Oxidation and mobilization of naturally occurring chromium in soils of the Sacramento Valley, California

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Outline

- Chromium toxicity and sources – importance of speciation
- Naturally occurring Cr(VI) in groundwater – a global issue
- Natural Cr distribution in Sacramento Valley soils
- Cr(VI) in vadose zone soils and sediments
- Natural Cr(VI) generation in soils
- Oxidation reactivity of natural versus fertilizer-derived Cr(III)

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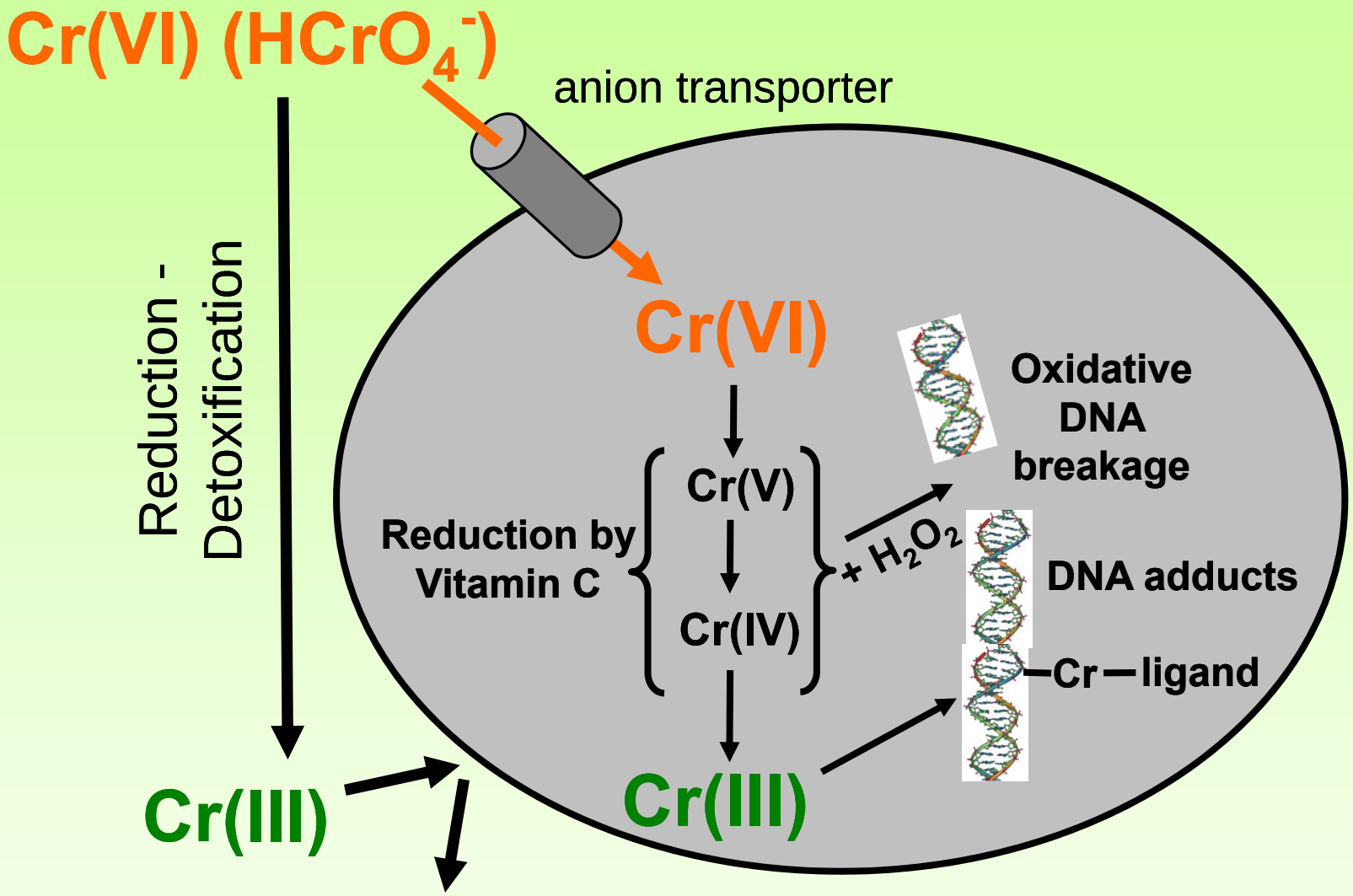
Toxicity and carcinogenesis of chromium



National Toxicology Program

USGS

Salnikow & Zhitkovich, 2008, Chem. Res. Toxicol.

Sources of chromium in soil and water

- **Anthropogenic**
  - **Industrial waste – often Cr(VI)**
    - Primary contaminant at over ½ of Superfund sites
    - Tanneries
    - Corrosion inhibitors
    - Metal plating
    - Wood Preservatives
  - **Fertilizers – Cr(III)**
    - Inorganic
    - Biosolids
- **Natural – Cr(III)**
  - **Ultramafic Rocks**

Leather Tanning – Morocco

Trace Metal Concentrations in Rock Phosphates (mg/kg)

Cr	Ni	As
1 - 331	1 - 125	1-21

EPA 747-R-98-003 (1999)

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Pellerin & Booker (2000) *Environmental Health Perspectives*

Naturally occurring Cr(VI) in the news

"Many cities in California have chromium 6 in their water at higher levels than Beachwood, says lawyer Stephen Lewis, who represents the plant's former owners. He argues that the chromium 6 in Beachwood's water could be naturally present or the result of activity unrelated to the plant."
–San Francisco Chronicle, 12-14-08

"Hexavalent chromium is not naturally occurring; though industry lobbyists and their PR machines have done a great job making you believe it does. Hexavalent chromium is pollution;…"
–Erin Brockovich, 2-15-2011, comment on CA Proposed Public Health Goal for Cr(VI) in drinking water (0.02 mg L^{-1})

"The Cr (VI) you identified in Honolulu's water supply, as is probably the case for every other city you tested, is not industrial "pollution" — it's Mother Nature."
–Roger Brewer, Ph.D., 6-7-2011, letter to the Editor in response to EWG report on Cr(VI) in municipal drinking water, Norman (OK) Transcript

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Naturally occurring Cr(VI) in groundwater–global distribution

World Health Organization
MCL = 50 μg L^{-1}

La Spezia, Italy

73 μg L^{-1}

Fantoni et al. (2002) *Env. Geol.*

United Arab Emirates

400+ μg L^{-1}

Wood et al. (2009) *Ground Water*

Mojave Desert , CA

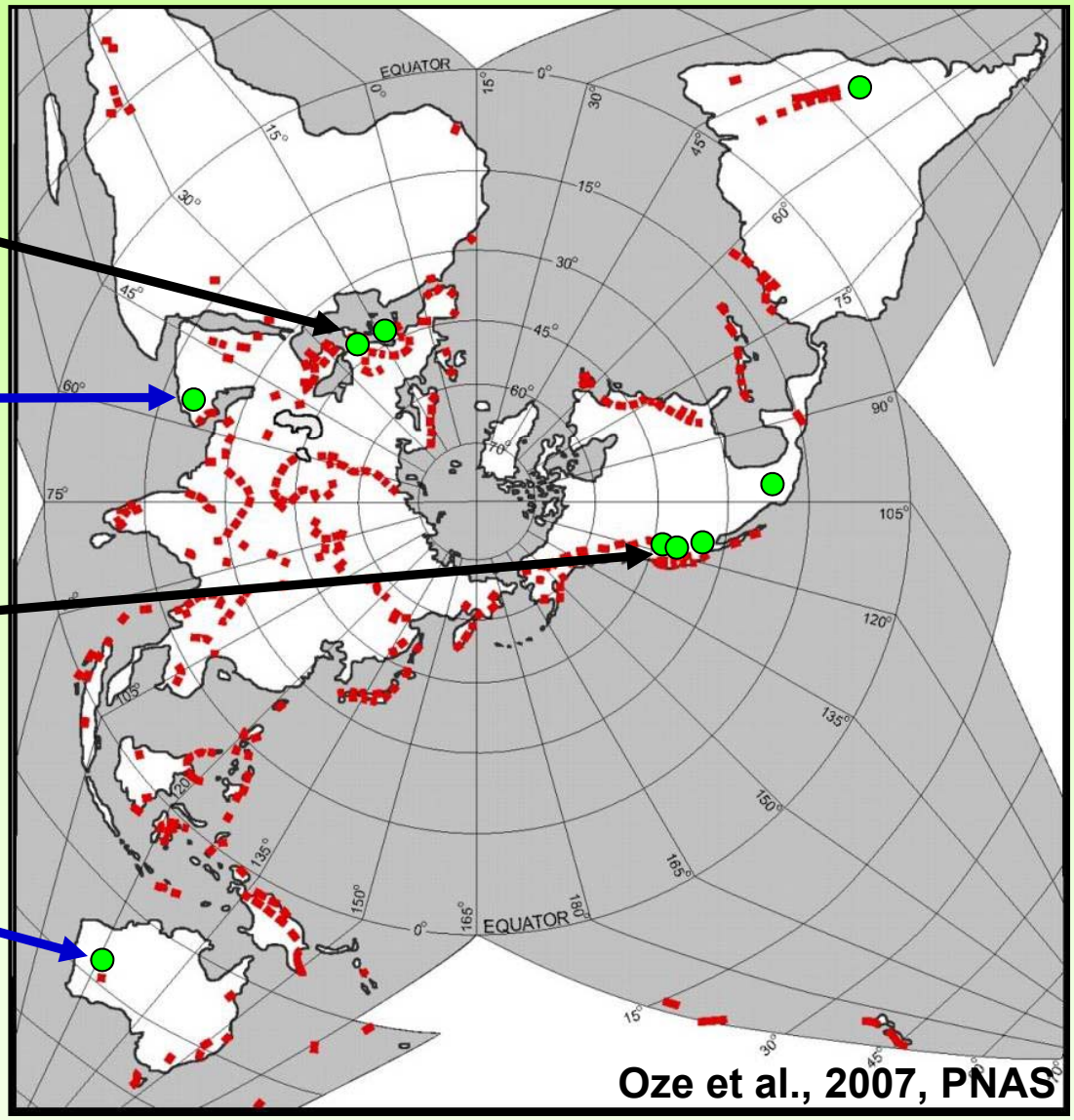
60 μg L^{-1}

Izbicki et al. (2008) Appl. Geochem.

Yilgarn Craton

430 μg L^{-1}

Gray (2003) Geochem. Explor. Environ. Anal.



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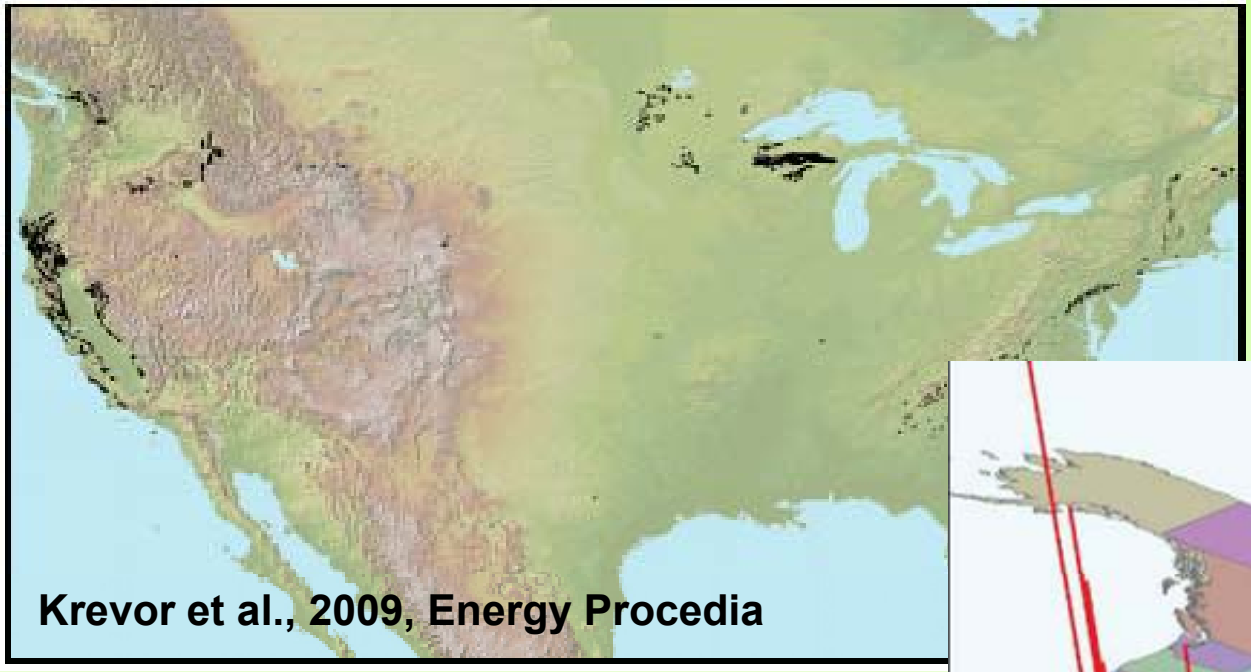
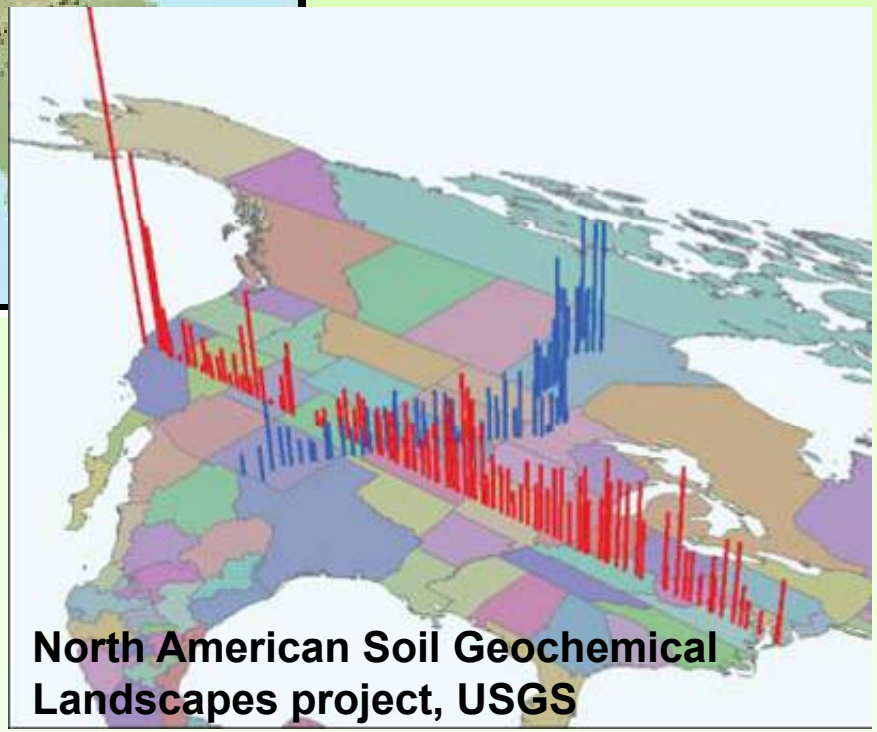
Cr concentrations northern California surface soils are extremely high



Krevor et al., 2009, Energy Procedia



North American Soil Geochemical Landscapes project, USGS

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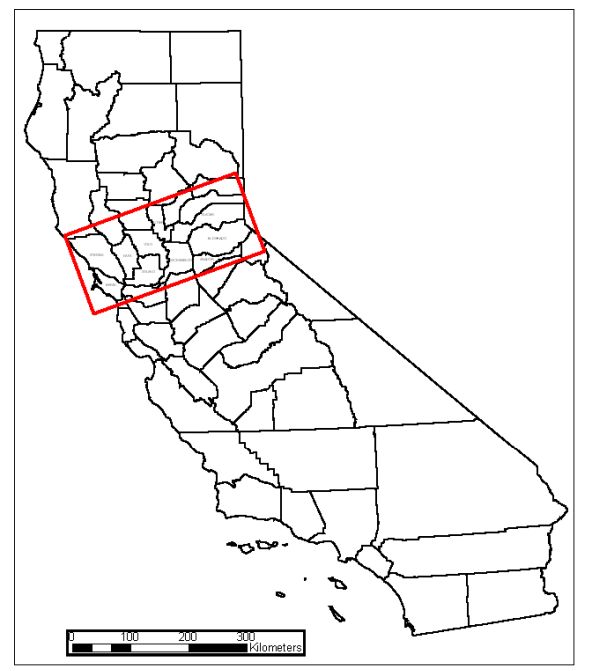
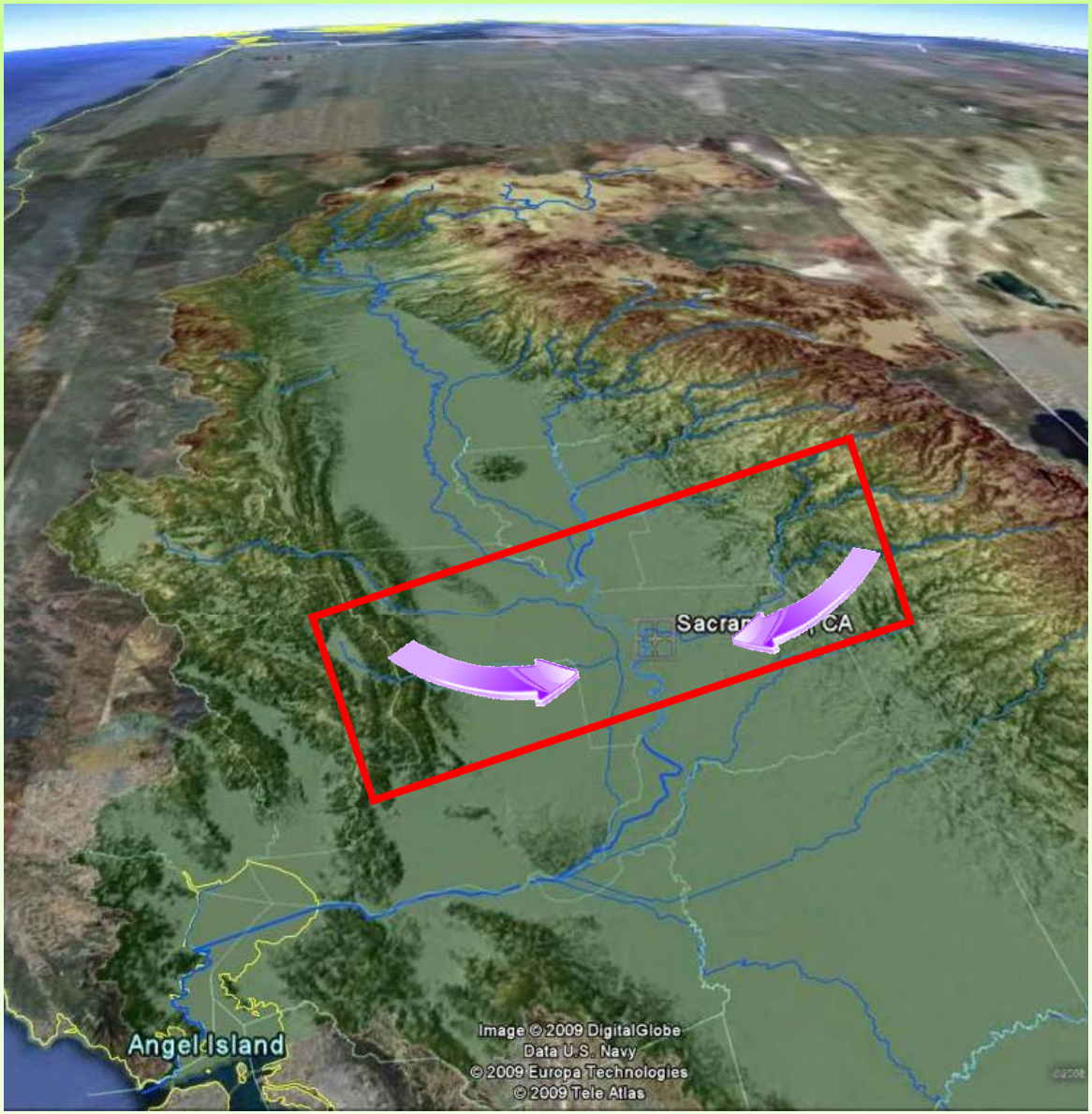
Regional-scale soil geochemistry of northern California





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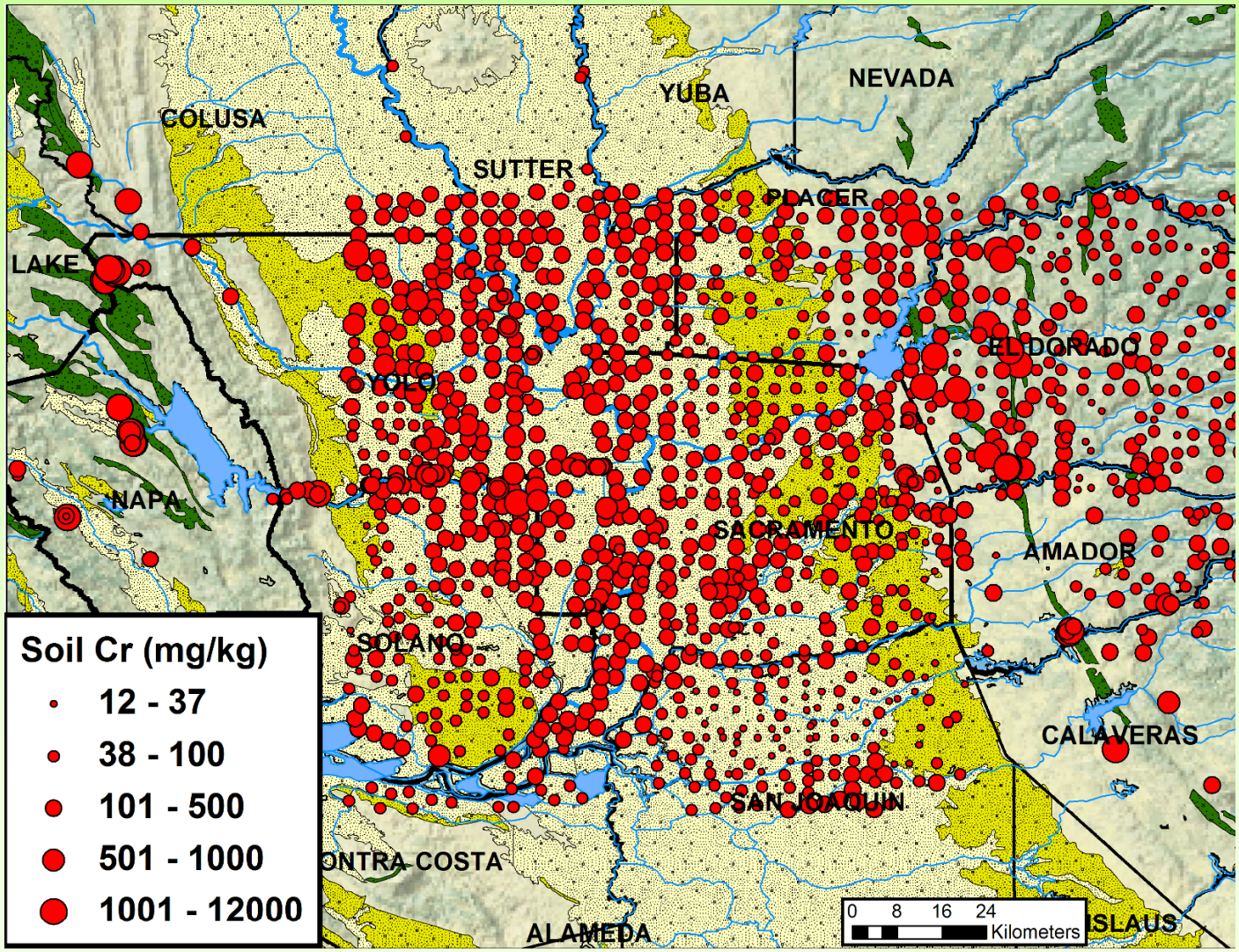

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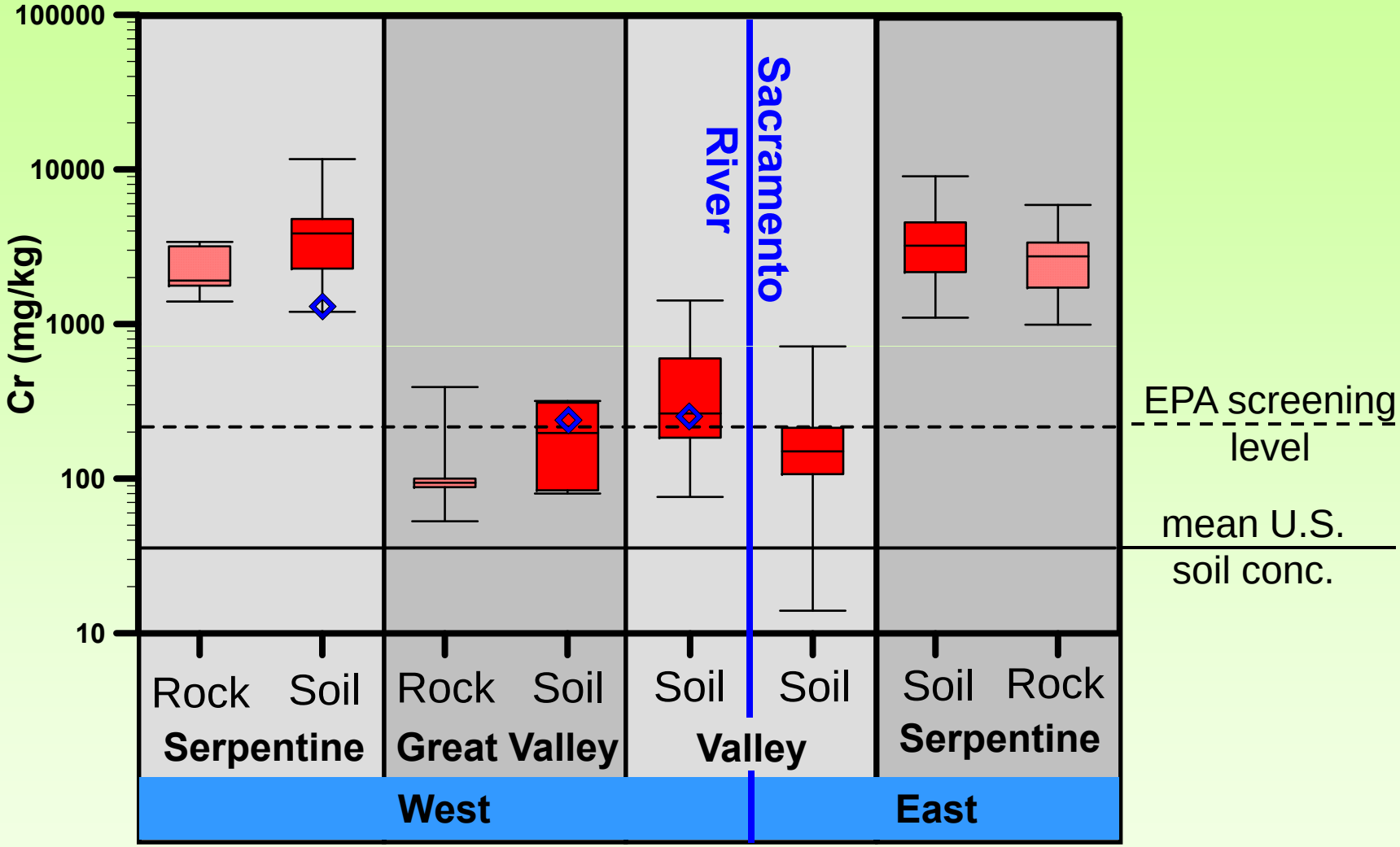
Morrison et al., 2009, Appl. Geochem.

Rock and surface soil total Cr concentrations



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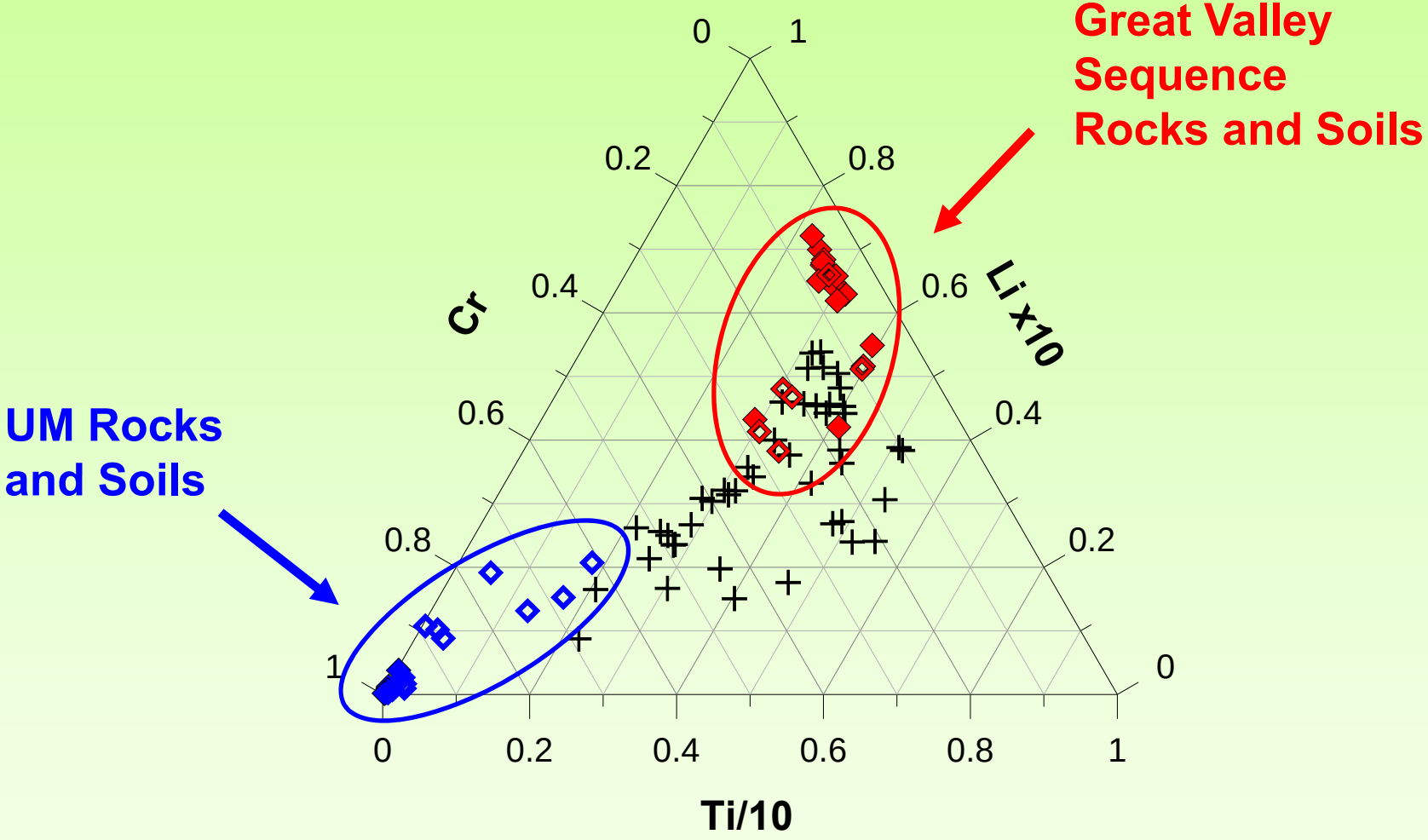
Morrison et al., 2009, Appl. Geochem.

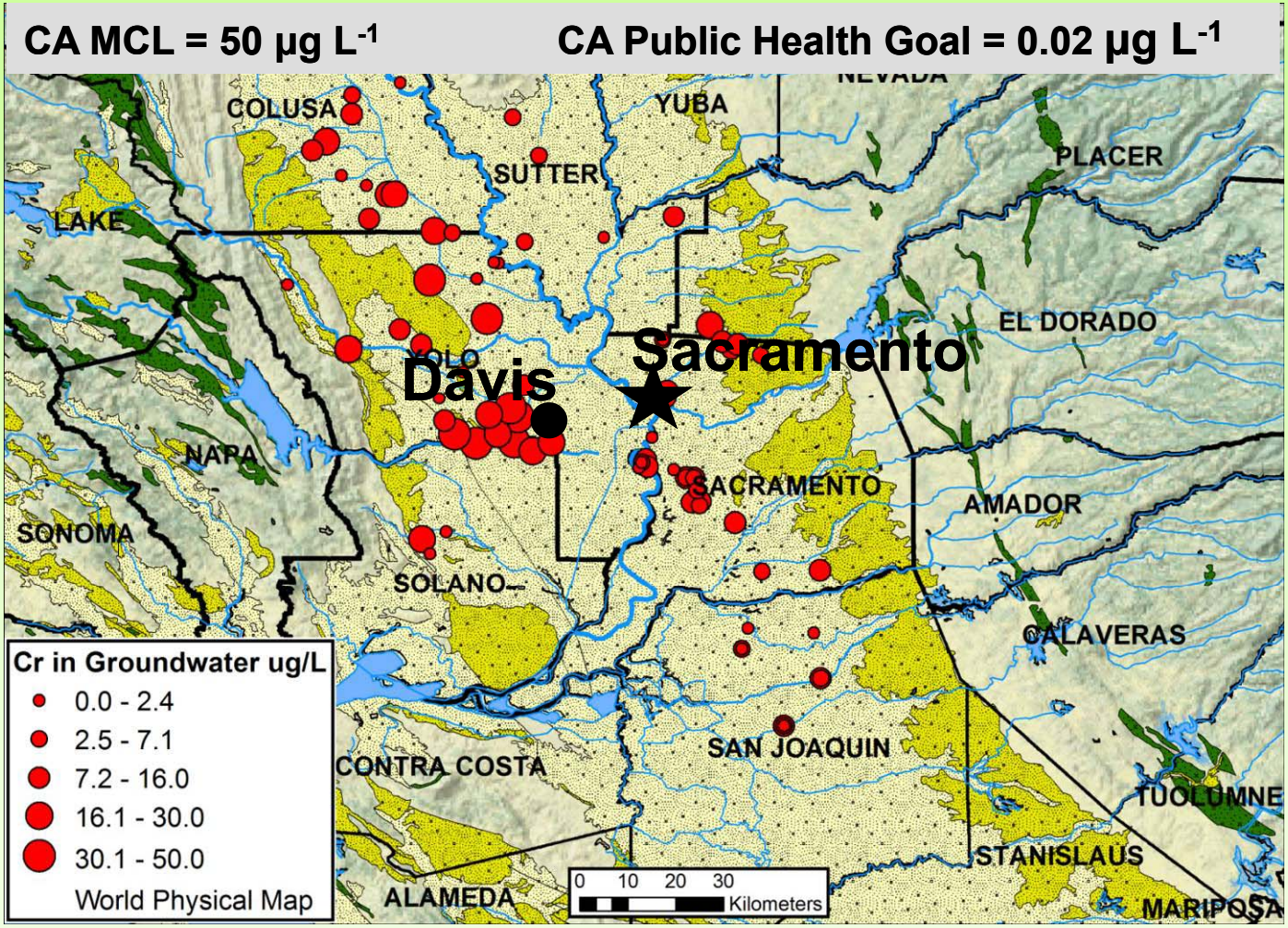
Contributions of source materials to western valley soils



USGS

Morrison et al., 2009, Appl. Geochem.

Cr(VI) in valley groundwater is a health concern



Morrison et al., 2009, Appl. Geochem.

Wanty et al., 2009, Appl. Geochem.

Dawson et al., 2008, USGS Data Series

USGS

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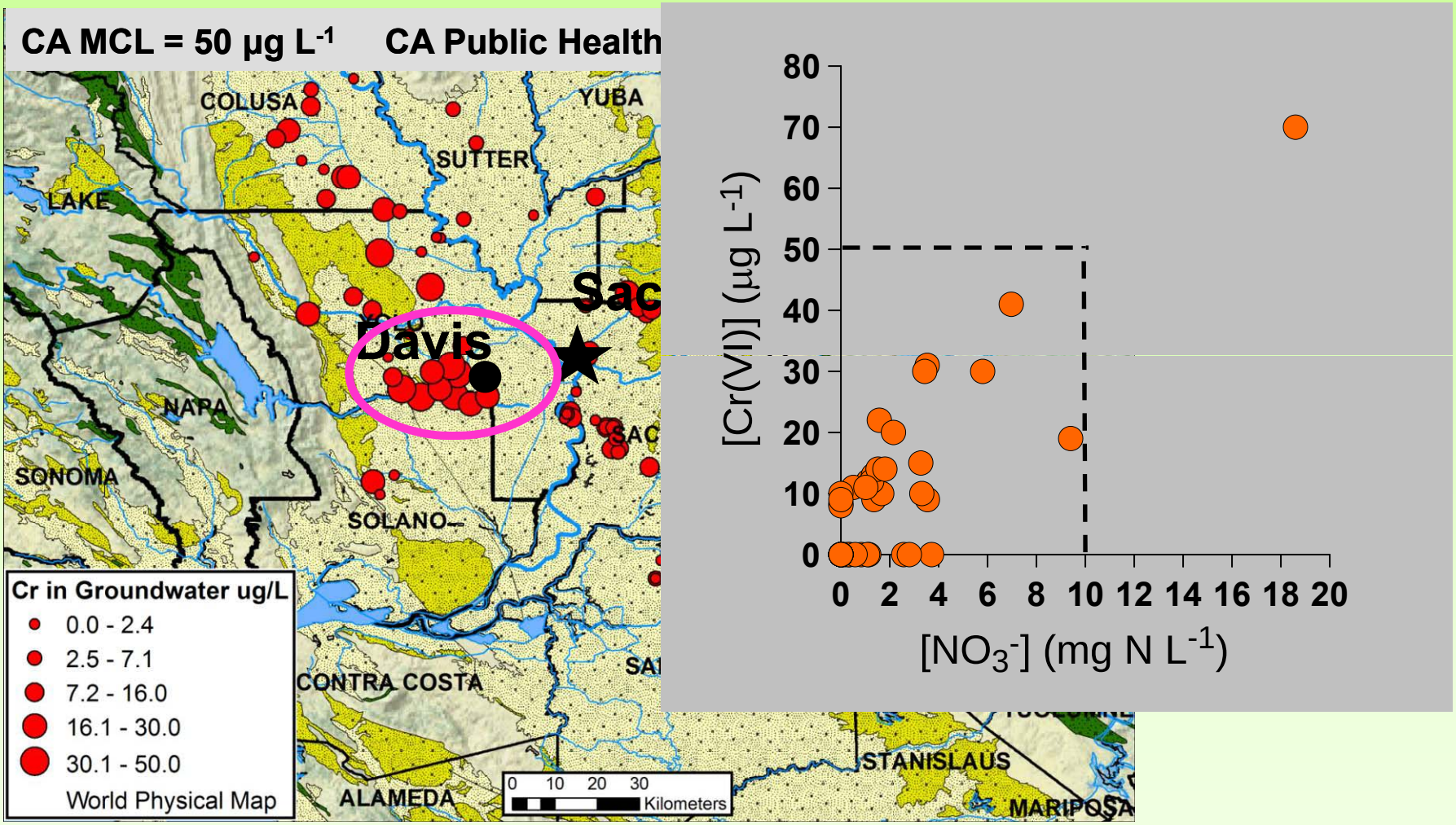

Morrison et al., 2009, Appl. Geochem.

Wanty et al., 2009, Appl. Geochem.

Dawson et al., 2008, USGS Data Series

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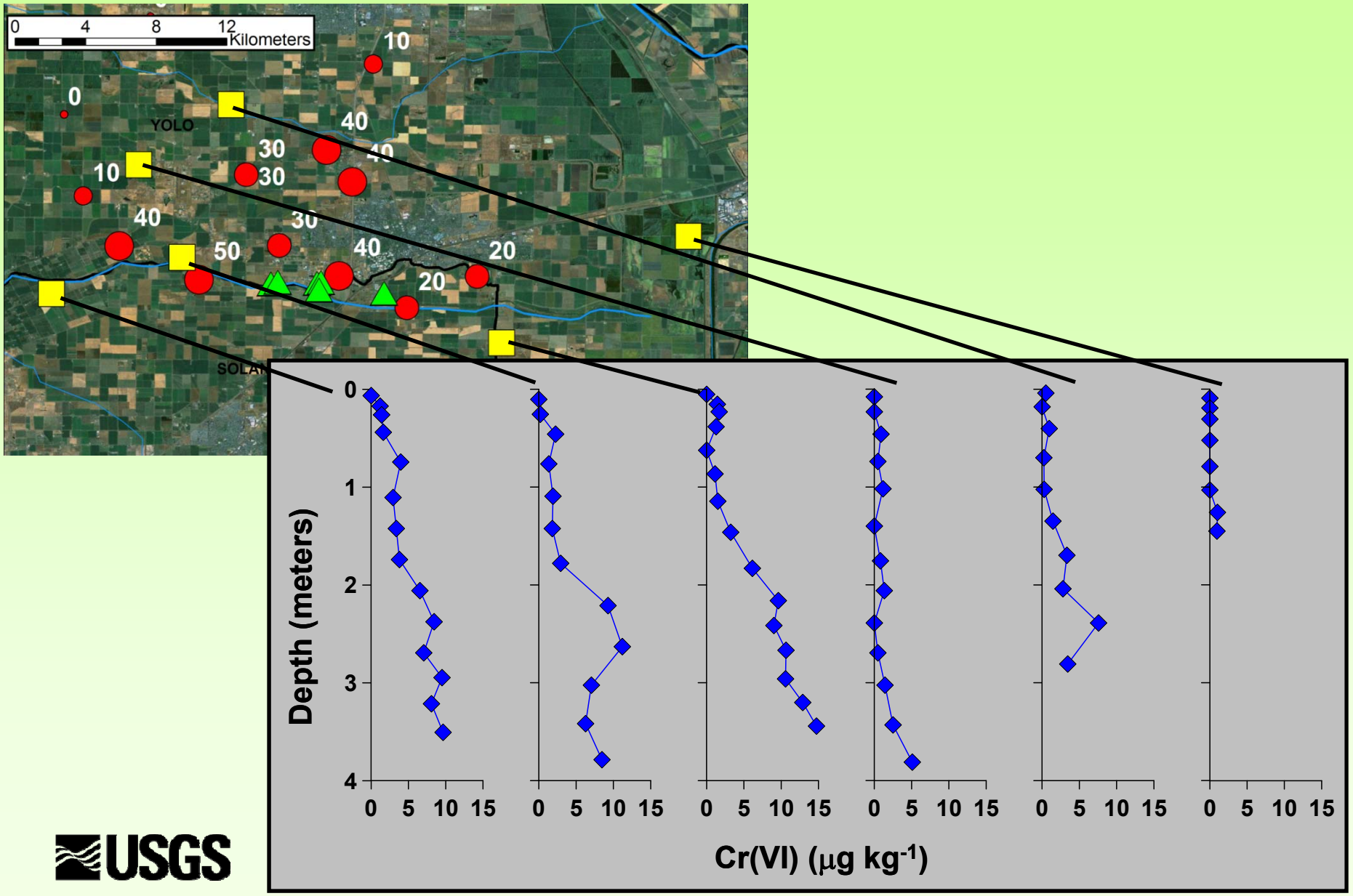
Cr(VI) increases with depth in shallow soils



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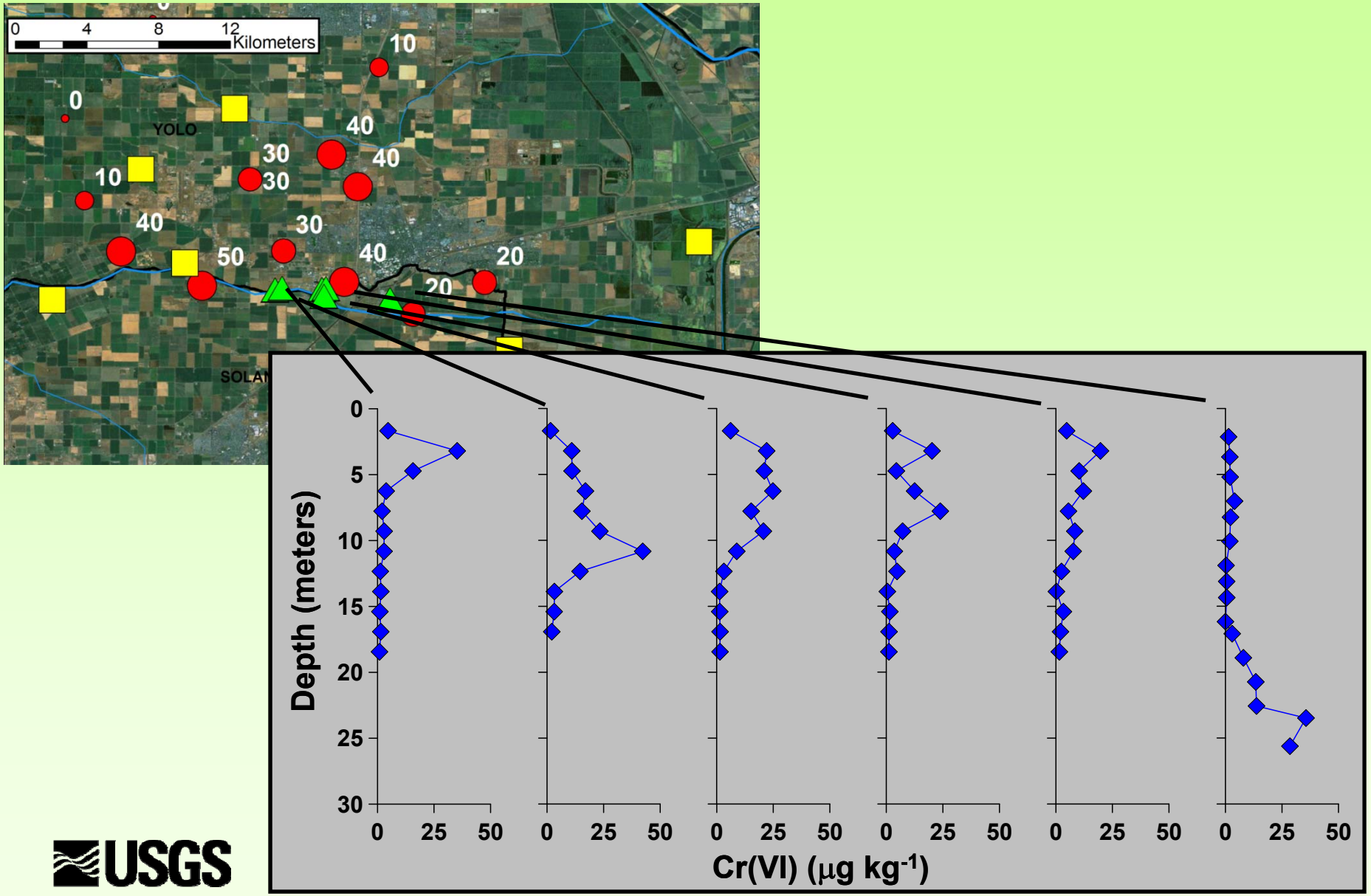
Mills et al., 2011, Appl. Geochem.

Cr(VI) is elevated in deeper soils/sediments



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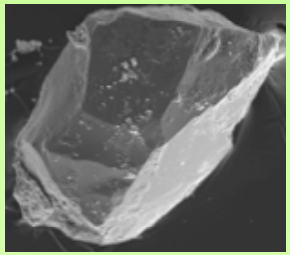
Mills et al., 2011, Appl. Geochem.

Chromium cycling in natural environments



Chromite ($FeCr_2O_4$)

dissolution

Cr(III)

e.g. $Cr(OH)_3$, $CrOH^{2+}$

Cr(VI)

e.g. $HCrO_4^-$, CrO_4^{2-}

Mn Oxides

- Fe^{2+}
- Organic Carbon
- Sulfides

dissolution/ precipitation

sorption

e.g. $Cr(OH)_3(s)$

clays and oxides

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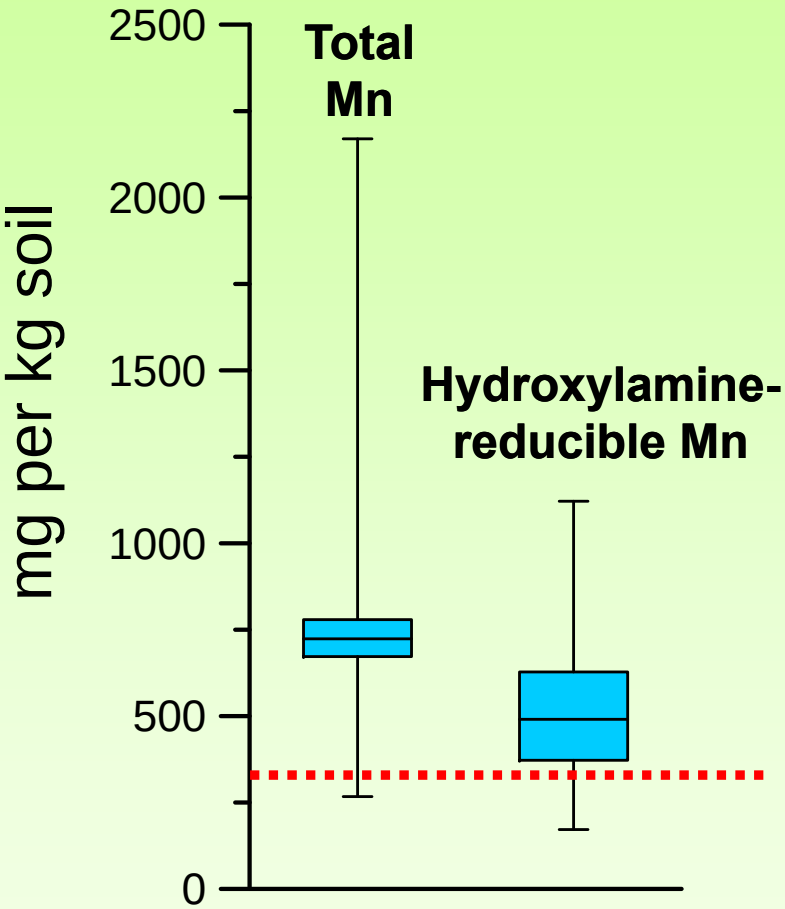
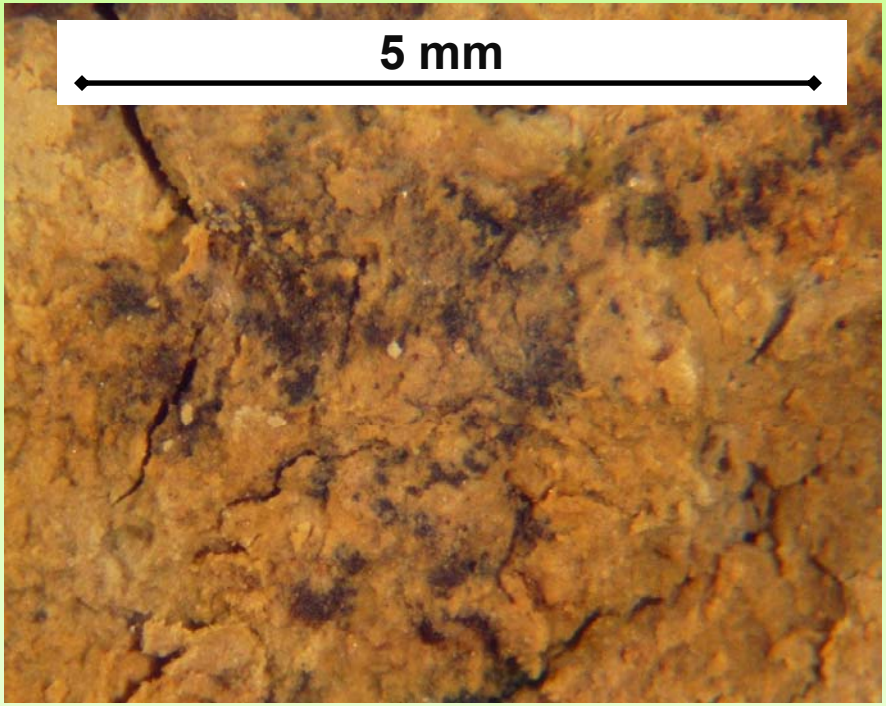
Mn oxides are abundant in valley soils



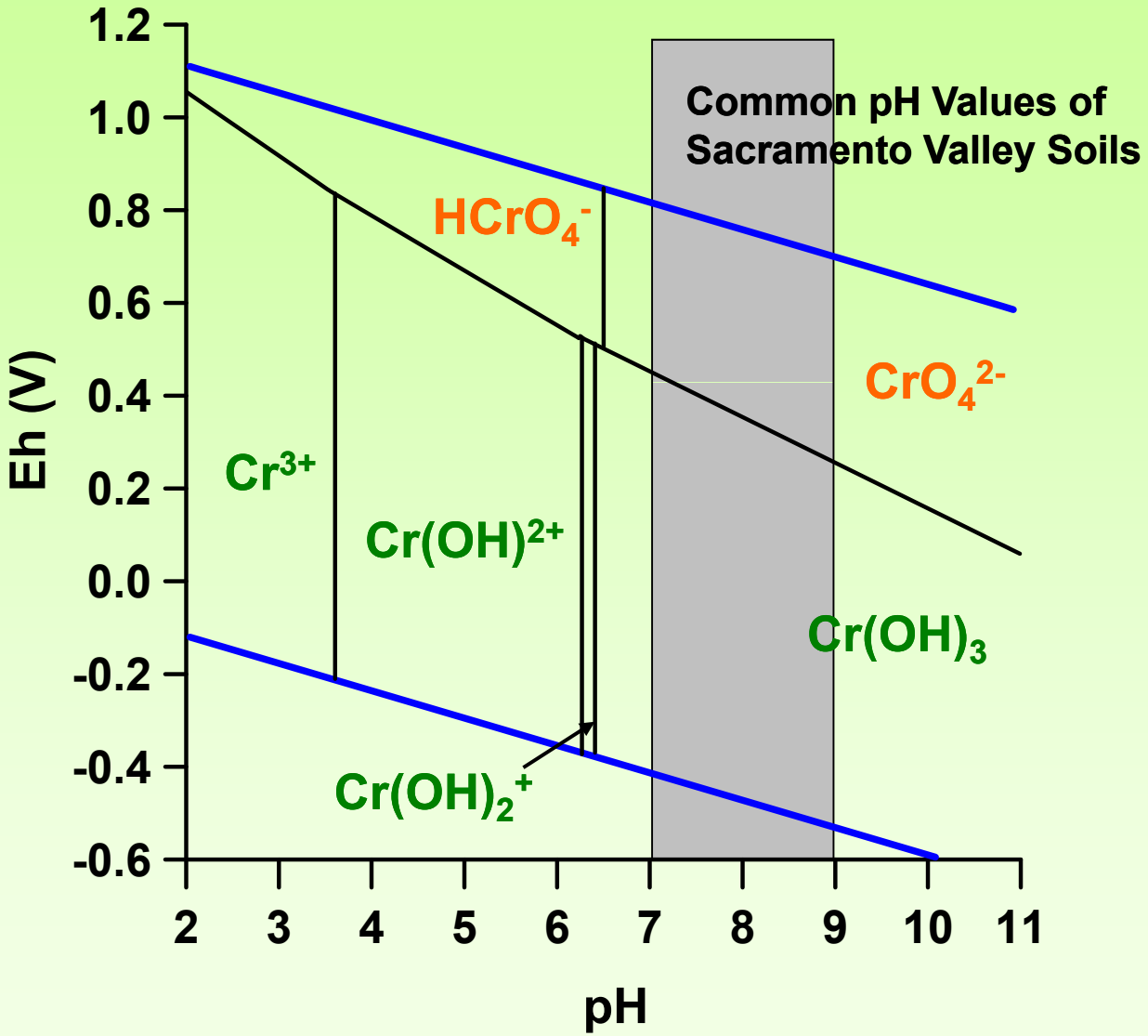


Geometric Mean for Total Mn in U.S. surface soils (Shacklette and Boerngen, 1984)

USGS

Mills et al., 2011, Appl. Geochem.

Soil pH is a major control on Cr cycling



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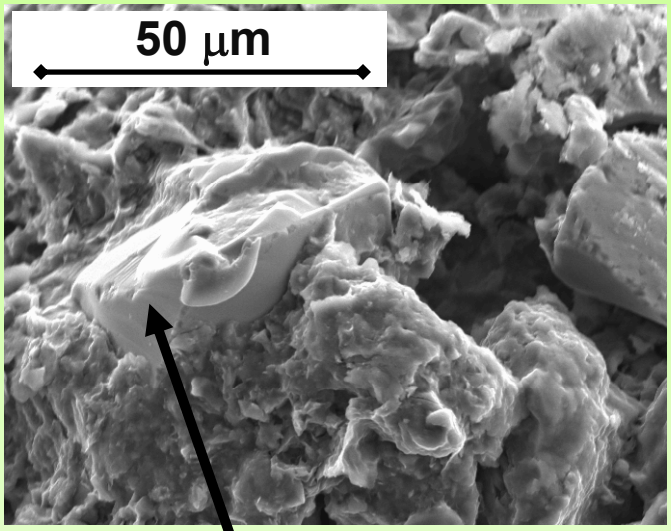
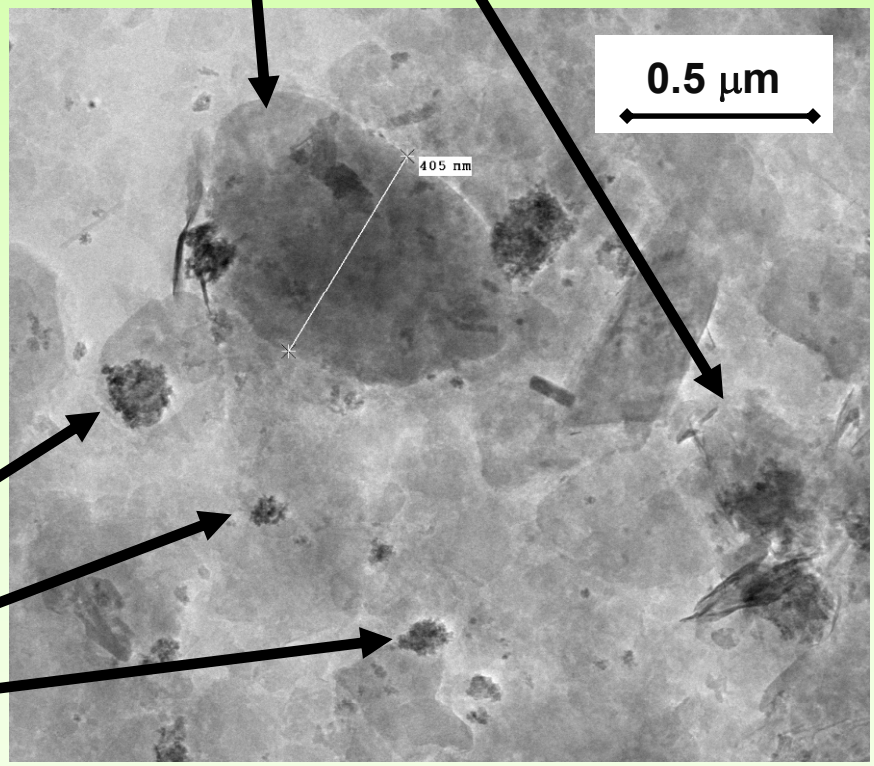
Several distinct residences of Cr in valley soils



Chromite
($FeCr_2O_4$)

Smectite/Illite
(~300 ppm Cr)



Nano-crystalline
Iron oxides
(300-500 ppm Cr)

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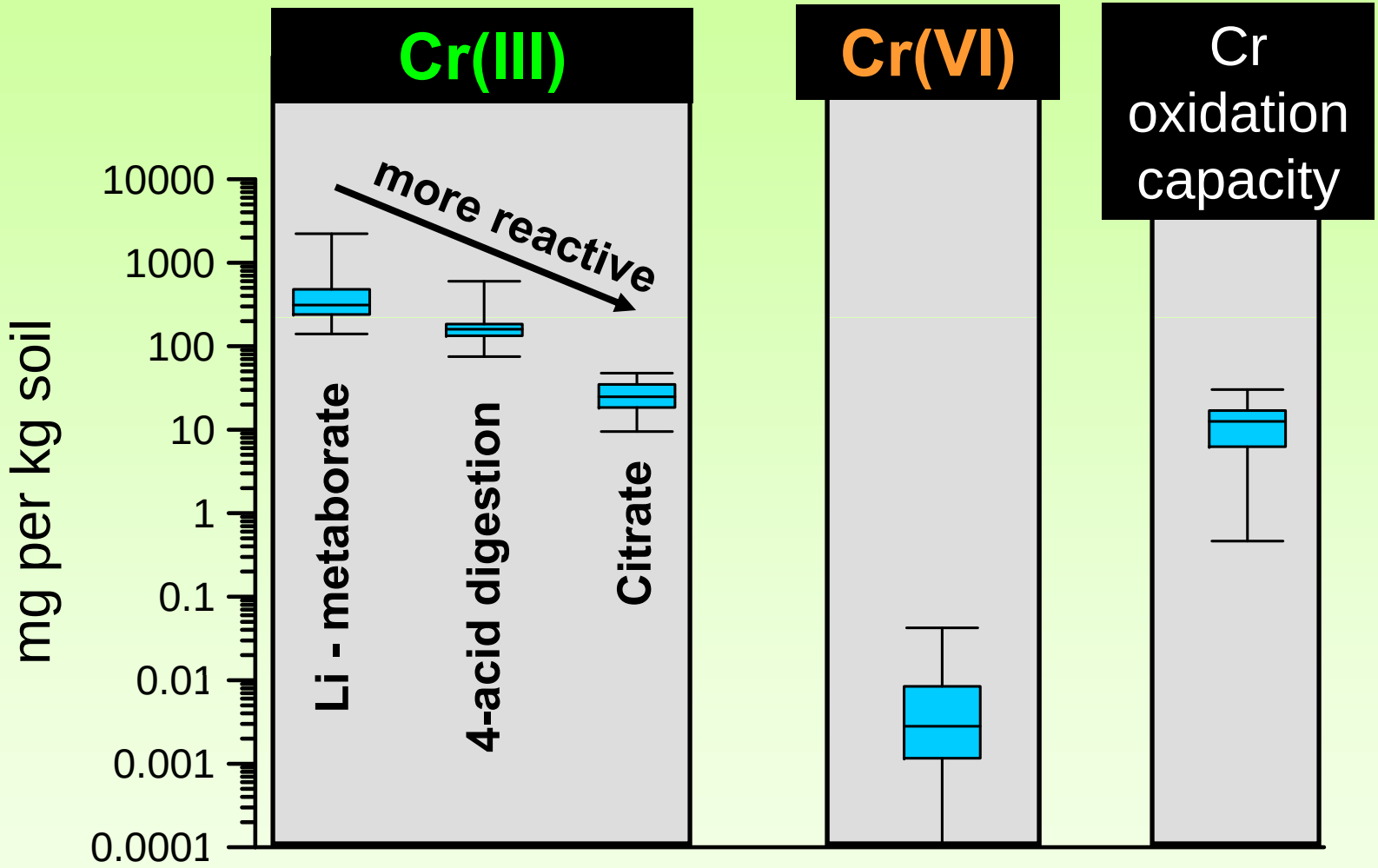
Morrison, 2010, Ph.D. Thesis – Colorado School of Mines

Concentrations of different Cr residences vary widely



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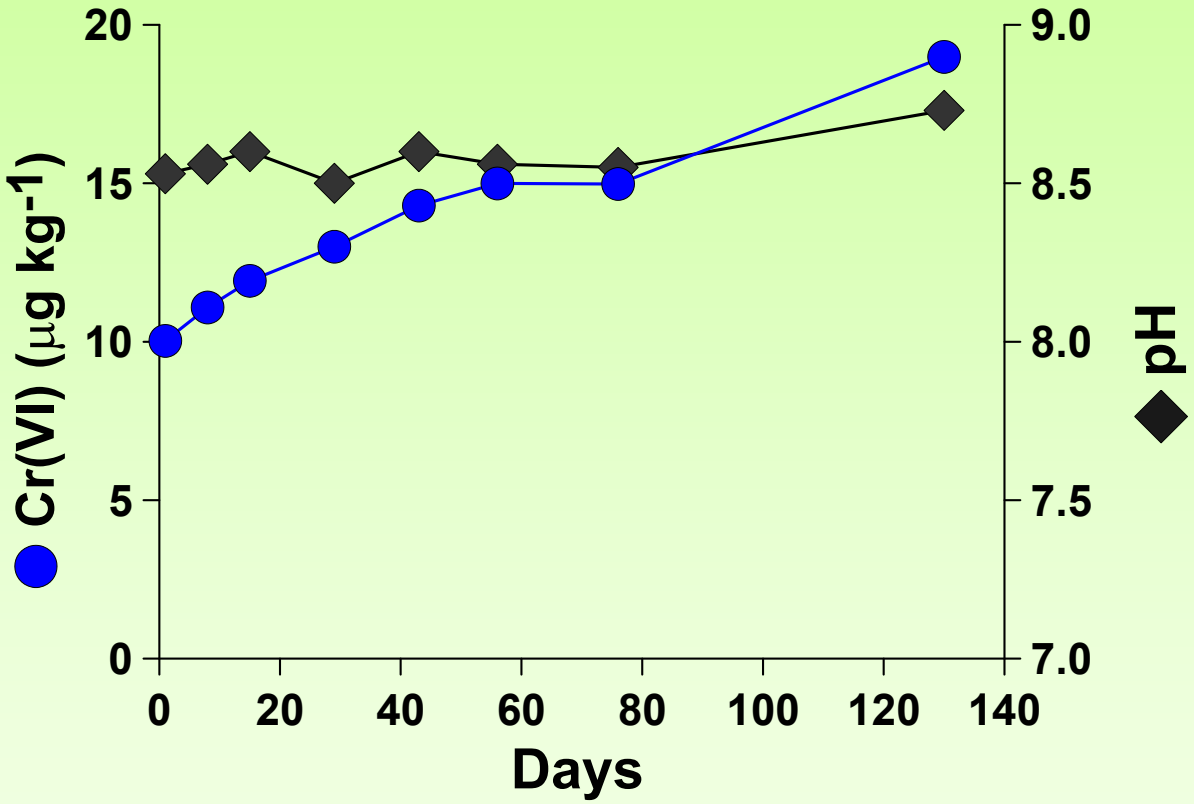
Mills et al., 2011, Appl. Geochem.

Cr(VI) generated during incubation of subsoil



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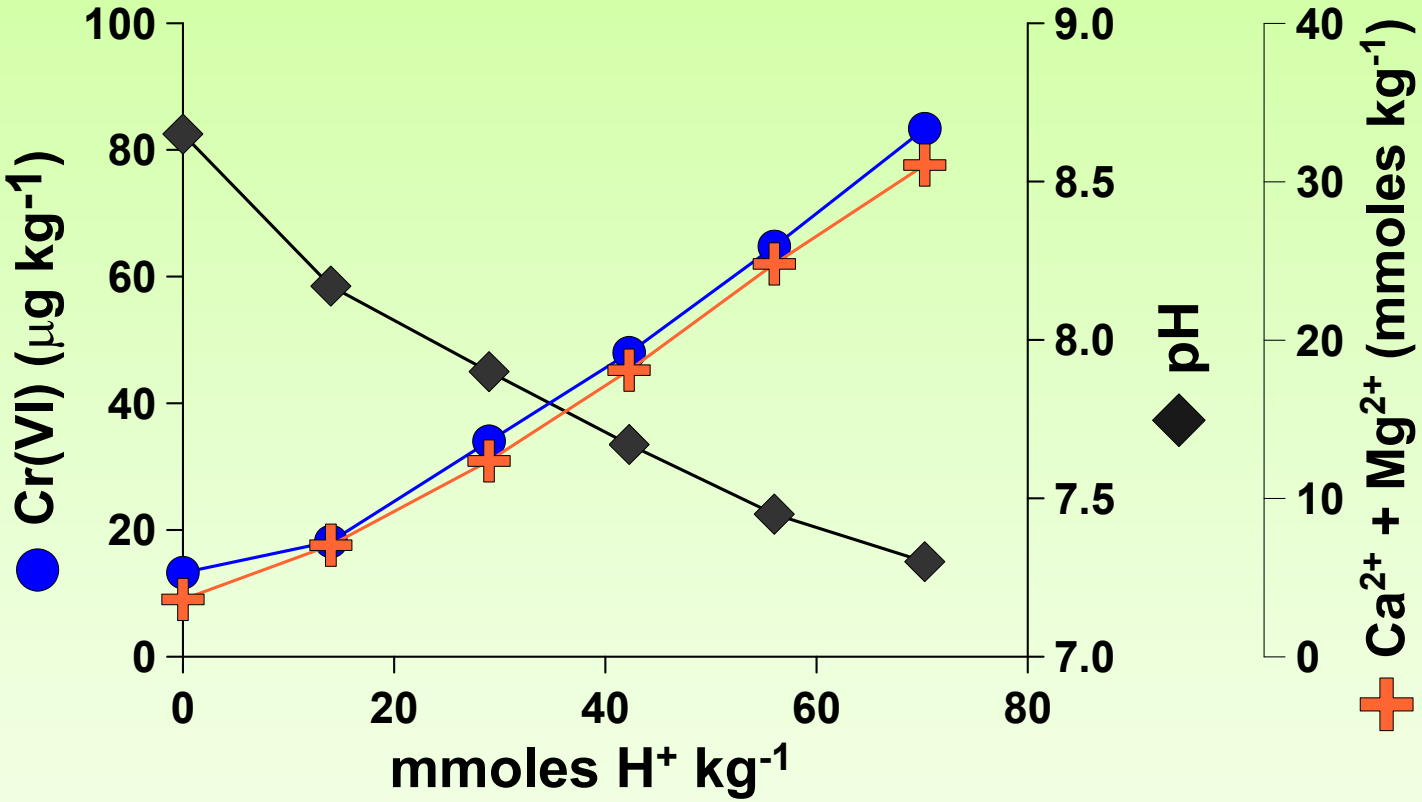
Mills et al., 2011, Appl. Geochem.

H^+ – Cr^{3+} exchange results in enhanced Cr(VI) generation

Soils ammended with HCl and incubated for two weeks



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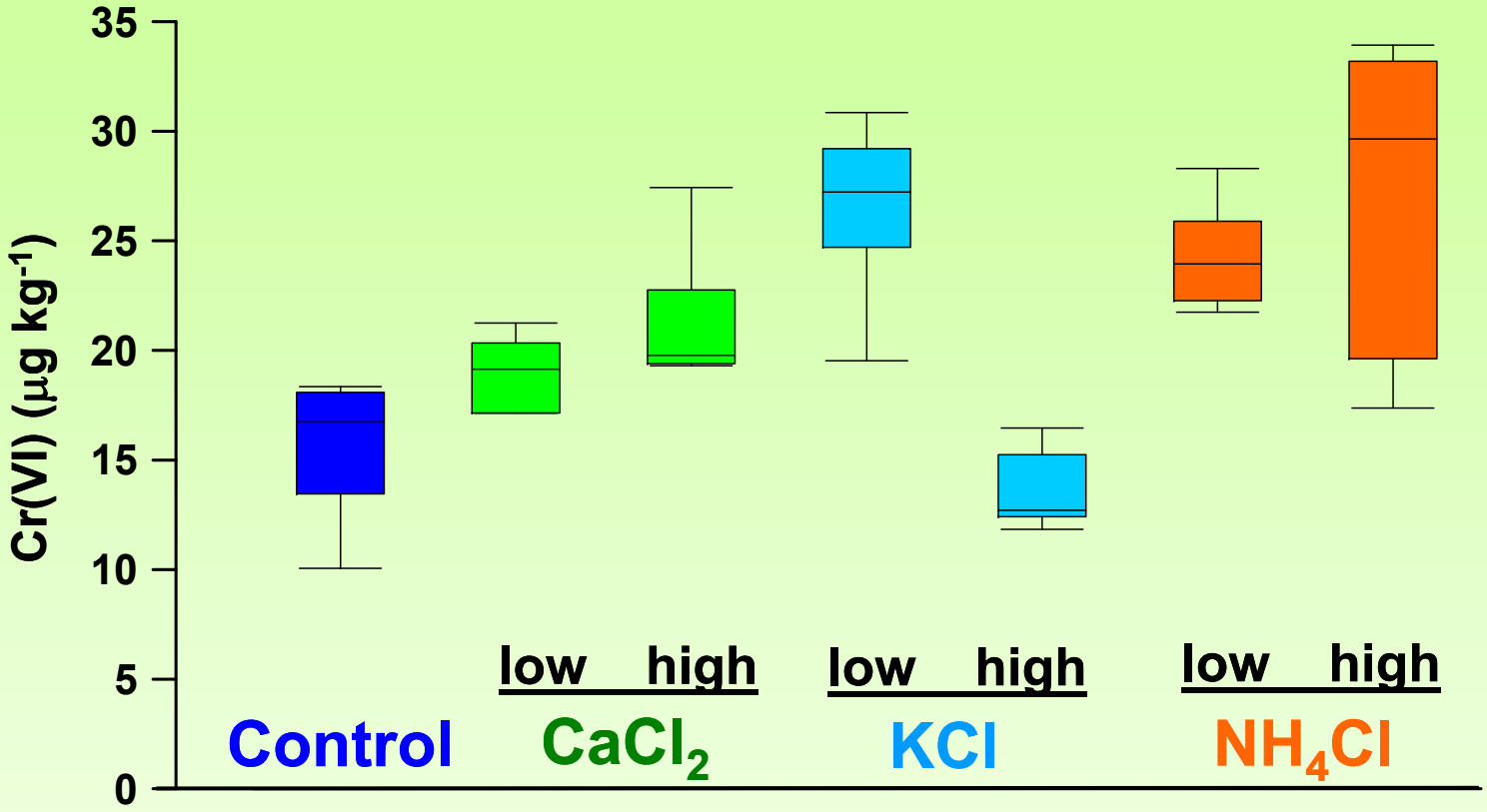
Mills et al., 2011, Appl. Geochem.

Other salt additions affect Cr(VI) generation



Low = 45 mequivalents kg^{-1} **High=128 mequivalents kg^{-1}**

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Multiple effects of $(NH_4)_2SO_4$ on Cr(VI)

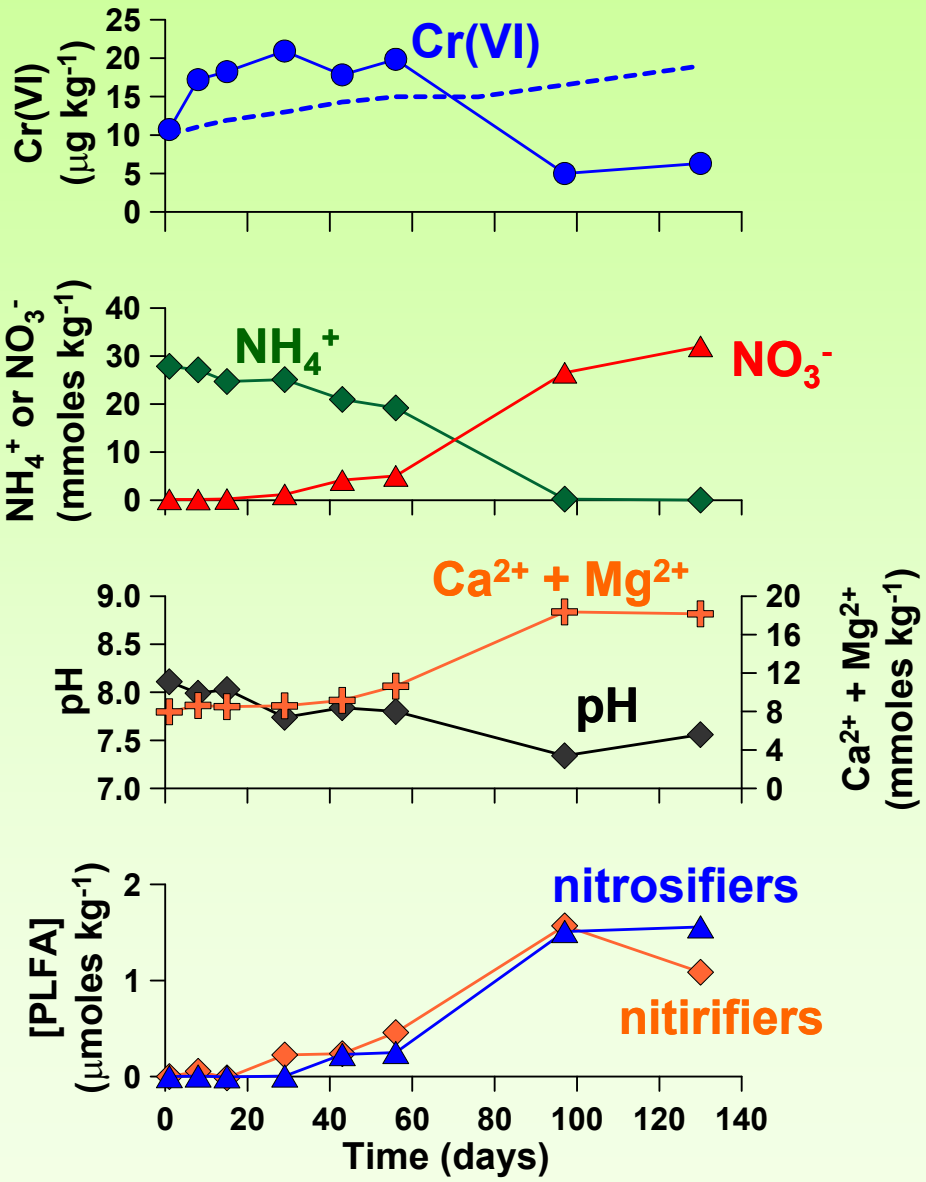
70 mequivalents NH_4^+ kg^{-1}

NITRIFIERS

$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2\ H^+ + H_2O$

NITROSIFIERS

$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$



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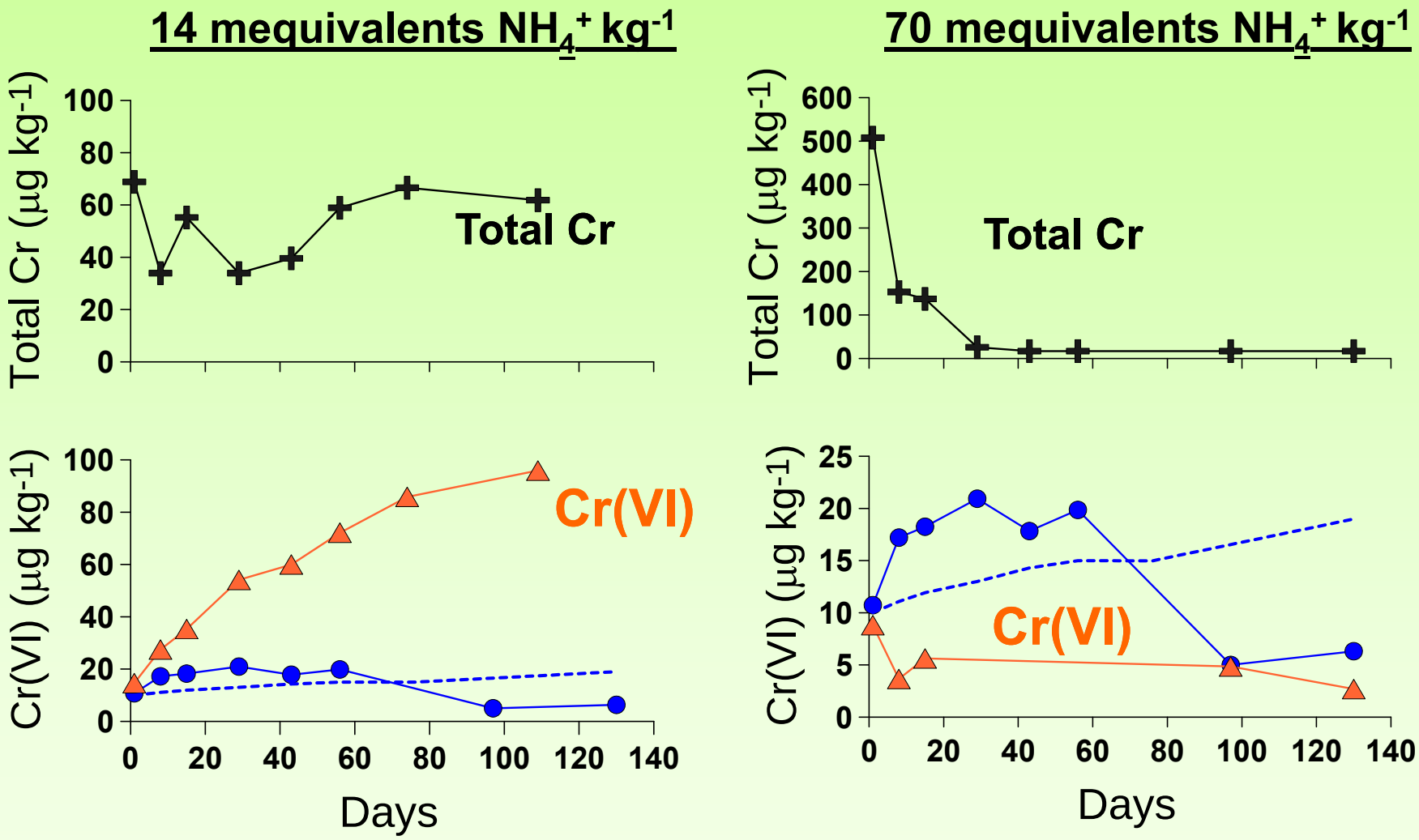
Cr(VI) generation from Cr(III) in ammonium polyphosphate fertilizer



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Conclusions

- Sacramento valley soils are elevated in Cr and Mn due to weathering of ultramafic rocks in surrounding mountains
- Natural Cr is mostly present as Cr(III) in chromite
- Natural Cr(VI) generation occurs but is kinetically limited by Cr(III) mobility
- Addition of protons and other cations increases Cr(VI) generation rates
- Higher concentrations of some cations/anions appear to shut down Cr(III) oxidation mechanism
- Organic carbon produced by nitrifying bacteria can reduce Cr(VI)
- Oxidation of Cr(III) in ammonium polyphosphate occurs faster than oxidation of natural Cr(III)

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Acknowledgements

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