Speciation Methods Used to Assess Potential Health Effects of Toxic Metals in Environmental Materials

By Ruth E. Wolf, Suzette A. Morman, and Geoffrey S. Plumlee

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Speciation Methods Used to Assess Potential Health Effects of Toxic Metals in Environmental Materials

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Abstract

Assessing potential exposures to toxic metals or metalloids such as arsenic and chromium in environmental materials is important in protecting public health. The chemical form of an element in, or released from, a material is also important, since some forms, such as Cr(VI), are more toxic than others, for example, Cr(III). We have used a variety of procedures to assess potential exposures to hexavalent chromium in ash and burned soils from October 2007 southern California wildfires. Synthetic lung-fluid and de-ionized water extractions simulate release in the lungs and potential environmental releases due to rainfall. Extracts were analyzed for specific chromium and arsenic species using HPLC-ICP-MS methodology. Results indicate that the highly oxidizing environment in wildfires promotes some chromium conversion to Cr(VI), and that the caustic alkalinity of ash enhances Cr(VI) release and stability in lung fluids and rainfall.

Introduction

This Open-File Report contains illustrative materials, in the form of a PDF file of a PowerPoint slide presentation, used for an oral presentation given at the 11th Annual Force Health Protection Conference (*https://usachppm.apgea.army.mil/fhp/*) held August 9–15, 2008, in Albuquerque, N. Mex. The conference is sponsored by the U.S. Army Center for Health Promotion and Preventative Medicine (USACHPPM) and is focused on providing tools to anticipate, recognize, evaluate, and counter occupational and environmental health and disease threats affecting the health, fitness, and readiness of America’s worldwide deployed forces. This presentation was given in the Science and Technology Track of the conference, which focuses on current research and new and emerging technology to protect the health and performance of deployed forces and the associated military community, including advances in medical geology.

The material presented in the report provides a brief overview why speciation analysis (determining the chemical form of an element) is important when determining the possible effects of exposure to potentially toxic elements on human health, as well as some areas of research currently underway at the U.S. Geological Survey (USGS). One such area of research includes work on an analytical method to determine the inorganic forms of arsenic, As(III) and As(V); selenium, Se(IV) and Se(VI); and chromium, Cr(III) and Cr(VI), in waters, soil and fire ash extracts, and simulated biological fluids. The method discussed in the presentation is an adaption of a previously published method (Wolf and others, 2007) for the determination Cr(III) and Cr(VI) in waters and soil extracts. The method consists of the separation of the individual species using high performance liquid chromatography

(HPLC), under the same chromatographic conditions, followed by detection using inductively coupled plasma mass spectrometry (ICP-MS) instrumentation. Method validation and performance data is presented in the slides as well as some operational considerations in performing analyses using this method.

In simple terms, medical geology is an emerging science that studies the links between the geologic environment and potential impacts on human health. Example data is presented for chromium showing the relationship between the underlying geology of a study area in California and the resulting mean observed soil and water chromium levels. Also presented are some of the potential processes by which naturally-occurring chromium from the weathering of rocks and soils could be converted to the more toxic hexavalent, Cr(VI), form.

The presentation also discusses the growing concern over the number and frequency of wildfires in recent years in the United States. Wildfires can have negative impacts on human and ecosystem health. In regards to impacts on human health, there are immediate effects due to exposure to gases and particulates released during a fire. There are also post-fire and long-term effects that can result from exposure to potentially caustic dusts that can raise soil and water pH levels and possible exposure to chemicals and metals liberated by the fire. These effects may be of particular concern to USACHPPM scientists as military personnel are often called upon to assist in fighting major forest fires. For purposes of illustration, data from ash and burned soils from about 28 sites in southern California wildfire areas (Harris, Witch, Ammo, Santiago, Canyon, and Grass Valley) collected by USGS in November 2007 were presented. USGS researchers have applied a wide variety of analytical methods to these samples with the goal of helping to identify characteristics of the ash and soils from wild land and suburban burned areas that may be of concern for their potential to adversely affect water quality, human health, endangered species, and debris-flow or flooding hazards. These studies are part of the Southern California Multi-Hazards Demonstration Project, and preliminary findings have been discussed by Plumlee and others (2007).

Several tables of results taken from Plumlee and others (2007) are presented in the slides as well as maps depicting the fire and sampling locations. The slides also contain preliminary results for additional testing that was performed on sample leachates to determine the chemical form or speciation of the potentially toxic elements of interest present. In addition to the de-ionized water leaching method discussed by Hageman (2007), the samples were also leached using a near-neutral pH simulated lung fluid (Plumlee and others, 2006) to model potential chemical interactions of inhaled particles with fluids lining the respiratory tract.

The preliminary results presented in the slides show that in the de-ionized water leachate, all of the chromium present in the fire-impacted ash and soils is in the form of Cr(VI), and the resulting high pH tends to stabilize Cr(VI) from reduction to Cr(III). Analysis of the simulated lung fluid leachates indicates that the predominant form of chromium present in the near-neutral pH of lung fluid would be Cr(VI), which is of concern due to the high possibility of inhalation of the small ash and soil particulates, particularly by fire or restoration crews. The presence of Cr(VI) in leachates from the fire ash samples is of particular concern due to its known toxicity and carcinogenicity (Agency for Toxic Substances and Disease Registry, 2008). In the future, the collection of air-monitoring data, including particulates on air filters that may be analyzed for Cr(VI) content, would be useful in assessing the potential impact of the Cr(VI) present in fire-impacted soils and ash on the health of fire-fighting and restoration crews, including active duty military personnel, who are often called upon to assist in wild fire suppression efforts.

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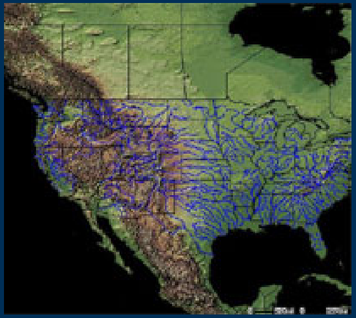
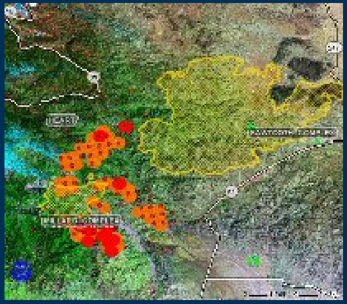
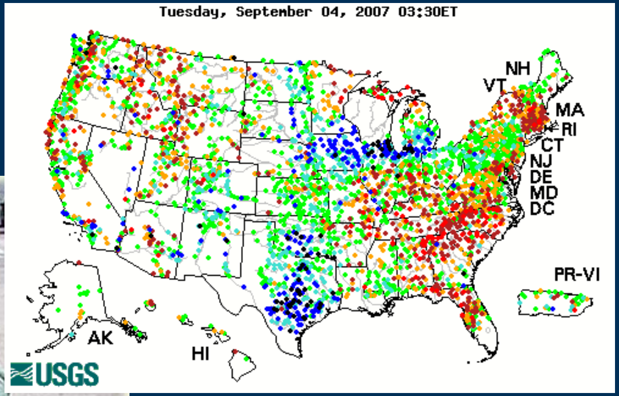




- Multi-disciplined science organization (Dept. of Interior) dedicated to unbiased study of the landscape, natural resources, and natural hazards (10,000 staff in 400 offices)
  - Biology: Trends in biological resources, invasive species
  - Geography: Landsat5, land remote sensing
  - Water: Water resources, water quality (NAQWA), toxics
  - Geospatial Information: National maps (www.geodata.gov)
  - Geology: Energy & mineral Assessments, geologic hazards, astrogeology, earth surface dynamics, coastal and marine geology
- Provides data that agencies use to make land and resource use decisions
  - Bureau of Land Management (BLM)
  - Environmental Protection Agency (EPA)
  - National Forest Service (NFS)
  - National Park Service (NPS)
  - State and local agencies



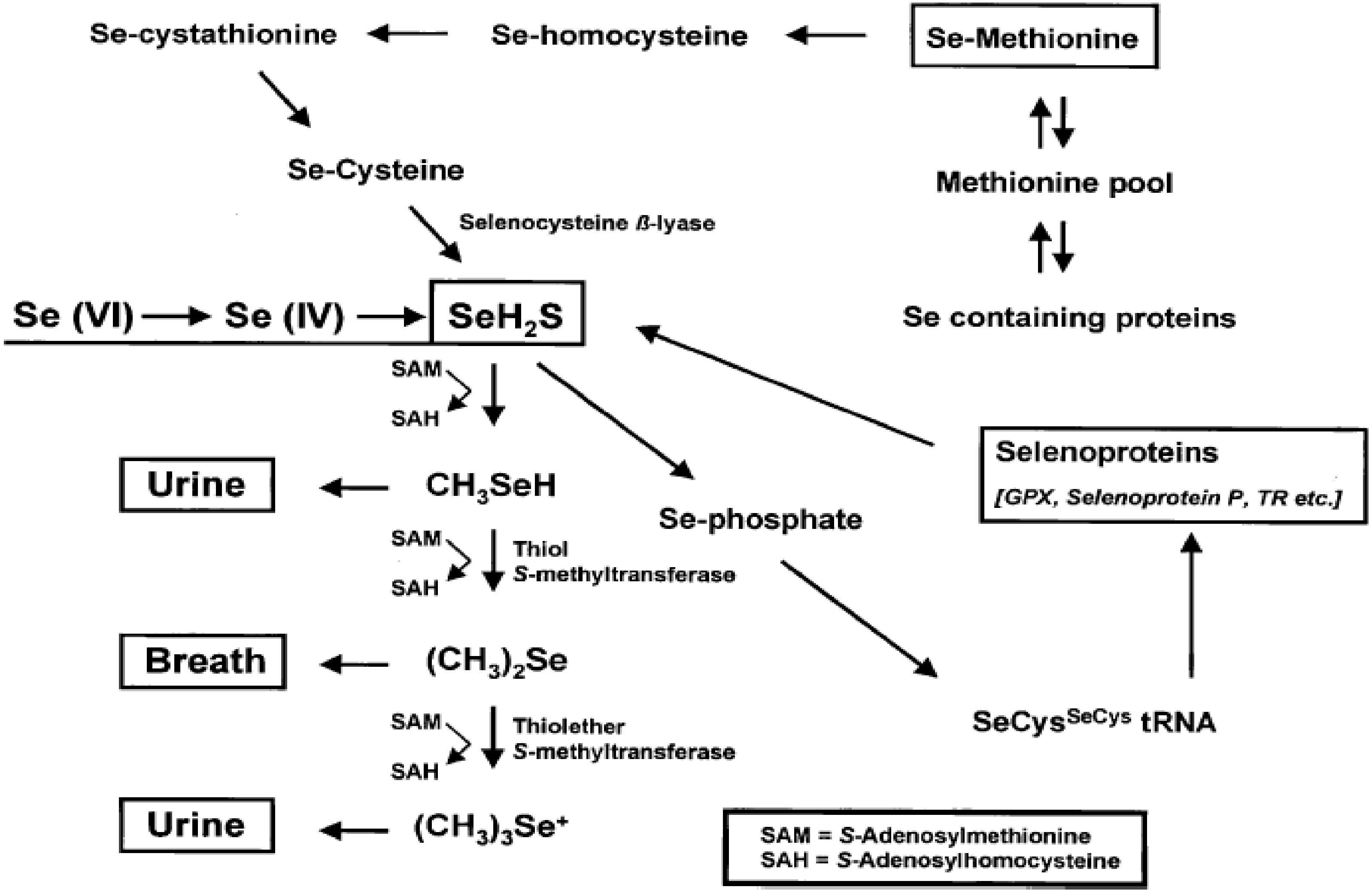
What is (chemical) speciation?

- The determination of the chemical form of an element
  - Inorganic vs. organic forms
    - Hg^0 vs. CH_3Hg (methyl mercury)
    - As(V) vs. trimethylarsonioacetate (arsenobetaine – AsB)
    - Se(VI) or selenite vs. selenoproteins, selenocystine, selenomethionine
  - Oxidation state
    - As(III) vs. As(V)
    - Cr(III) vs. Cr(VI)
    - Se(IV) vs. Se(VI)

Why is speciation important?

- Allows assessment of toxicity and bioavailability
  - Most toxic forms of Hg are methylated forms
    - Can cross biological membranes and accumulate in body
      - Huang, C.W. and Jiang, S.J., J. Anal. At. Spec., 1993, 8, 681
  - As(III) and As(V) are relatively toxic - arsenobetaine is not
    - Fish often banned for high Total As content when the As is most often in the form of arsenobetaine which is non-toxic
      - Larsen, E.H., Pritzl, G., and Hansen, S.H., J. Anal. At. Spec., 1993, 8, 557
  - Cr(III) is an essential element involved in glucose metabolism, however Cr(VI) is a known carcinogen
  - Selenium chemistry is extremely complex, some selenium compounds implicated in cancer prevention mechanisms

Proposed selenium metabolic route in mammals



Se-cystathionine

Se-homocysteine

Se-Methionine

Se-Cysteine

Methionine pool

Selenocysteine ß-lyase

Se (VI) → Se (IV) → SeH_2S

Se containing proteins

SAM

SAH

Selenoproteins

[GPX, Selenoprotein P, TR etc.]

Urine

CH_3SeH

Se-phosphate

SAM

SAH

Thiol *S*-methyltransferase

Breath

$(CH_3)_2Se$

SAM

SAH

Thiolether *S*-methyltransferase

$SeCys^{SeCys}$ tRNA

Urine

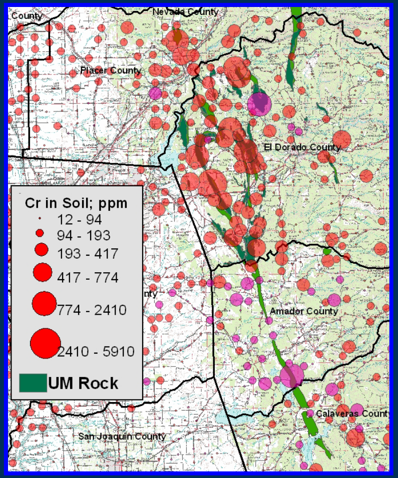
$(CH_3)_3Se^+$

SAM = *S*-Adenosylmethionine
SAH = *S*-Adenosylhomocysteine

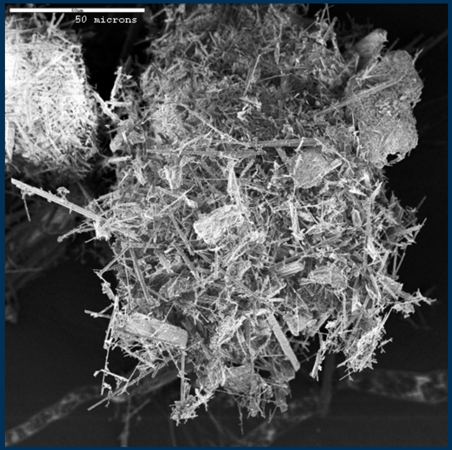
From B'Hymer and Caruso, J. Chromatography A, 1114 (2006), 1-20.

Why USGS and speciation?

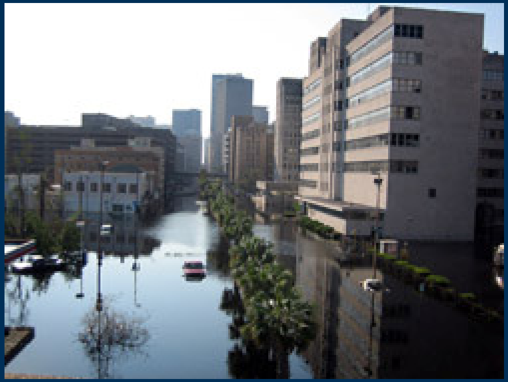
- Watershed and environmental monitoring
- Study of natural weathering processes
  - Does Cr(VI) occur naturally?
- Disaster response
  - Were the high As values in water/fish after Hurricane Katrina inorganic As or the non-toxic arsenobetaine?
- Biological response and ecosystem health studies
- Remediation strategies for contaminated sites



Cr in soils in Western Metamorphic Belt, CA



Asbestiform amphiboles (Libby, MT)



Hurricane Katrina floodwaters

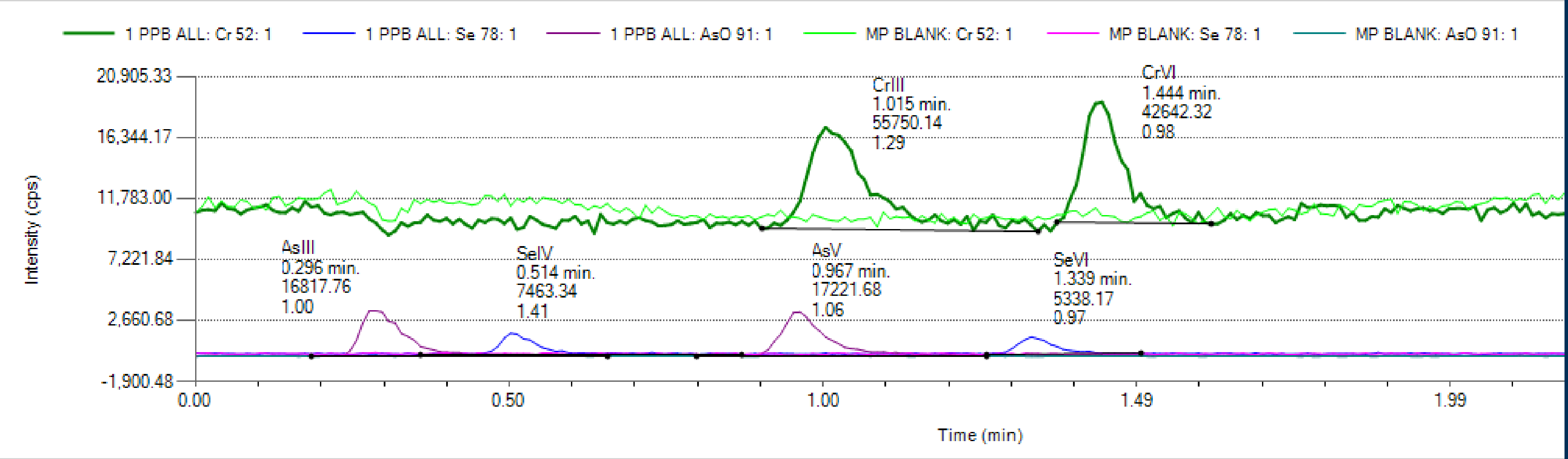
California wildfires, October 2007, NASA

Current Areas of Research

- Method for rapid analysis of waters/leachates to determine inorganic species of As, Se, and Cr
- Occurrence and stability of Cr(VI)
  - Can Cr(VI) occur naturally in the environment through weathering of ultramafic rocks?
    - Relationship of soils in Northern CA from Western Metamorphic Belt to lung cancer clusters in vicinity
  - Is Cr(VI) present in ashes/soils affected by wildfires?
    - Highly oxidizing environment of fires known to convert Cr(III) to Cr(VI)
    - Potential impact on human health - responders and clean-up
  - Interaction of Cr(VI) containing materials with simulated biological fluids

Analytical Method for Speciation of As, Cr, Se

- Determines Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6} in a single analysis
  - HPLC-DRC-ICP-MS method (3cm-C8, RP/ion-pairing, TBAOH/MeOH) †
  - Rapid method < 2 minutes (allows stability/time studies)
  - Detection limits ~50-100 ppt in aqueous samples
- Tested in waters, soil leaches, simulated bio-fluid leaches
- Sample collection/storage protocols being evaluated



Chromatogram of 1 ppb standard of Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6}

†Complete description in Wolf, Morrison, and Goldhaber, JAAS, 2007, 22, 1051-1060

Method Validation – Waters/Extracts

- Reference water samples diluted 1:1 with mobile phase
  - Allows Cr(III) to form anionic EDTA complex – 30 minutes
  - Provide well-characterized samples to check matrix effects
- Waters spiked at 2.5 ppb
  - Diluted 1:1 with 5 ppb standard in MP
- Recoveries within ± 20% with a few exceptions
  - Cr(VI) in M-178 and M-180
    - Samples have high Fe and SO_4^{2-} levels

	Cr(III) Recovery		Cr(VI) Recovery		As(III) Recovery		As(V) Recovery		Se(IV) Recovery		Se(VI) Recovery	
Sample	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr	PP-2Hr	PP-24Hr
MP spike	109	106	104	100	107	104	105	95	109	97	101	100
M-170	98	107	94	88	92	103	106	102	102	96	101	99
M-172	99	99	95	87	100	105	107	104	106	97	101	96
M-174	103	98	78	81	104	82	103	122	101	97	104	105
M-176	100	99	80	85	106	97	101	102	106	93	101	97
M-178	97	112	33	31	102	107	91	89	87	86	96	83
M-180	104	104	64	57	104	98	95	88	99	92	101	94

USGS

Method Validation – Dust Samples

- NIST 2701 – Cr(VI) contaminated soil
  - Micronized and loaded onto air filter and extracted
  - 506.6 ± 30.2 µg/g – 92%
    - Certificate Value: 551.2 ± 34.5 µg/g
- BCR 545 – Cr(VI) in welding dust
  - Supplied as air monitoring filter
  - 41,030 ± 2600 µg/g – 102%
    - Certificate Value: 40,200 ± 600 µg/g
- Ultrasonic extraction for 3 hours in 10mM $Na_2CO_3/NaHCO_3$ buffer solution at pH 9

Sample Analysis Schemes

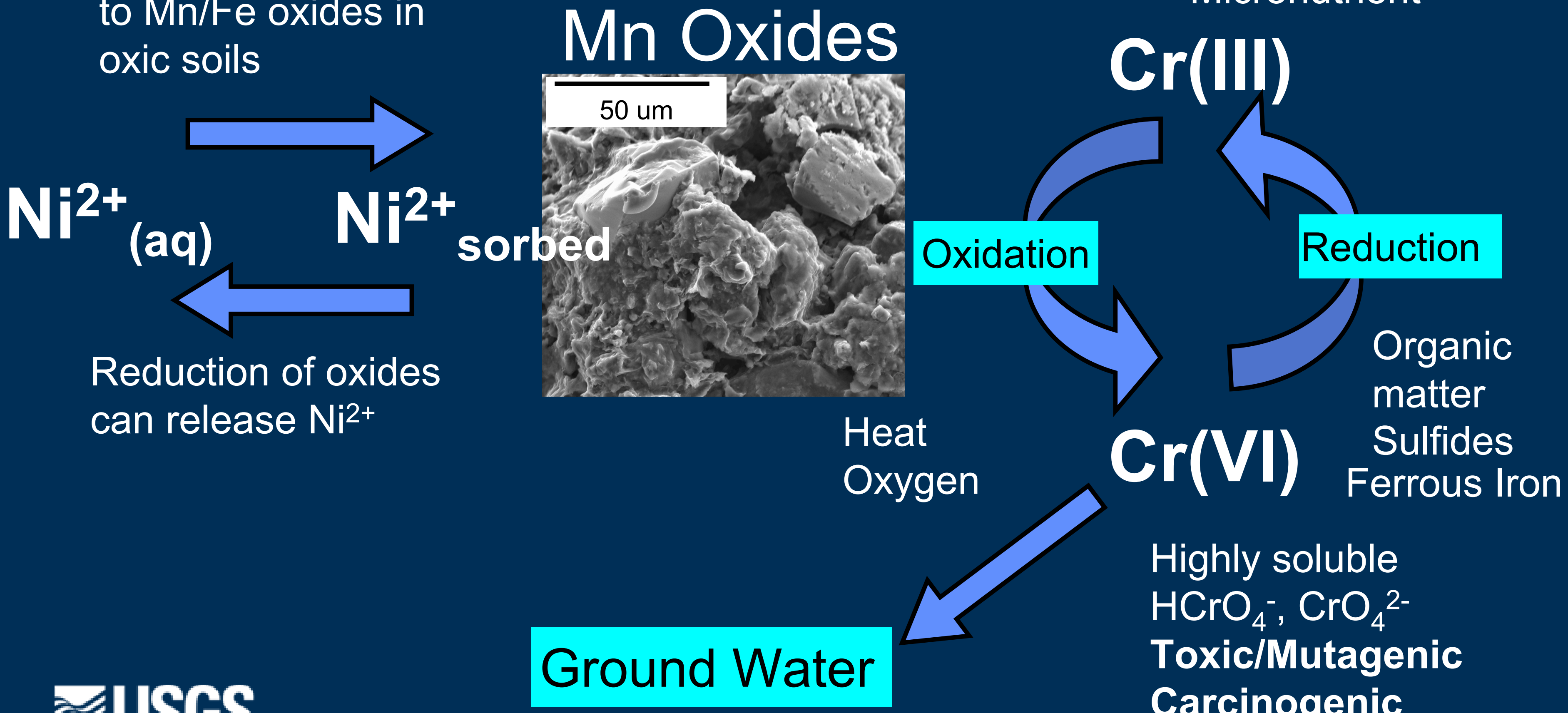
- Waters – diluted 1:1 with mobile phase and analyzed directly

- Soils and dusts – must be leached to extract analytes
  - De-ionized (DI) water leaches – soluble Cr(VI)
    - Short: 1 g sample in 20 mL DI water for 5 minutes, centrifuge, 0.45 µm filter
    - Extended: 1 g sample in 40 mL DI water , 20 hours, centrifuge at 3800 rpm for 20 minutes, 0.45 µm filter
  - Simulated gastric leach fluid
    - pH 1-2 HCl solution to simulate stomach environment
    - 1 part soil to 100 parts leachate fluid, rotated at 37ºC for 2 hours, filtered and analyzed for pH and metals
  - Cell line fluid leach – "simulated lung fluid"
    - Serum-based carrier fluid used in toxicity tests
    - Simply proxy for a near neutral pH solution with amino acids and proteins that could be encountered along an inhalation pathway
    - 0.5 g sample in 20 mL for 24 hours at 37ºC
  - EPA Method 3060A – pH 13 sodium carbonate/ hydroxide, 1 hour, 95ºC

- Air Filters
  - Sonicate in 10mM Na_2CO_3/$NaHCO_3$ buffer at pH 9
    - 3 hours, filter, dilute 1:1 with MP and analyze

USGS

Does Cr(VI) occur naturally?
Weathering Processes for Chromium



Strongly adsorbed to Mn/Fe oxides in oxic soils

$Ni^{2+}_{(aq)}$ Ni^{2+}_{sorbed}

Reduction of oxides can release Ni^{2+}

Mn Oxides

Relatively insoluble
Stable
Micronutrient

Cr(III)

Oxidation

Reduction

Heat
Oxygen

Cr(VI)

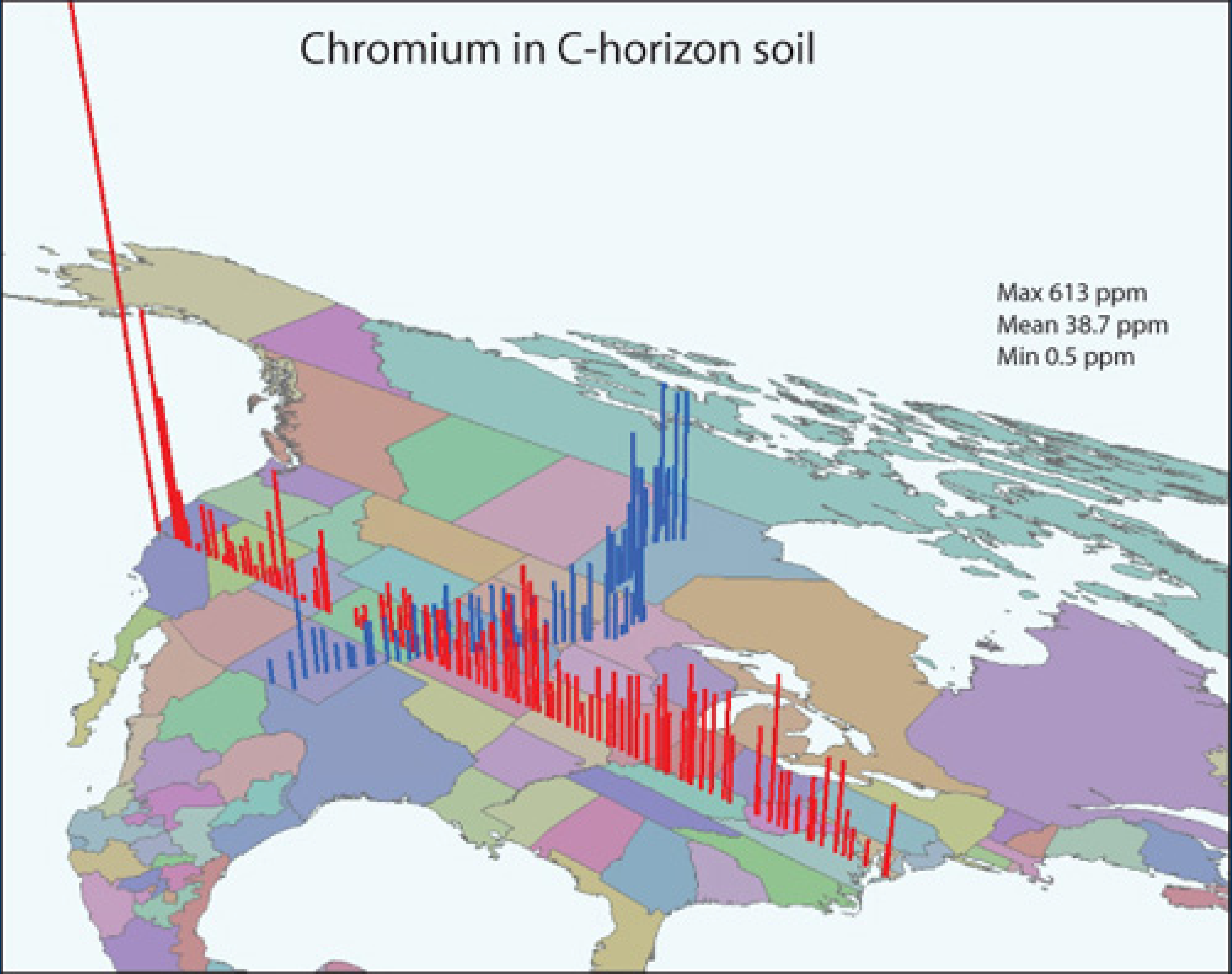
Organic matter
Sulfides
Ferrous Iron

Highly soluble
$HCrO_4^-$, CrO_4^{2-}
Toxic/Mutagenic
Carcinogenic
(inhalation)

Ground Water

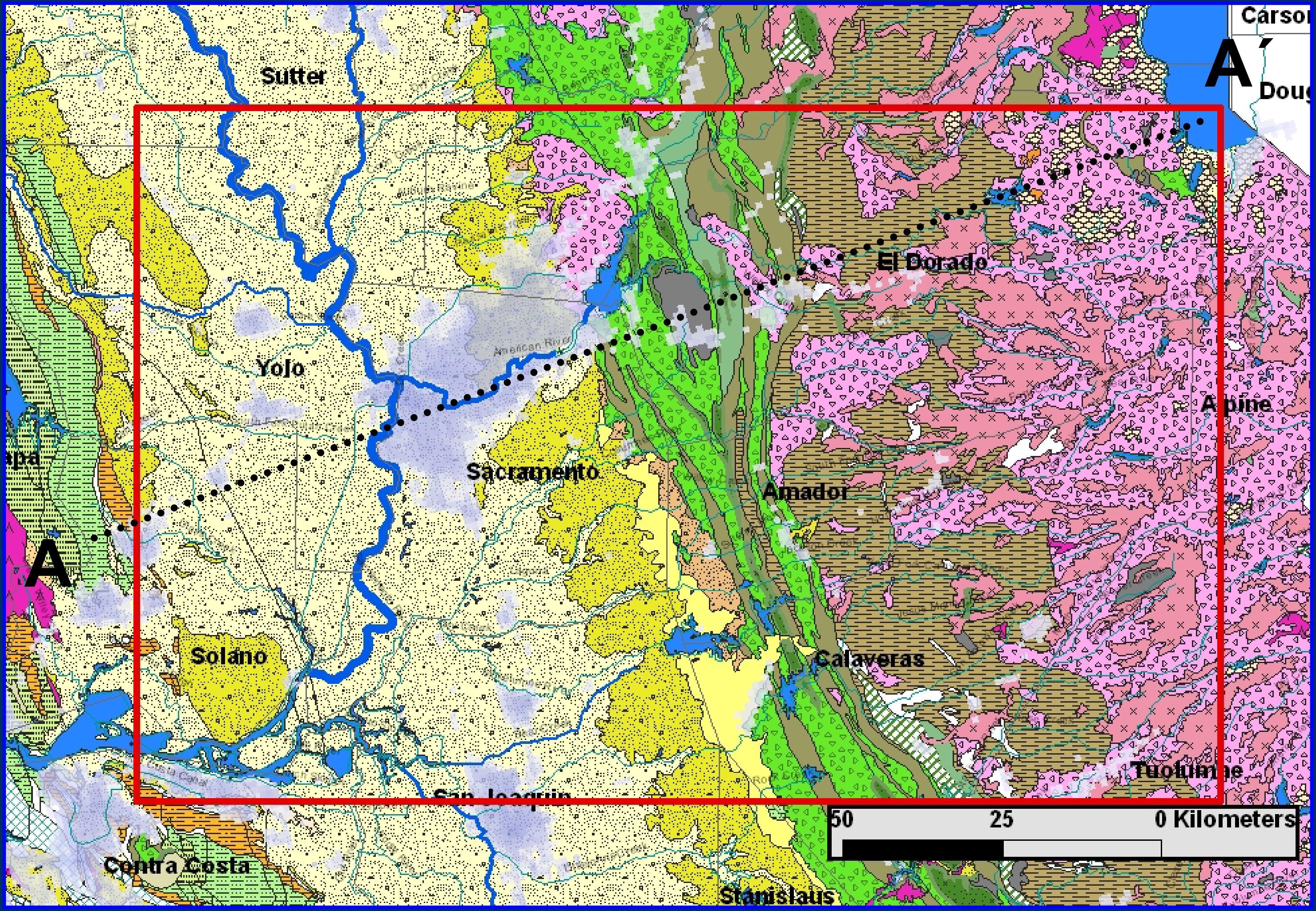
USGS

Chromium in C-horizon soil



Max 613 ppm
Mean 38.7 ppm
Min 0.5 ppm

Geologic map of Northern California study area

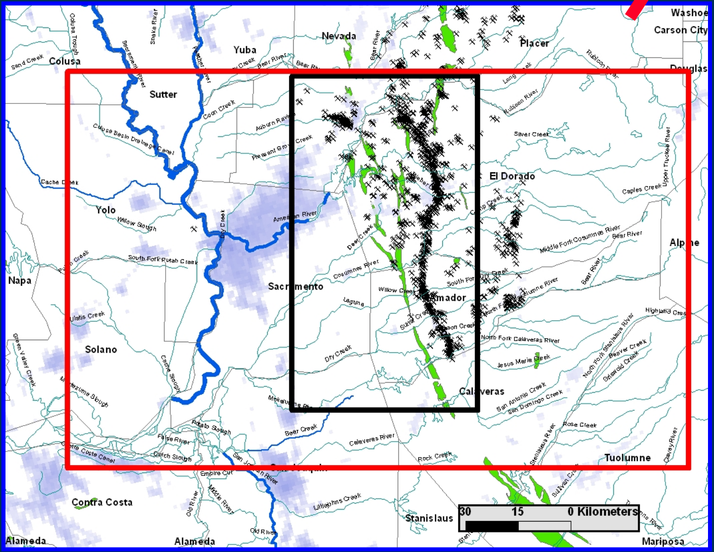


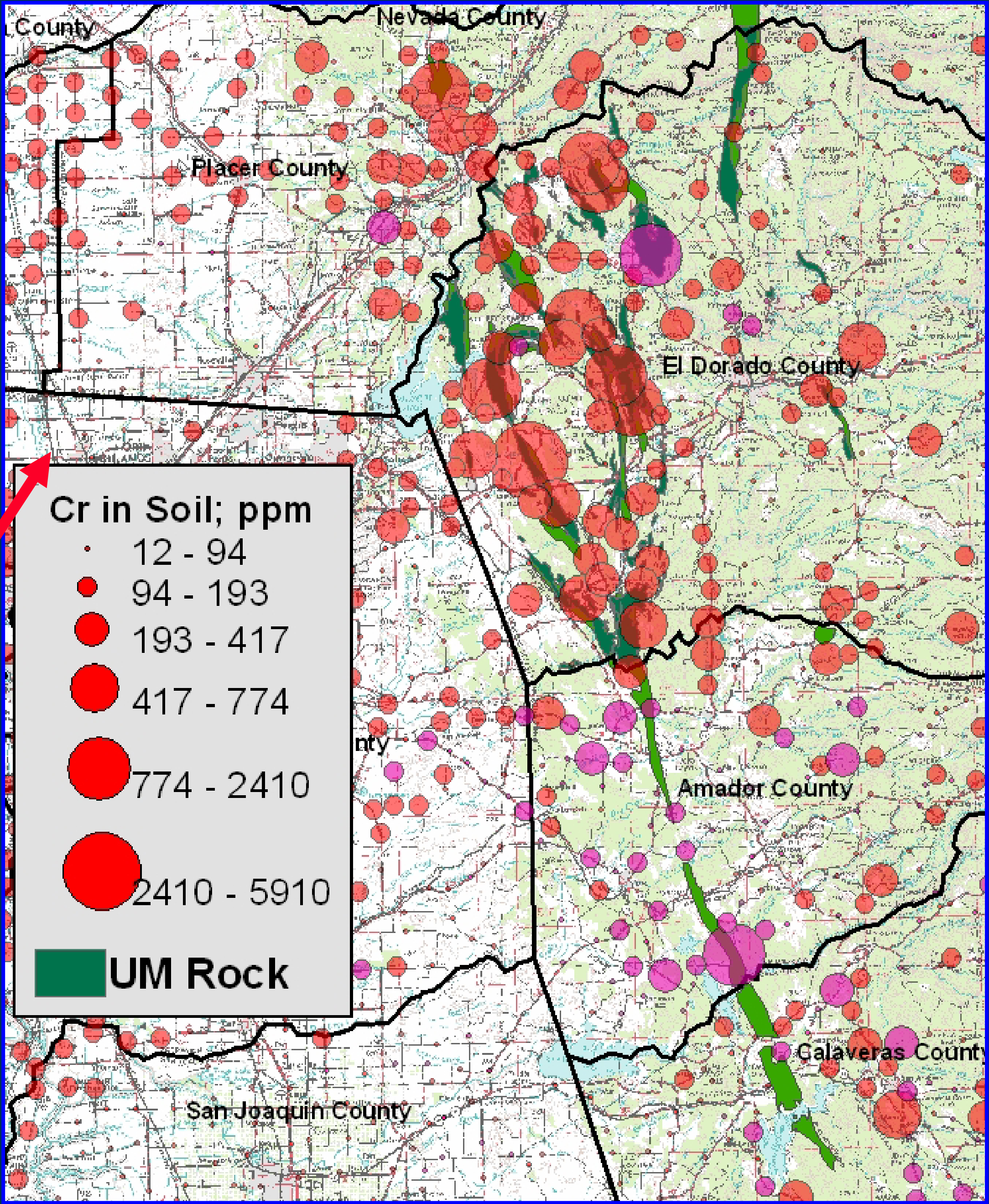
Elevations along A-A´

USGS

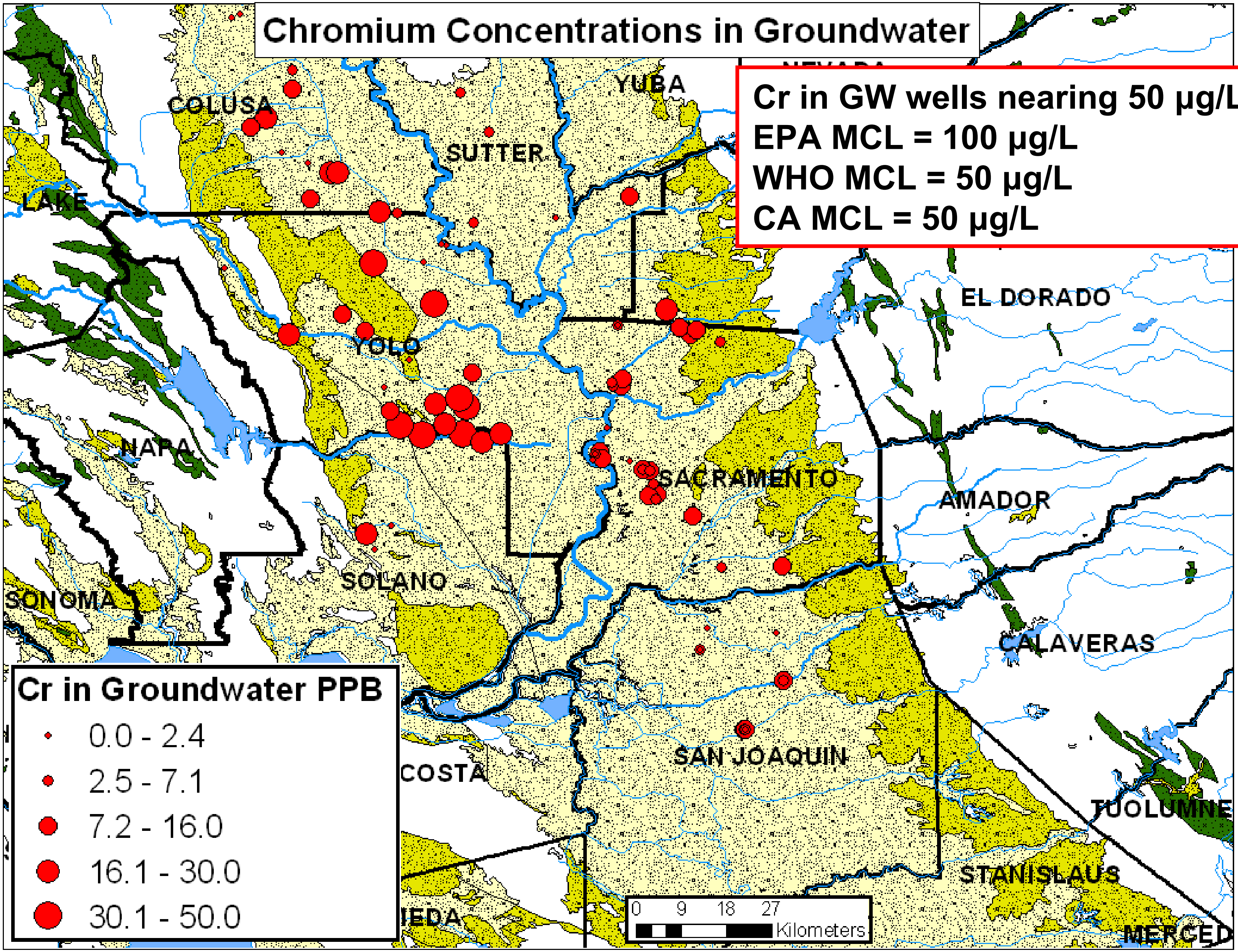
Chromium Results

- Soil and stream sediments
- U.S. Mean = 37 ppm
- Correlation between ultramafic rocks and high total chromium values





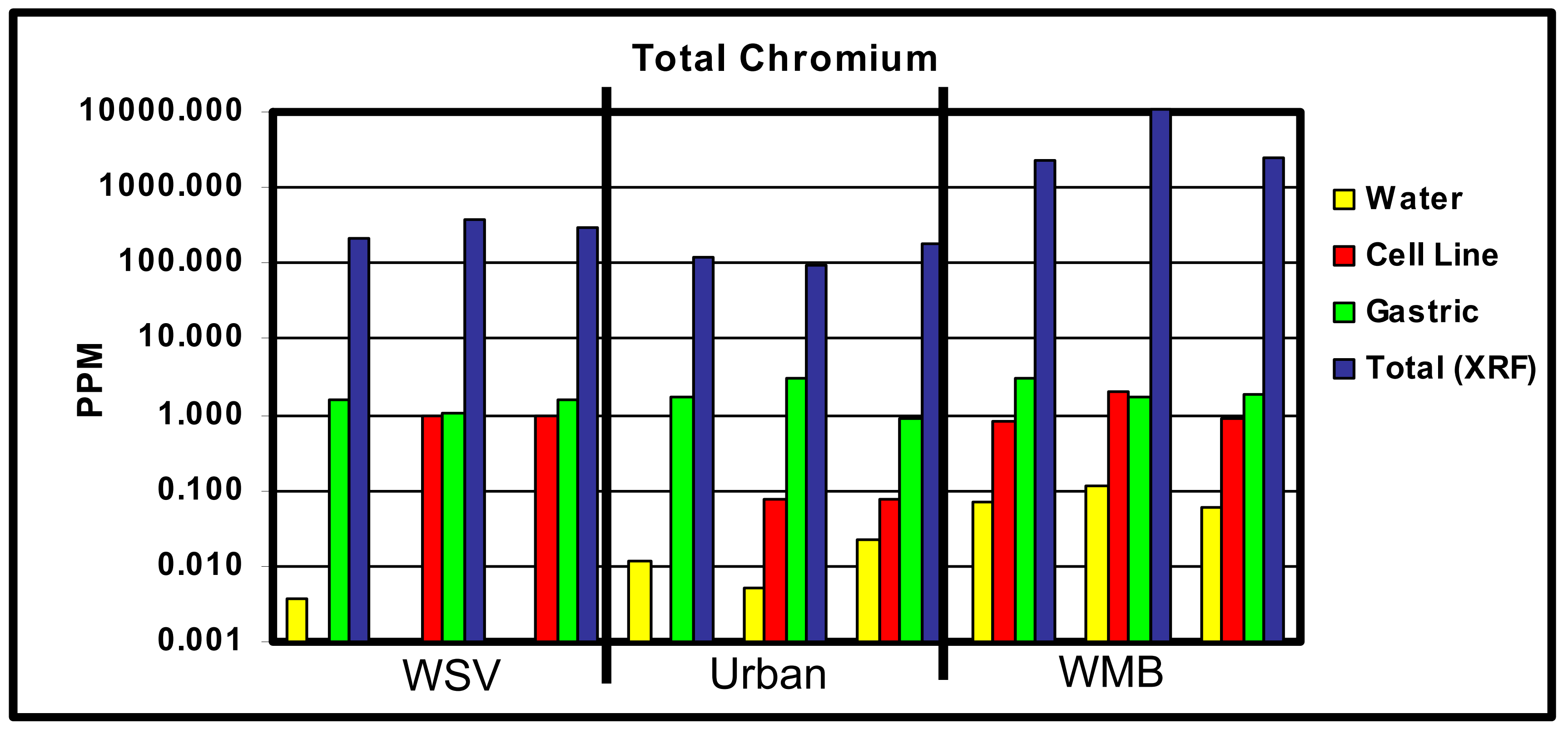
Chromium Concentrations in Groundwater



Cr in GW wells nearing 50 µg/L
EPA MCL = 100 µg/L
WHO MCL = 50 µg/L
CA MCL = 50 µg/L

Leach Tests for Total Chromium

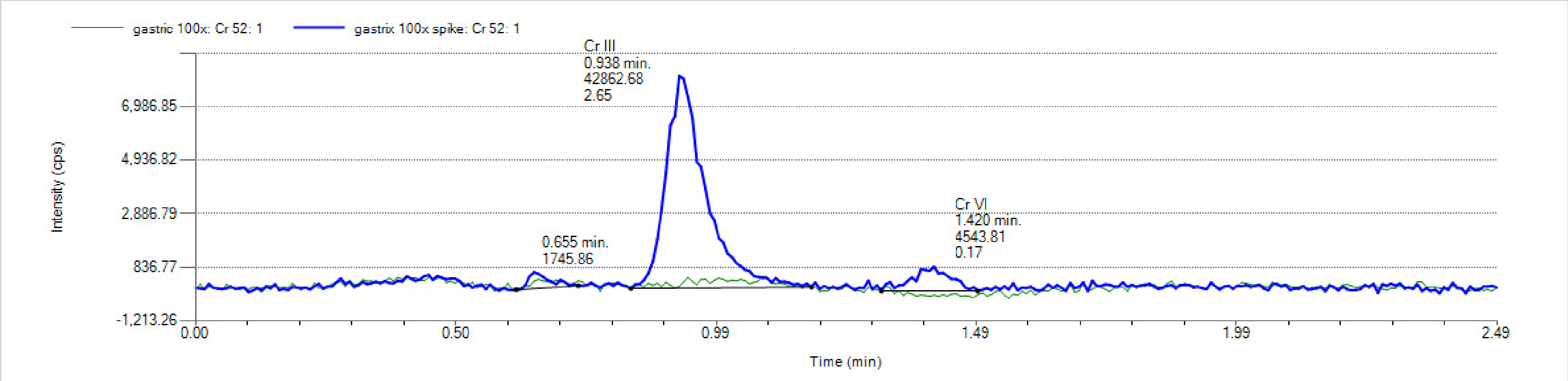
- Gastric leach results in most Total Cr
  - Preliminary studies show Cr(VI) is rapidly converted to Cr(III) in simulated gastric fluid
  - Precipitates as $Cr(OH)_3$ - non-toxic



Simulated Gastric Fluid Spike Stability

- Dilute HCL and glycine – adjusted to pH=1.2
- Diluted 1:100 with mobile phase prior to spiking at ~2 ppb
- Solution at room temp 15 minutes then in AS tray ~1 hour
  - Cr(VI) is rapidly converted to Cr(III)
  - Cr(III) = 132%, Cr(VI) = 8.5%
    - Some Cr(III) might be caught in filters in HPLC

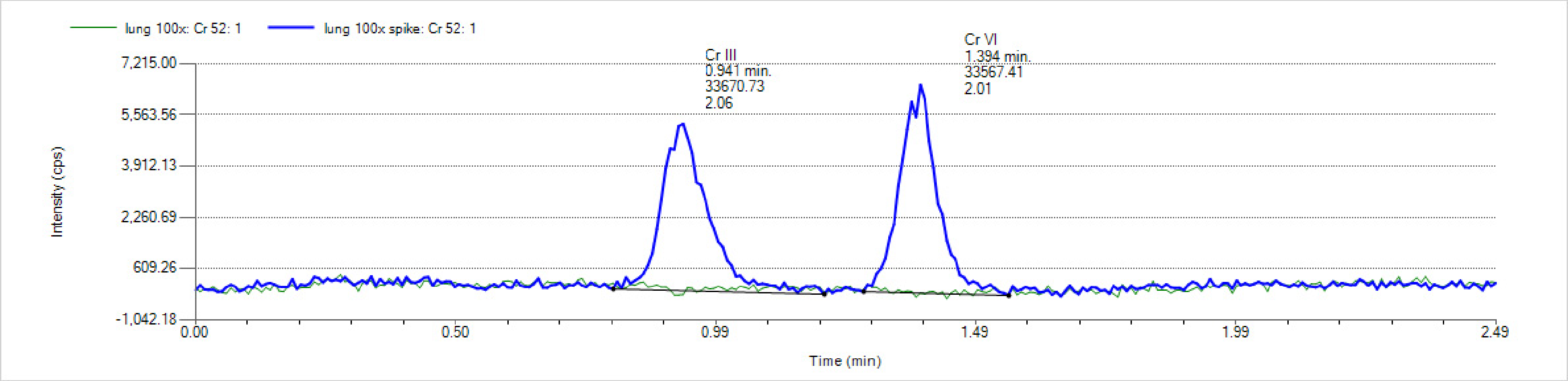
- Analytical method will allow further time studies to be carried out on stability of Cr(VI) in gastric and intestinal fluids



Simulated Lung Fluid Spike Stability

- Fluid adjusted to pH 7.4
- Diluted 1:100 with MP (pH =7.51) prior to spiking (2 ppb)
- Cr(III) = 108%, Cr(VI) = 106% recovery
- Both species stable in lung fluid

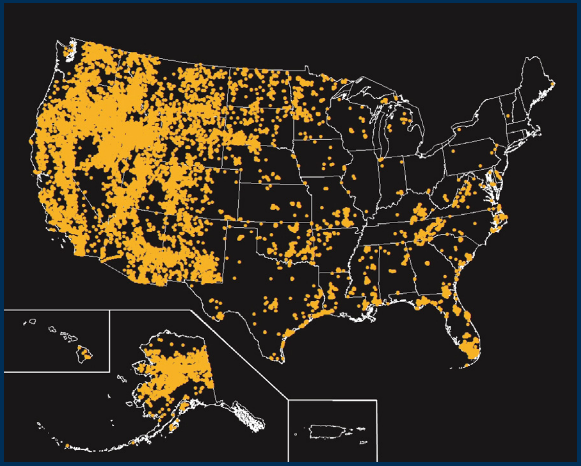
- Implies Cr(VI) more stable in lungs
  - Higher potential for exposures via inhalation than from ingestion



USGS

Wildfires a Growing Concern

- **More land affected by wildfires in recent years since 1960s**
- **In 2007 > 9 million acres burned**
  - **~36,500 km^2 > Belgium (30,528 km^2)**
  - **1.1M acres in California (1% of total)**
  - **1.9M acres in Idaho (4% of total)**
  - **Over 0.5M acres each in Alaska, Florida, Georgia, Nevada, Montana, Oregon, and Utah**
- **Fires in 2003 burned over 5,700 structures**
  - **4,090 primary residences**



Locations with wildfires > 250 acres (1 km^2) from 1980-2003. Sources: BLM, USFS, USFWS, BIA, NPS, USGS.

Year	*# Fires*	*# Acres*
2007	85,822	9,321,326
2006	96,385	9,873,429
2005	66,753	8,689,389
2004	not listed	6,800,000
2003	85,943	4,900,000

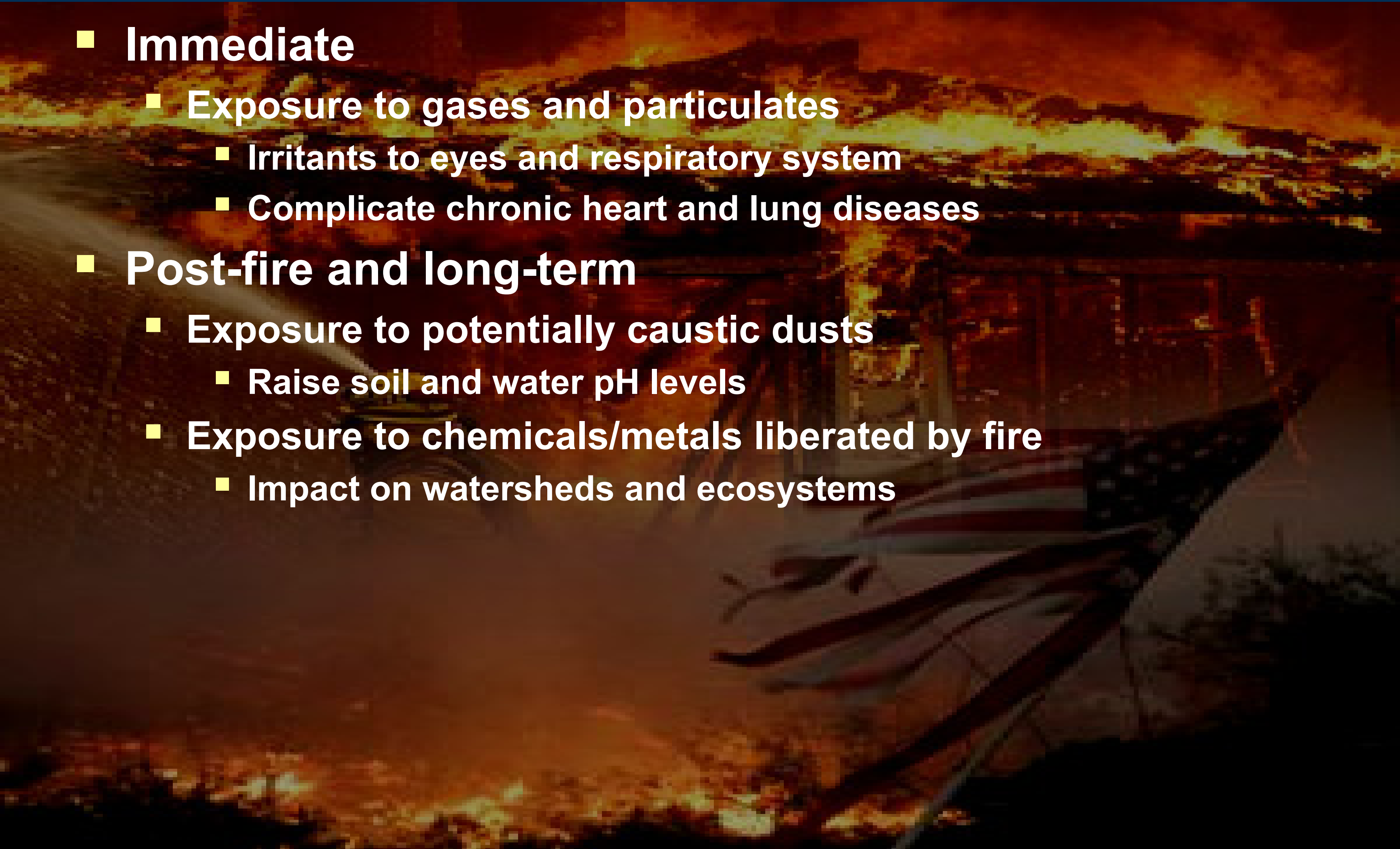
Source: http://www.nifc.gov/fire_info.html

Analysis of Fire Ash/Soil Leachates

- Large forest fires in California, Fall 2007
  - Burned many homes
- USGS asked to assess potential risks to human health from residential and non-residential fire ash
  - Expected to vary with particle size and speciation
- Preliminary Report
  - http://pubs.usgs.gov/of/2007/1407/

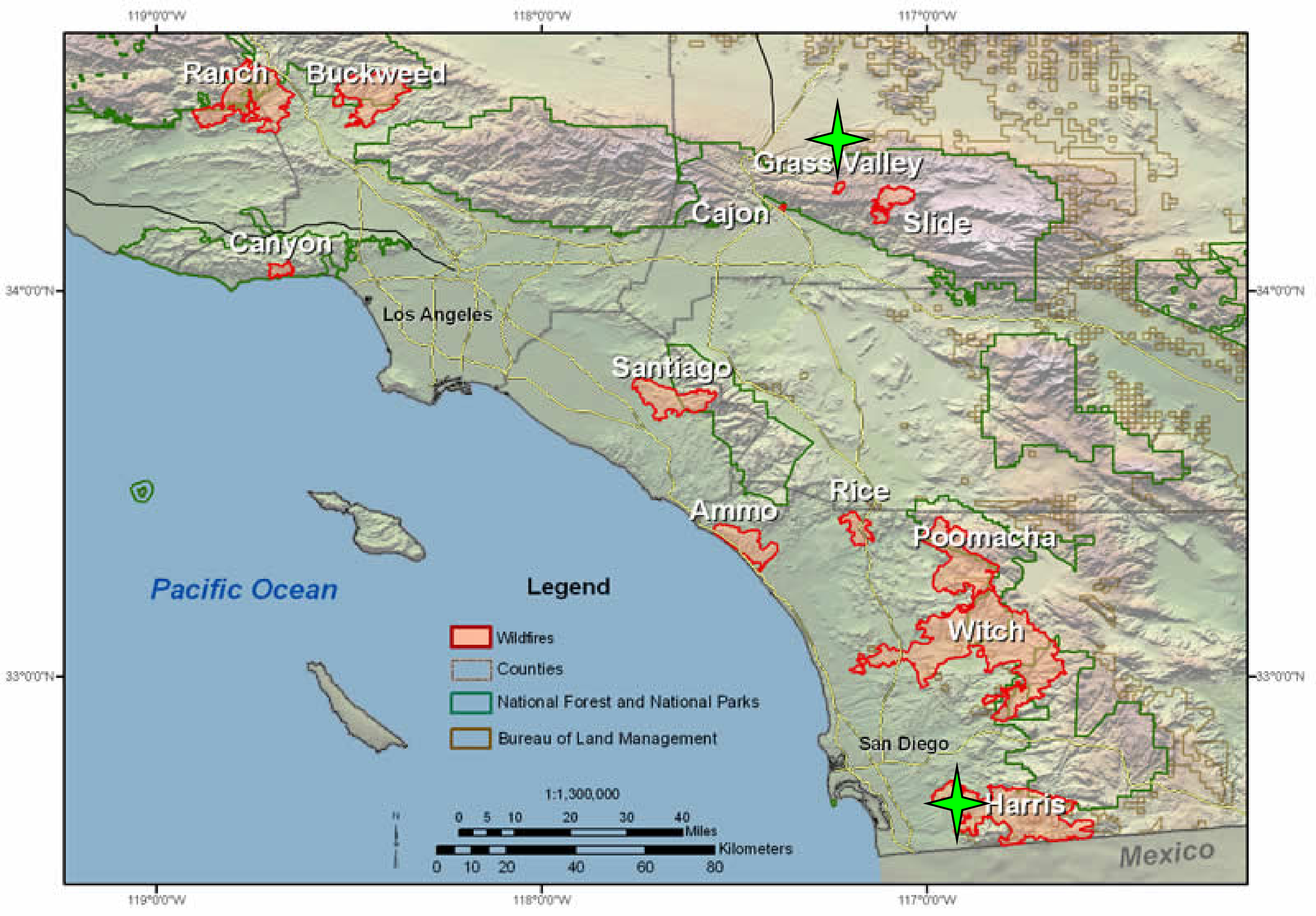
USGS

Effects of Fires on Health



- Immediate
  - Exposure to gases and particulates
    - Irritants to eyes and respiratory system
    - Complicate chronic heart and lung diseases
- Post-fire and long-term
  - Exposure to potentially caustic dusts
    - Raise soil and water pH levels
  - Exposure to chemicals/metals liberated by fire
    - Impact on watersheds and ecosystems

2007 California Burn Areas



Fire Ash Studies – 2007 California Fires

- Samples from burned wildland and residential areas
  - Primary focus on residential ash and soil samples at request of Burned Area Emergency Rehabilitation (BAER) Team
  - Report available at: http://pubs.usgs.gov/of/2007/1407/

Source: http://pubs.usgs.gov/of/2007/1407/

News Release

December 4, 2007	Catherine Puckett Heidi Koontz	352-264-3532 303-202-4763	cpuckett@usgs.gov hkoontz@usgs.gov

USGS Study Finds Ash from Southern California Fires May Pose Problems to Health and the Environment

Ash from last month's southern California fires may pose problems to health and the environment, according to preliminary results from a U.S. Geological Survey (USGS) study released to the Multi-Agency State and Federal Task Force.

Samples collected from two residential areas burned by the Grass Valley and Harris wildfires indicate that the ash contains caustic alkali materials and can contain somewhat elevated levels of metals such as arsenic, lead, zinc and copper. Ash from burned wildlands can also contain caustic alkali materials, though at lower levels than the residential ash.

"These findings are consistent with the scientific knowledge about wildfire ash that has led counties in California to issue advisories regarding appropriate precautionary measures to avoid health problems associated with exposure to the ash," said Dr. Geoffrey Plumlee, a USGS lead author of the study.

"The study results also indicate that rain-water runoff from burned areas may adversely affect ecosystems and the quality of surface drinking water supplies," said Deborah Martin, a USGS wildfire ash specialist and study co-author. Additionally, critical habitat for some aquatic species may be affected by spikes in alkalinity as rainwater mixes with ash to form surface runoff.

Key Findings
Preliminary Fire Ash Study

- Water leach tests generate pH levels > 12
  - Suggest ash can generate caustic alkalinity in contact with rain water or bodily fluids (for example sweat, fluids in respiratory tract)
    - Rate of neutralization has not been studied
- Residential ash has elevated levels of metals
  - As (140 mg/kg), EPA PRG (soil) 0.4-0.62 mg/kg
  - Pb (344 mg/kg), EPA PRG 150-400 mg/kg
  - Sb (32 mg/kg), EPA PRG 31 mg/kg
  - Cu (1,370 mg/kg), EPA PRG 3,100 mg/kg
  - Zn (2,800 mg/kg), EPA PRG 23,000 mg/kg
  - Cr (354 mg/kg)
    - EPA PRG 210 mg/kg (Cr^{+6}/Cr^{+3} = 0.17), 30 mg/kg if all Cr(VI)

      - PRG = Preliminary Remediation Goal

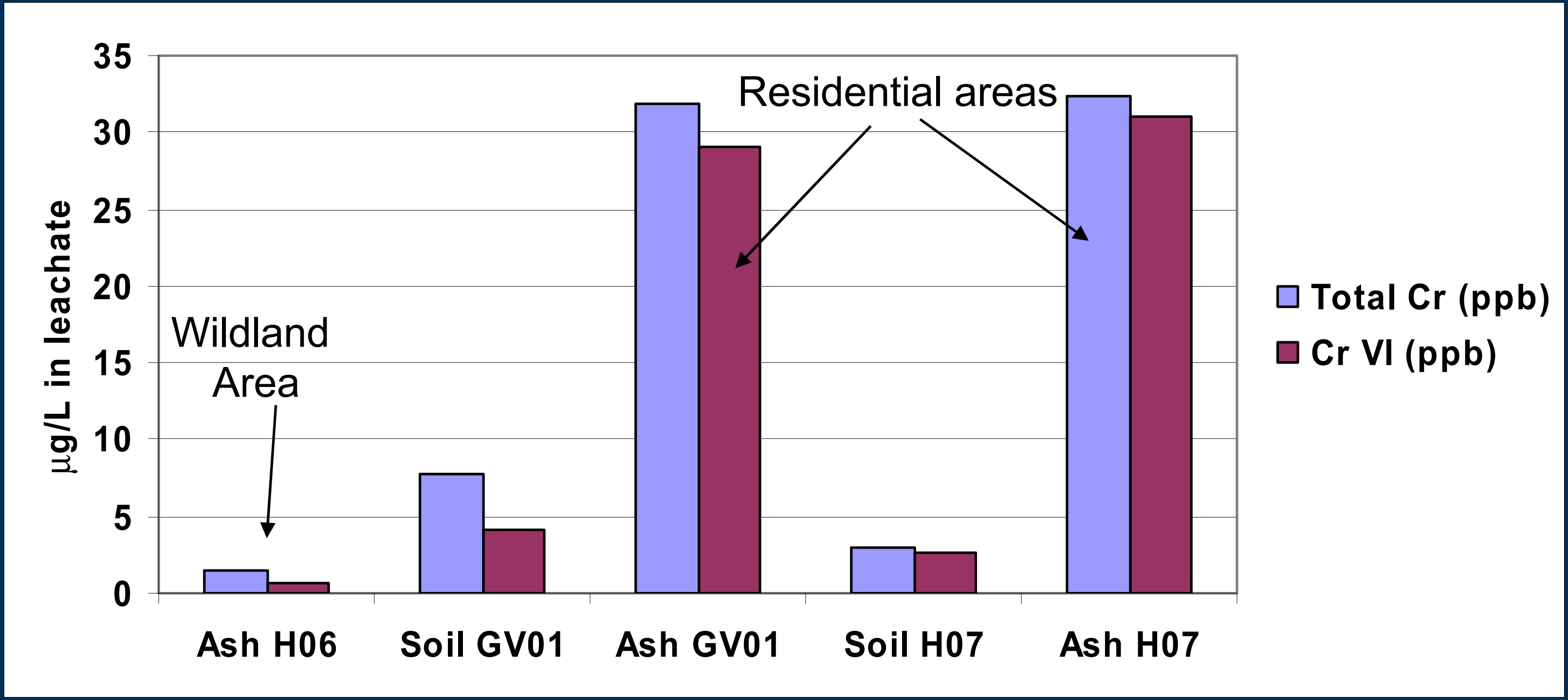
Elemental Content in DI-Leaches

- Total elemental analysis in 5 minute DI-water leach
  - Limited information on actual potential for toxicity or impacts on human heath and environment
- Toxicity depends on chemical form of element
  - Cr(VI) >> Cr(III), Cr(VI) a known carcinogen (lung)
    - Cr(VI) regulated in several industries with potential for inhalation of Cr(VI) containing dusts, for example, welding, refining, plating
  - As(III) > As(V), aquatic species

Sample	Location Description	pH	As (µg/L)	Cr (µg/L)	Se (µg/L)
Harris 06 Ash	Steep hillside	10.9	1	1.5	7.2
Grass Valley 02 Soil	Hillside	8.2	1	<1	<1
Grass Valley 02 Ash	Hillside	9.8	1	1.4	3.1
Grass Valley 01 Soil	Modern homes	10.9	2	7.7	1.6
Grass Valley 01 Ash	Modern homes	12.7	2	31.9	3.6
Harris 07 Soil	Residential, mobile homes	10.6	219	3	2.7
Harris 07 Ash	Residential, mobile homes	12.5	13.5	32.4	6.3
Blank	De-ionized water	6	<1	<1	<1

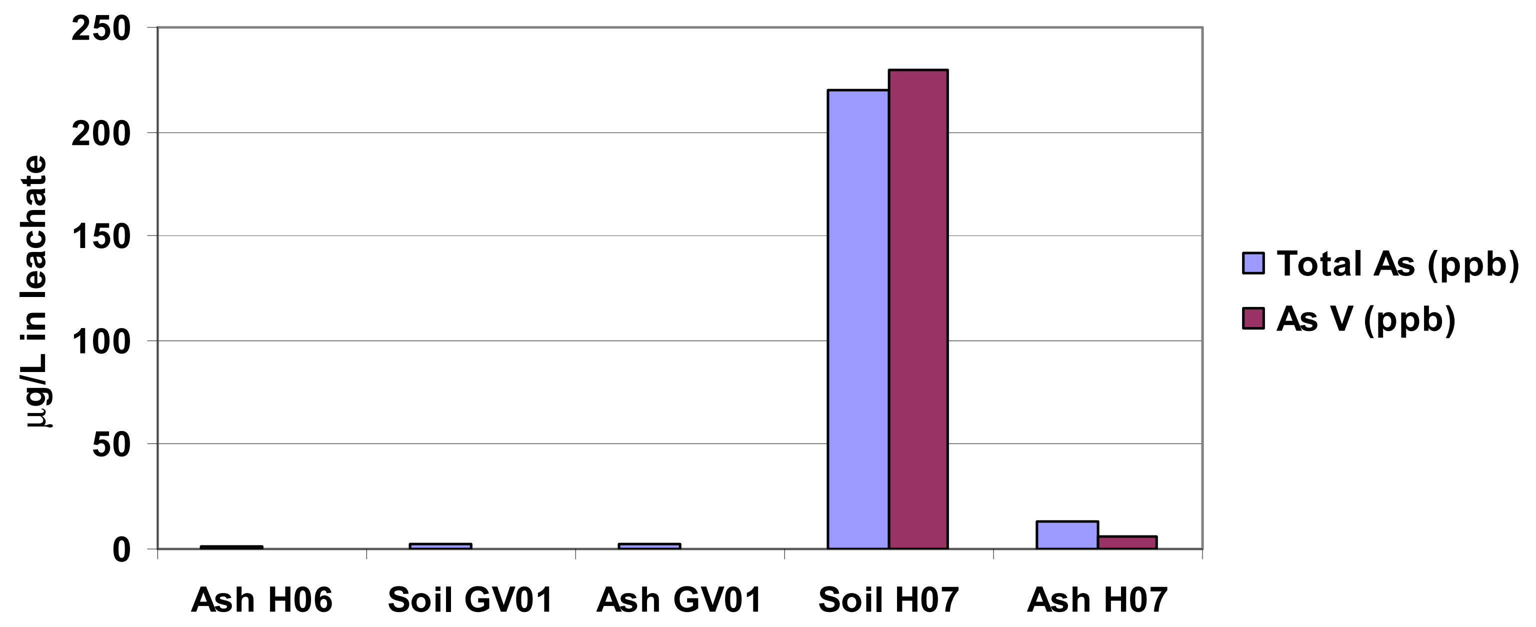
Total Cr vs. Cr(VI)

- In filtered DI-water leachate (~6 g to 125 mL, 5 minutes)
- pH > 10, Cr(III) precipitates – filtered out (0.45 µm filter)
- At pH > 8, Cr(VI) stable as CrO_4^{2-}



Total As vs. As(V)

- In filtered DI-water leachate
- Se < 2 ppb (all forms)



Simulated Lung Fluid Leach

- Estimates effects of particulates (<38 µm) taken into lungs and in contact with pulmonary fluids at near neutral pH

- 0.5 g sample to 20 mL at 37ºC for 24 hours
  - 150 mM Na, 0.2 mM Ca, 10 mM NH_4^+, 6 mM glycine, 67 mM formaldehyde, 20 mM methanol, 126 mM chloride, 0.5 mM sulfate, 27 mM hydrogen carbonate, 1.2 mM phosphate, 0.2 mM citrate, adjusted to pH 7.4

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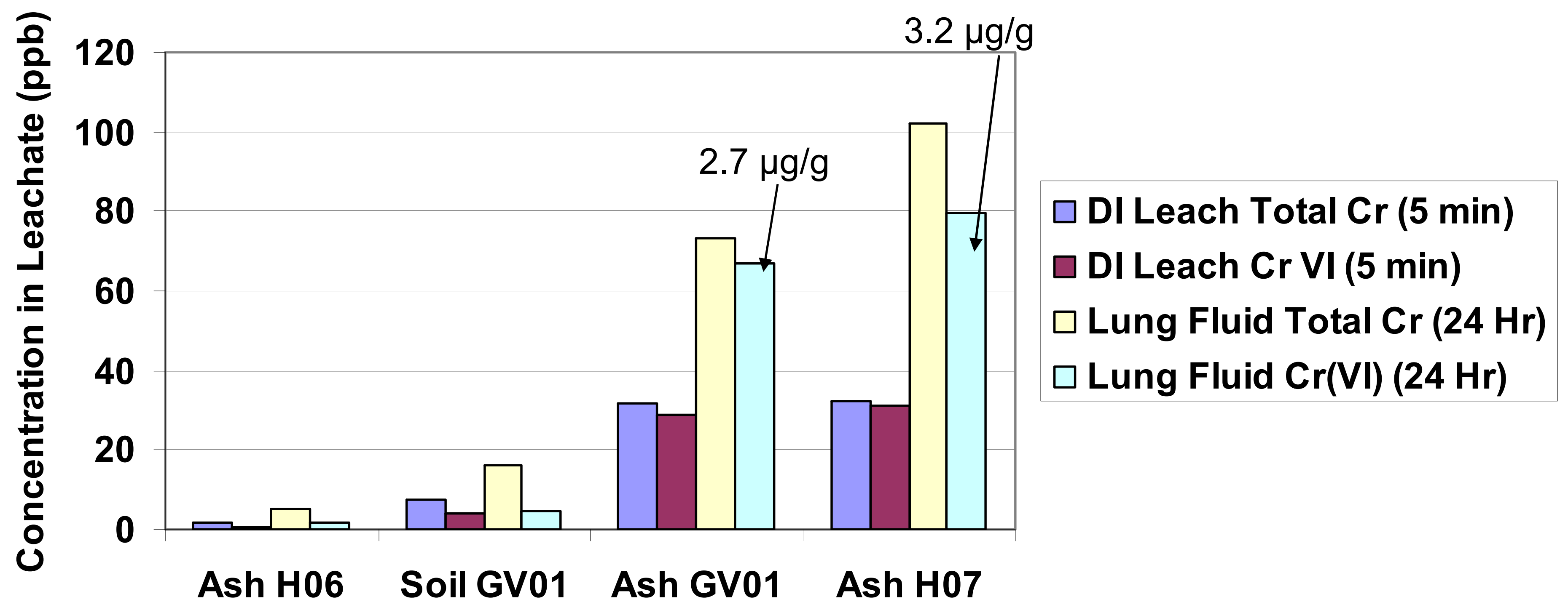
Cr in DI-Water and Lung Fluid Leaches

- More Cr is leached out in lung fluid leach
- Ash samples liberate much higher Cr values
  - Significant portion of it is Cr(VI)
    - OSHA PEL (8 Hr) Cr(VI) = 5 µg/m^3



Conclusions

- Analytical method can be used to determine inorganic forms of As, Se, and Cr in a variety of matrices
- Soil and water Cr concentrations appear to be linked to Cr content in underlying rock
  - Further study needed to assess potential for forming Cr(VI) by natural weathering processes
- Soils and ashes from residential areas have higher Cr(VI) levels than wildland area
- Predominant form of Cr found in fire-impacted soil and ash samples is Cr(VI)
  - Alkaline pH resulting from contact of ash with water and water-based fluids may have a stabilizing effect on Cr(VI)
- Potential human health impact from high pH and for exposure to Cr(VI)-containing ash and soils by first-responders and clean-up crews
  - Particularly for inhaled ash particles that are high in Cr
- Air monitoring tests for Cr(VI) should be done during fire clean-up/recovery operations to assess potential exposure to Cr(VI)

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