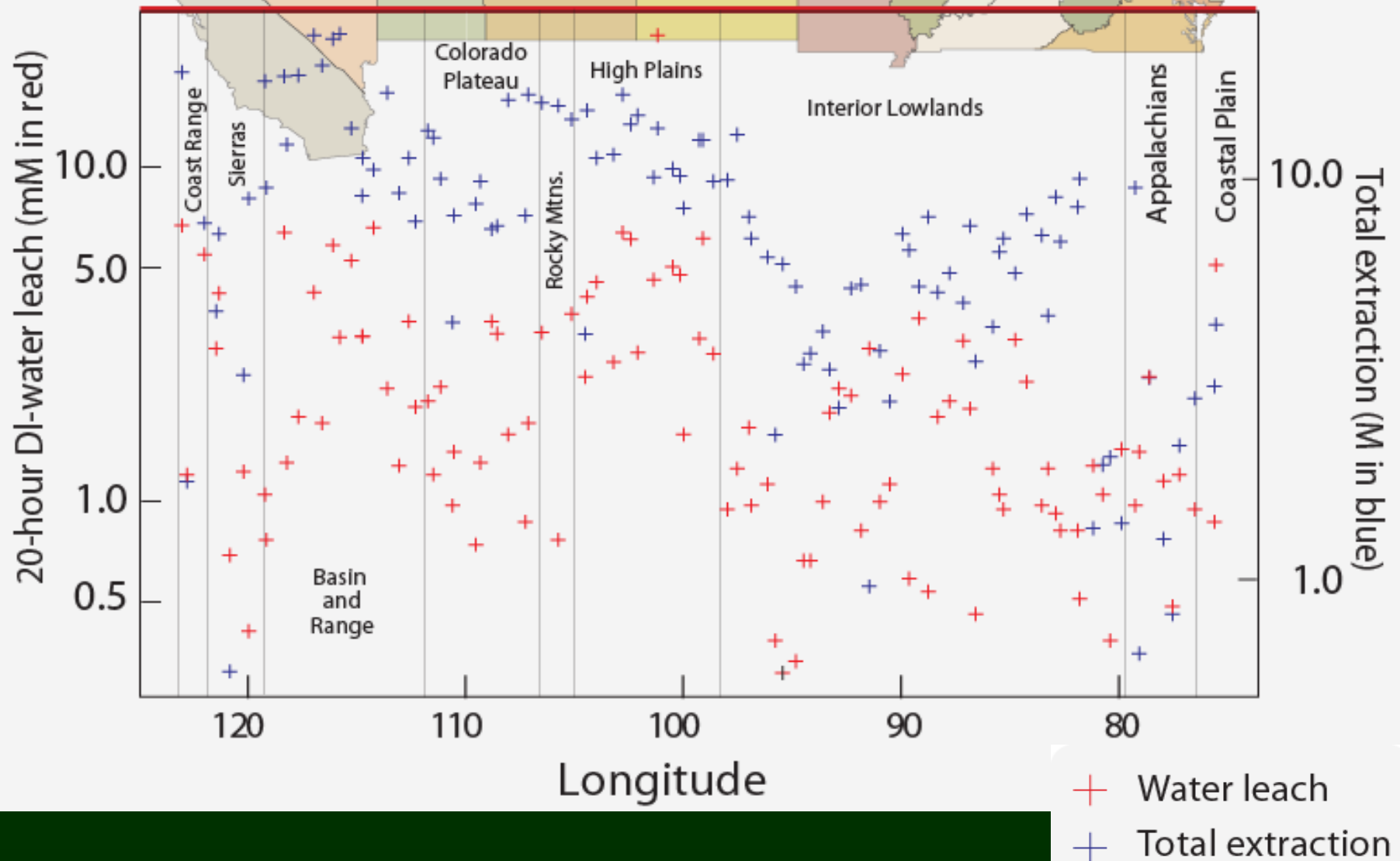
# K total vs. water extraction: E-W transect

K in <2 mm A-horizon soil

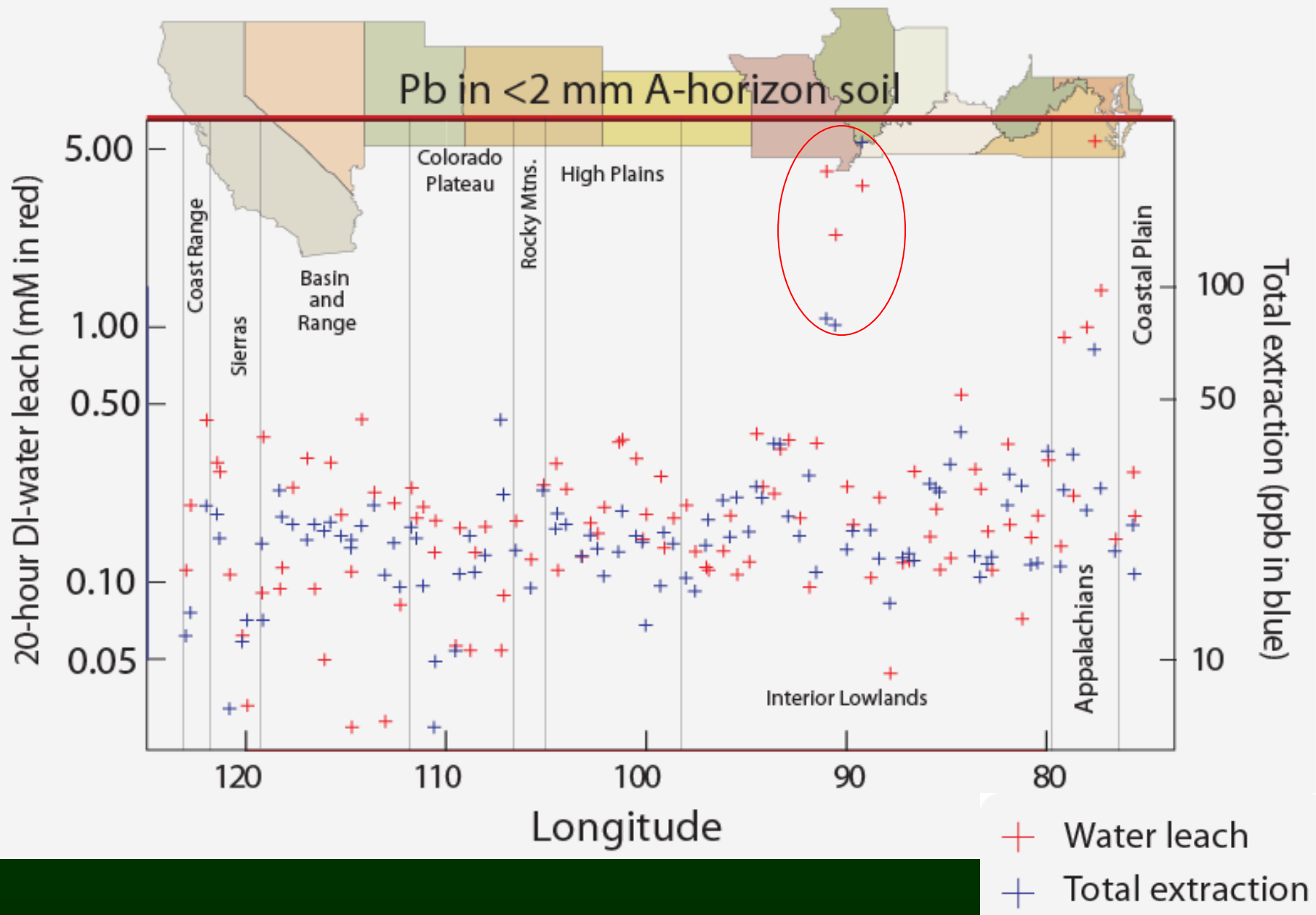


# K total vs. water extraction: E-W transect

K in <2 mm A-horizon soil



# Pb total vs. water extraction: E-W transect

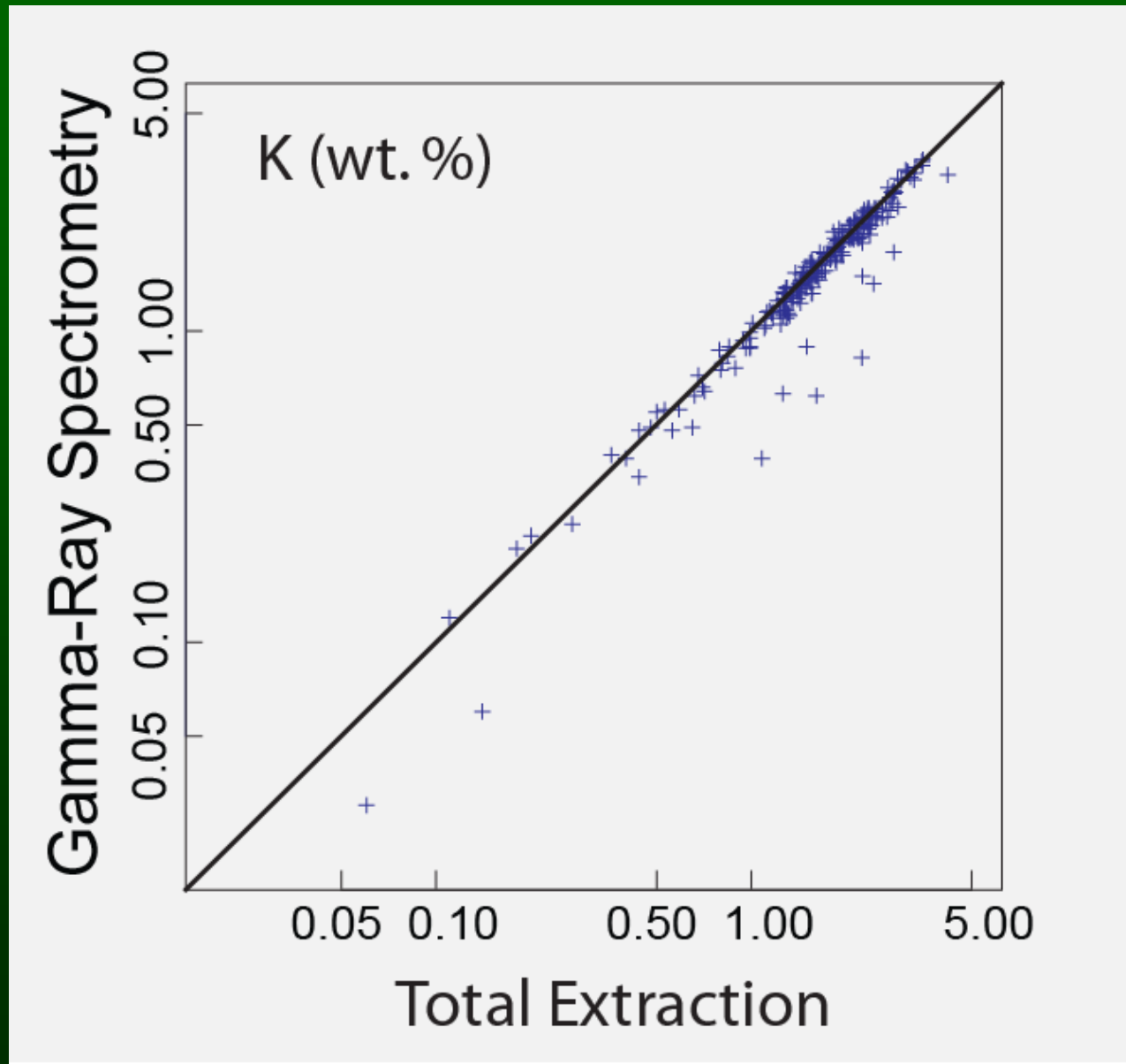




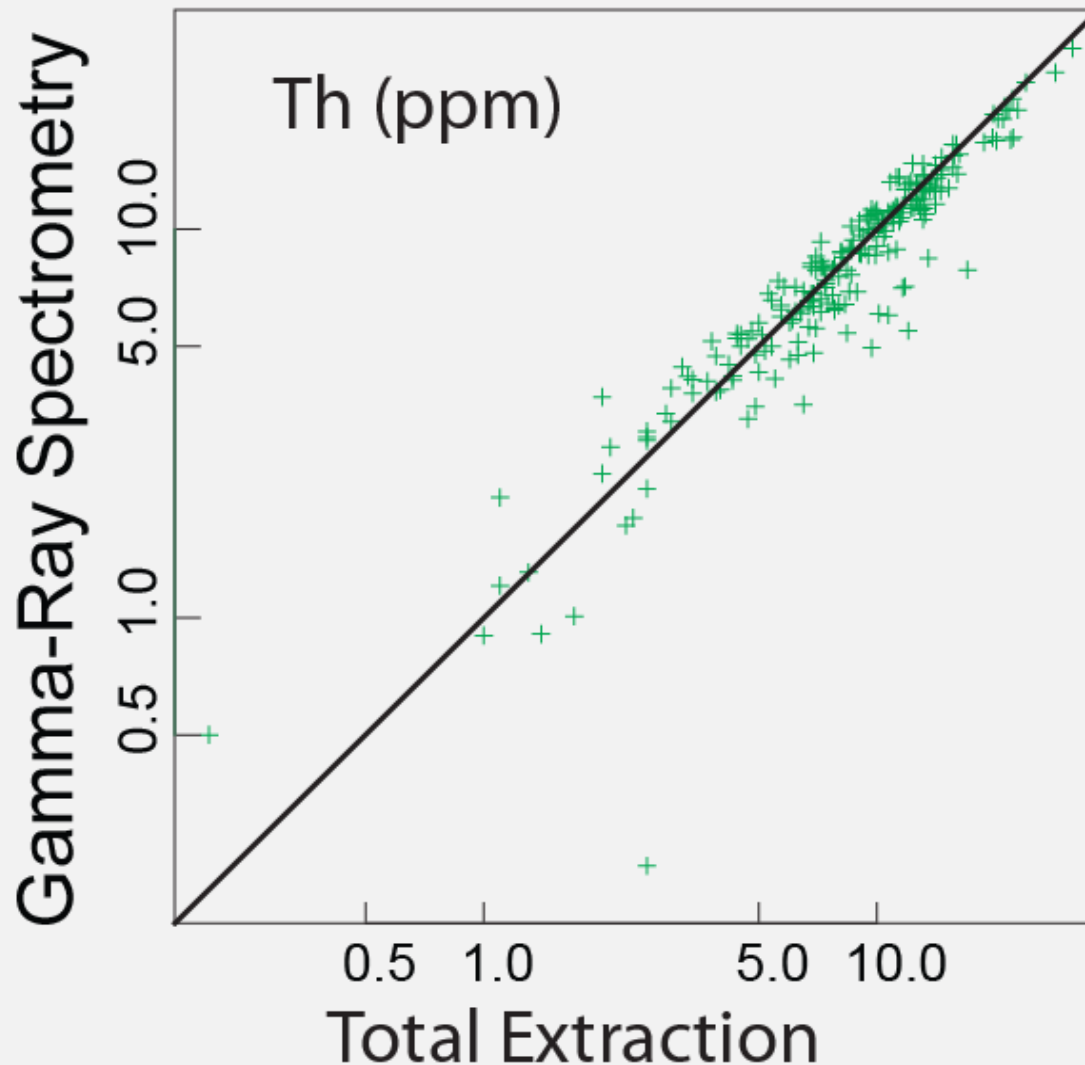
# Gamma-ray spectrometry

- Measure natural radiation from decay of  $^{40}\text{K}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$
- 155 to 432 grams of < 2 mm soil from A-, C-horizons, and 0-5 cm
- Sealed in metal cans to ensure no Rn escape; stored for 3 weeks to ensure equilibrium
- Each sample counted for 20 minutes and 1024 channel spectra recorded and archived
- IAEA-recognized standards used to develop run-specific calibrations from which K ( $^{40}\text{K}$ ), eTh ( $^{208}\text{Th}$ ) and eU ( $^{214}\text{Bi}$ ) were estimated

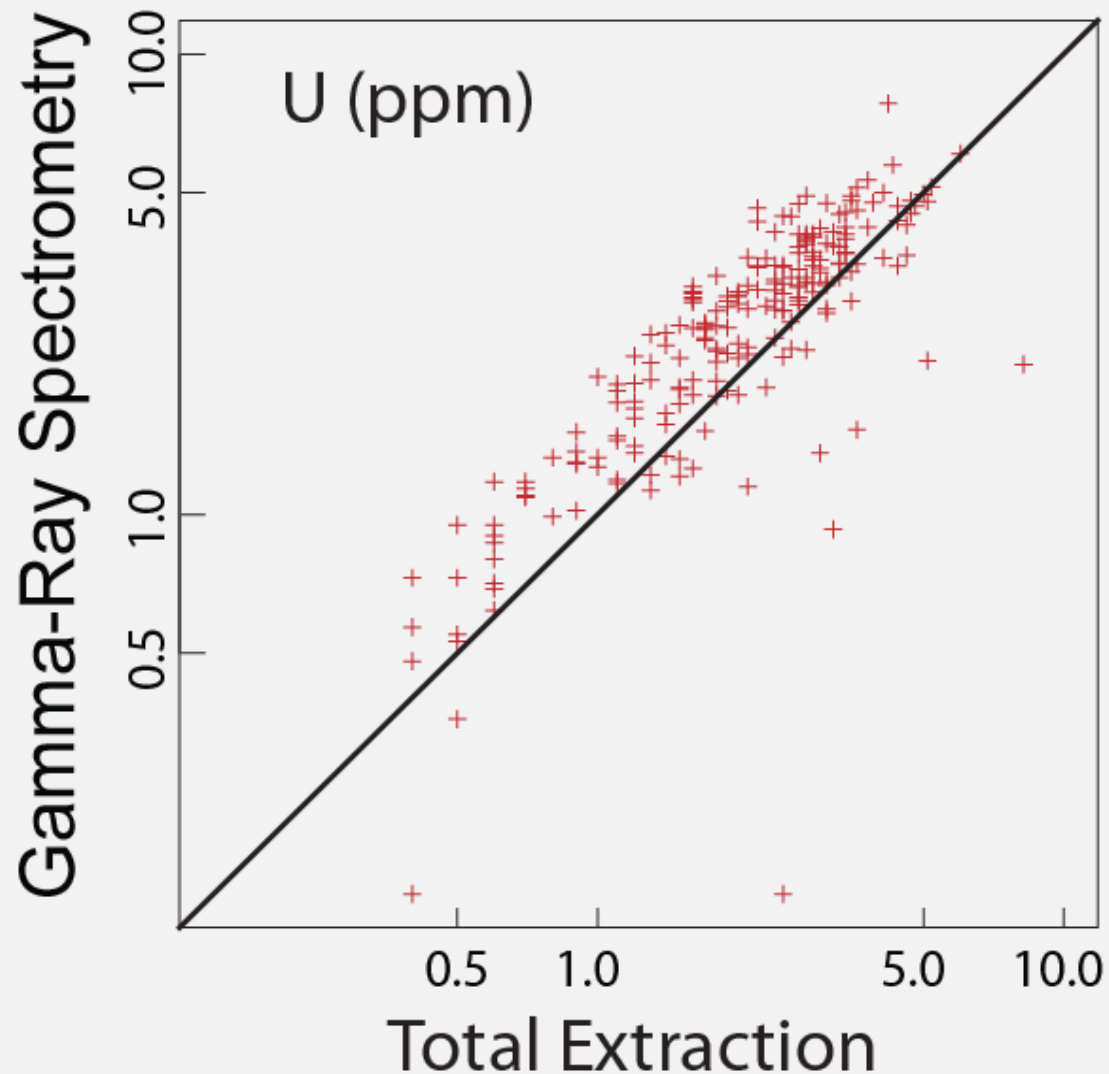
# Total extraction vs. Gamma-ray Spectrometry



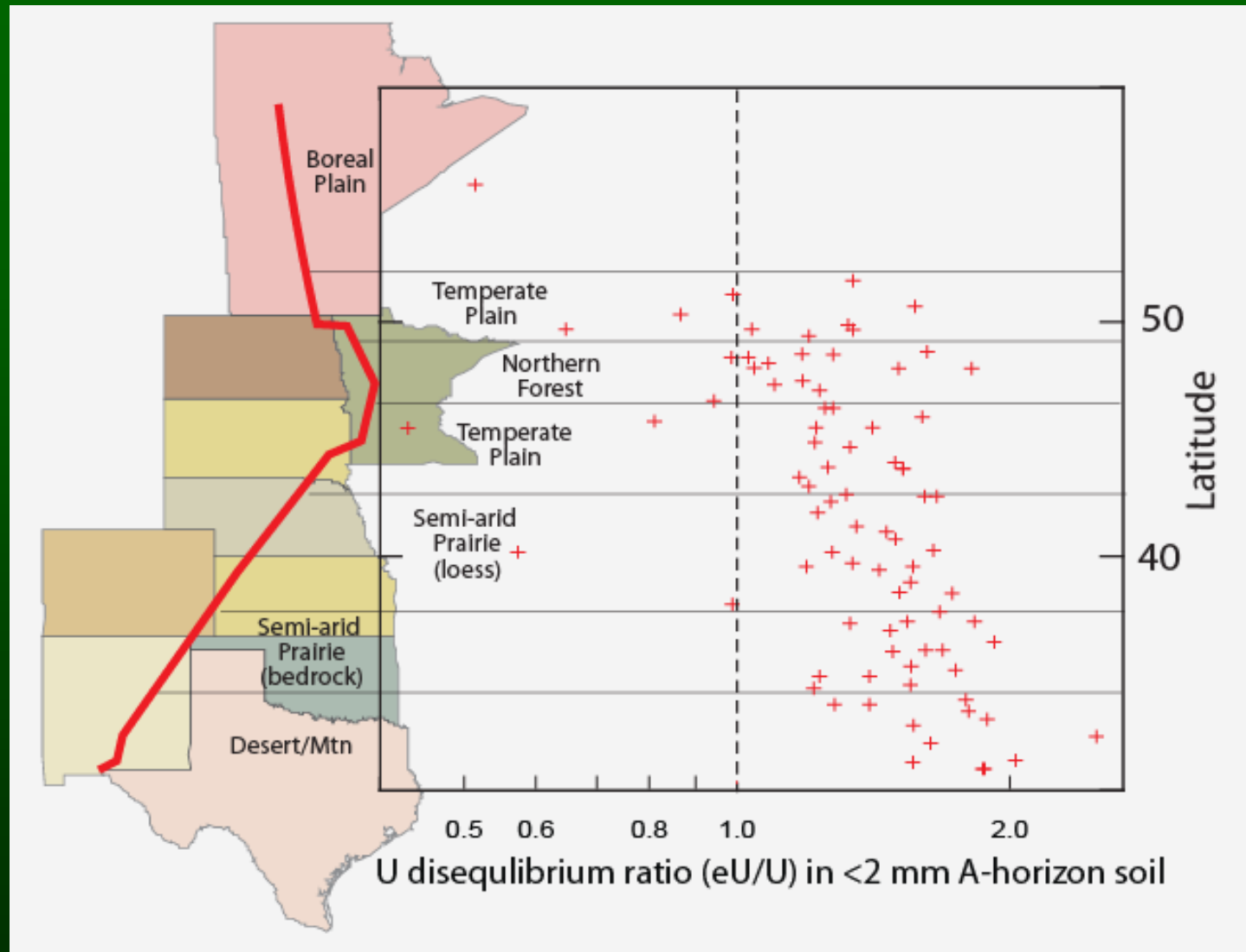
# Total extraction vs. Gamma-ray Spectrometry



# Total extraction vs. Gamma-ray Spectrometry



# U disequilibrium: N-S transect

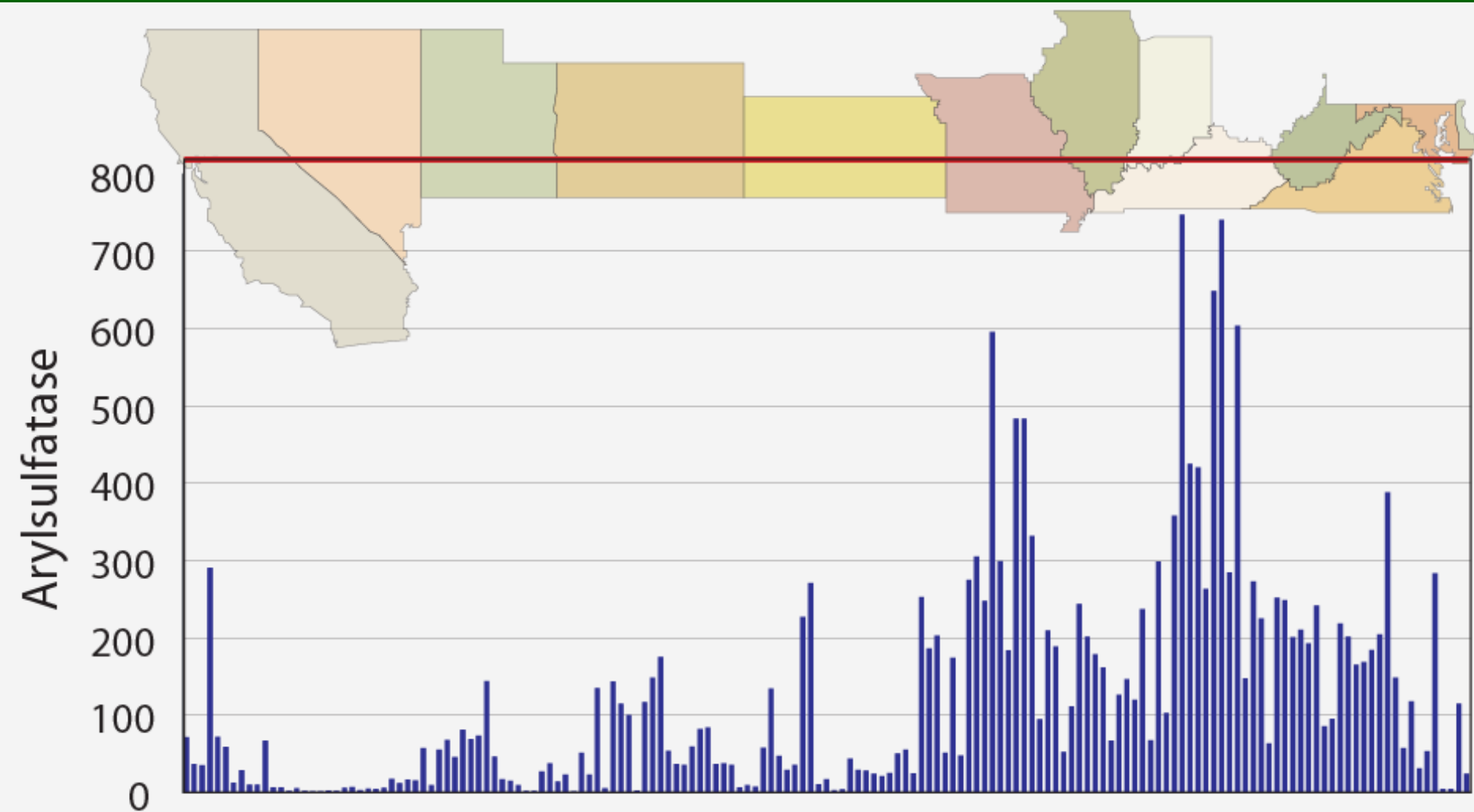


# Arylsulfatase

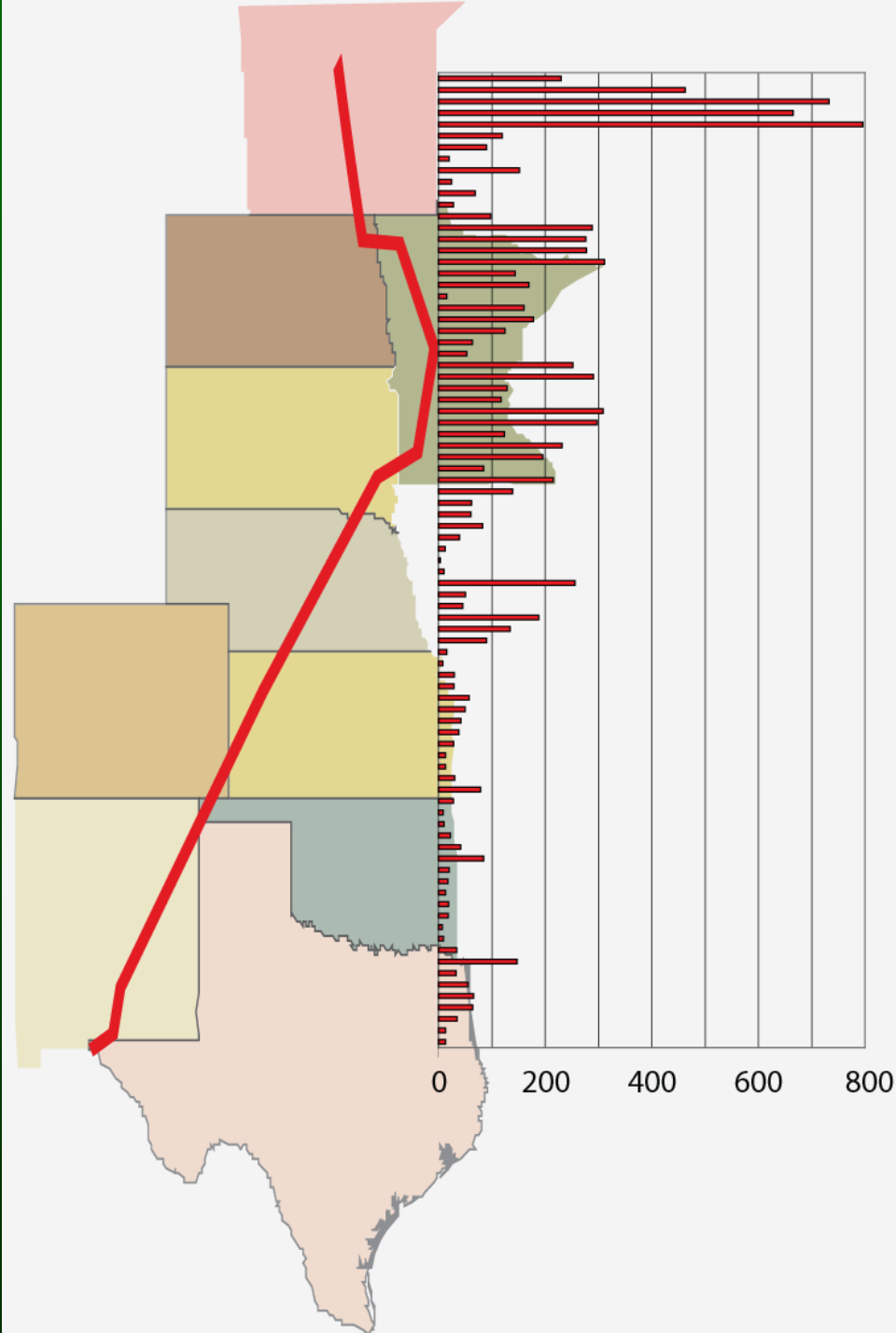
Releases sulfate, the plant-available form of sulfur, from various organic esters. Microbial ester sulfates found only in fungi and not in bacteria; thus, arylsulfatase highly correlated with fungal biomass. Useful soil quality index because elevated fungi indicative of high-quality soils.

Colorimetric determination in air-dried soil of the *p*-nitrophenol released upon hydrolysis of *p*-nitrophenyl sulfate.

# Arylsulfatase in A-horizon soils: E-W transect





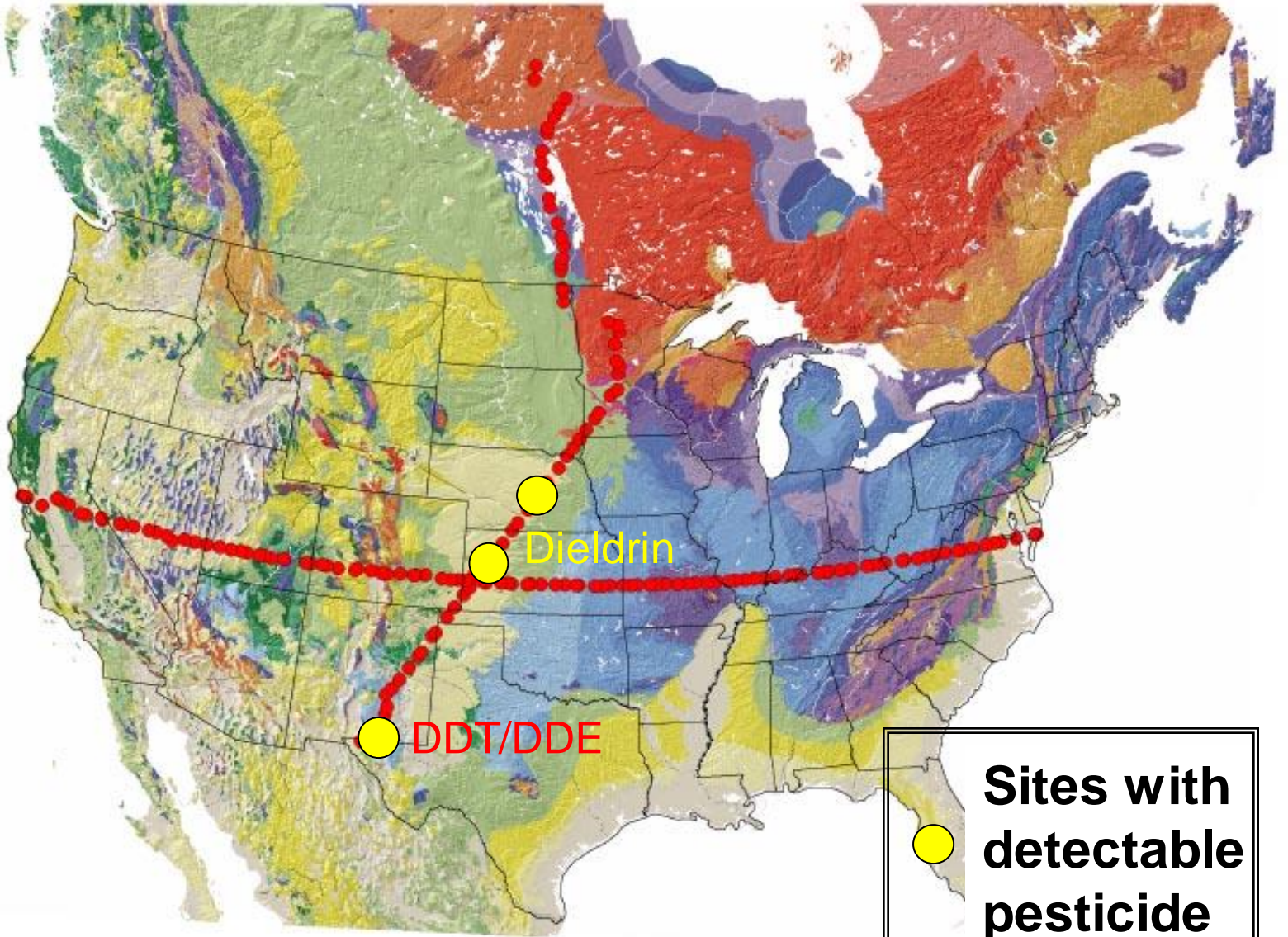


**Aryl-  
sulfatase  
in A-horizon  
soils: N-S  
transect**

# Organochlorine pesticides analyzed (73 US samples from N-S transect)

- Aldrin
- Alpha-BHC
- Beta-BHC
- Gamma-BHC (Lindane)
- Chlordane
- 4,4'-DDT
- 4,4'-DDD
- 4,4'-DDE
- Dieldrin
- Endrin
- Endrin aldehyde
- Endrin ketone
- Endosulfan I
- Endosulfan II
- Endosulfan sulfate
- Heptachlor
- Heptachlor epoxide
- Methoxychlor
- Toxaphene

Red indicates persistent organic pollutants (POPs)



# Human and agricultural pathogens (Preliminary results for N-S transect)

- *Brucella abortus* (in about 1% of sites)
  - Brucellosis (contagious abortion) in cattle
- *E coli* 0157:H7 (no hits)
  - Foodborne illness in humans (undercooked hamburger)
- *Cryptosporidium parvum* (no hits)
  - Parasite found in intestinal tract
- *Bacillus anthraxis* (1-4% of sites)
  - Anthrax

# Lessons learned from transects

- No need to collect or analyze separate 0-5 cm sample
- Sample spacing adequate to detect major (and minor) differences in chemistry across major physical, climactic, and geologic gradients
- One pH determination adequate
- For most elements, less than 1% of total concentration is leachable in water; leachability can vary significantly across the landscape
- Gastric fluid simulations (pH 1.5) extract greater amounts than water (pH 4-10), but % leached is variable for different soils
- eU/U disequilibrium, U has been leached from older soils
- Enzyme assays highly variable across the landscape
- Detectable pesticide and residue levels are rare

# Next Steps - 1

- Review of sampling strategy and design
  - USGS Denver April 11-12, 2006, with attendees from
  - USGS, NRCS, US-EPA, SREL, CDC, GSC and AAFC?
- Mexican partners to extend N-S transect south across Mexico, and complete an E-W transect in 2006
- Complete spatial variability and other studies
- Presentation at WSC 2006, Philadelphia
- Write up full field and analytical protocols
- Publication of science papers in 2007 in a special issue of GEEA

# Next Steps - 2

- USGS plans to commence sampling in 2007 in collaboration with State and Federal agencies
- Project approved for NRCan's ESS 2006-10 Environment & Health Program
  - Program and Division management need to identify/hire an individual to manage this project
  - Continue to collaborate with AAFC staff working in their "Soils Theme" to see this work integrated with their new "Pedons" project
  - Seek Federal and Provincial partners with whom to undertake the project, giving them full access to the data to meet their agency needs