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Release of Hexavalent Chromium by Ash and Soils in Wildfire-Impacted Areas

By Ruth E. Wolf, Suzette A. Morman, Geoffrey S. Plumlee, Philip L. Hageman, and Monique Adams

Open-File Report 2008–1345

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Abstract

The highly oxidizing environment of a wildfire has the potential to convert any chromium present in the soil or in residential or industrial debris to its more toxic form, hexavalent chromium, a known carcinogen. In addition, the highly basic conditions resulting from the combustion of wood and wood products could result in the stabilization of any aqueous hexavalent chromium formed.

Samples were collected from the October 2007 wildfires in Southern California and subjected to an array of test procedures to evaluate the potential effects of fire-impacted soils and ashes on human and environmental health (Plumlee and others, *http://pubs.usgs.gov/of/2007/1407/*). Soil and ash samples were leached using de-ionized water to simulate conditions resulting from rainfall on fire-impacted areas (Hageman and others, 2007, *http://pubs.usgs.gov/tm/2007/05D03/*). The resulting leachates were of high pH (10–13) and many, particularly those of ash from burned residential areas, contained elevated total chromium as much as 33 micrograms per liter. 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.

High Performance Liquid Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry (Wolf and others, 2007) was used to separate and detect individual species (for example, Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6}). These procedures were used to determine the form of the chromium present in the de-ionized water and simulated lung fluid leachates.

The results show that in the de-ionized water leachate, all of the chromium present is in the form of Cr^{+6}, and the resulting high pH tends to stabilize Cr^{+6} from reduction to Cr^{+3}. 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^{+6}, which is of concern due to the high possibility of inhalation of the small ash and soil particulates, particularly by fire or restoration crews.

Introduction

This Open-File Report contains illustrative materials, in the form of PDFs of PowerPoint slides, used for an oral presentation given at the Goldschmidt 2008 Conference held in Vancouver, British Columbia, in July 2008.

The individual slides summarize the growing concern over the number and frequency of wildfires in recent years in the United States. Wildfires can have negative effects on human and eco-system health. In regard to effects 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 due to exposure to potentially caustic dusts that can raise soil and water pH levels and possible exposure to chemicals and metals liberated by the fire. The U.S. Geological Survey collected ash and burned soils from about 28 sites in southern California wildfire areas (Harris, Witch, Ammo, Santiago, Canyon, and Grass Valley) in November 2007. U.S. Geological Survey researchers have applied a wide variety of analytical methods to these samples, with the goal of helping identify characteristics of the ash and soils from wildland and suburban burned areas that may be of concern for their potential to adversely affect water quality, human health, and endangered species and hazards from debris flows or flooding. 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.

High Performance Liquid Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry (Wolf and others, 2007) was used to separate and detect individual species (for example, Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6}). These procedures were used to determine the form of the chromium and arsenic present in the de-ionized water and simulated lung fluid leachates.

The preliminary results presented in the slides show that in the de-ionized water leachate, all of the chromium present is in the form of Cr^{+6}, and the resulting high pH tends to stabilize Cr^{+6} from reduction to Cr^{+3}. 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^{+6}, 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^{+6} (hexavalent chromium) 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).

Release of Hexavalent Chromium by Ash and Soils in Wildfire Impacted Areas

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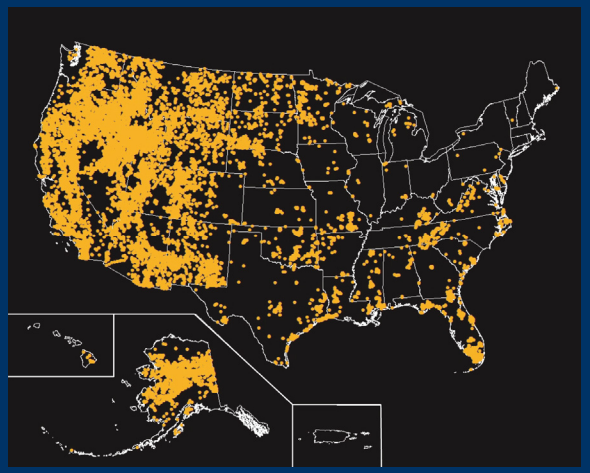
Wildfires a Growing Concern

- 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
- 2003 fires burned over 5700 structures
  - 4090 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

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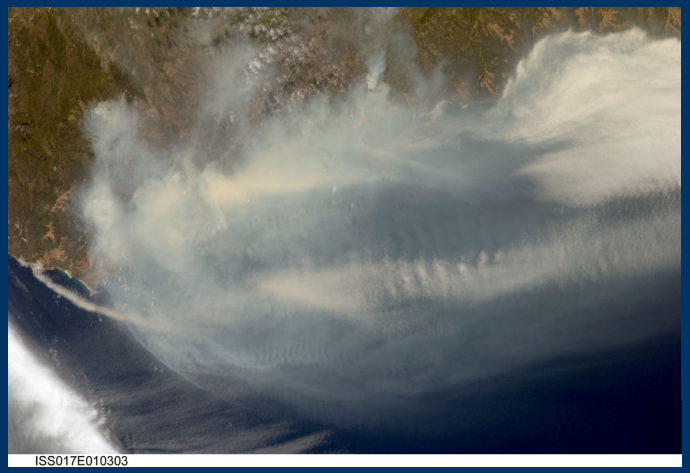
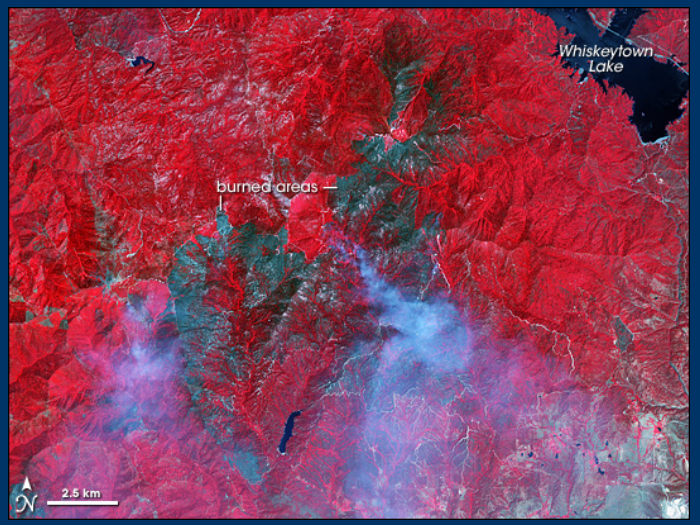
Impact of Wildfires Widespread

- Destruction of timber and wildlife habitats
  - Immediate and long-term
- Increased potential for flooding, debris flows, landslides
- Negative impacts on watersheds and water quality
- Human health effects
  - Smoke, particulates, etc.



California Wildfires Seen by the International Space Station on 4 July 2008. Photo: NASA



ASTER image of burned areas near Redding, CA. Red - vegetation. Grey - burned areas. Photo: NASA

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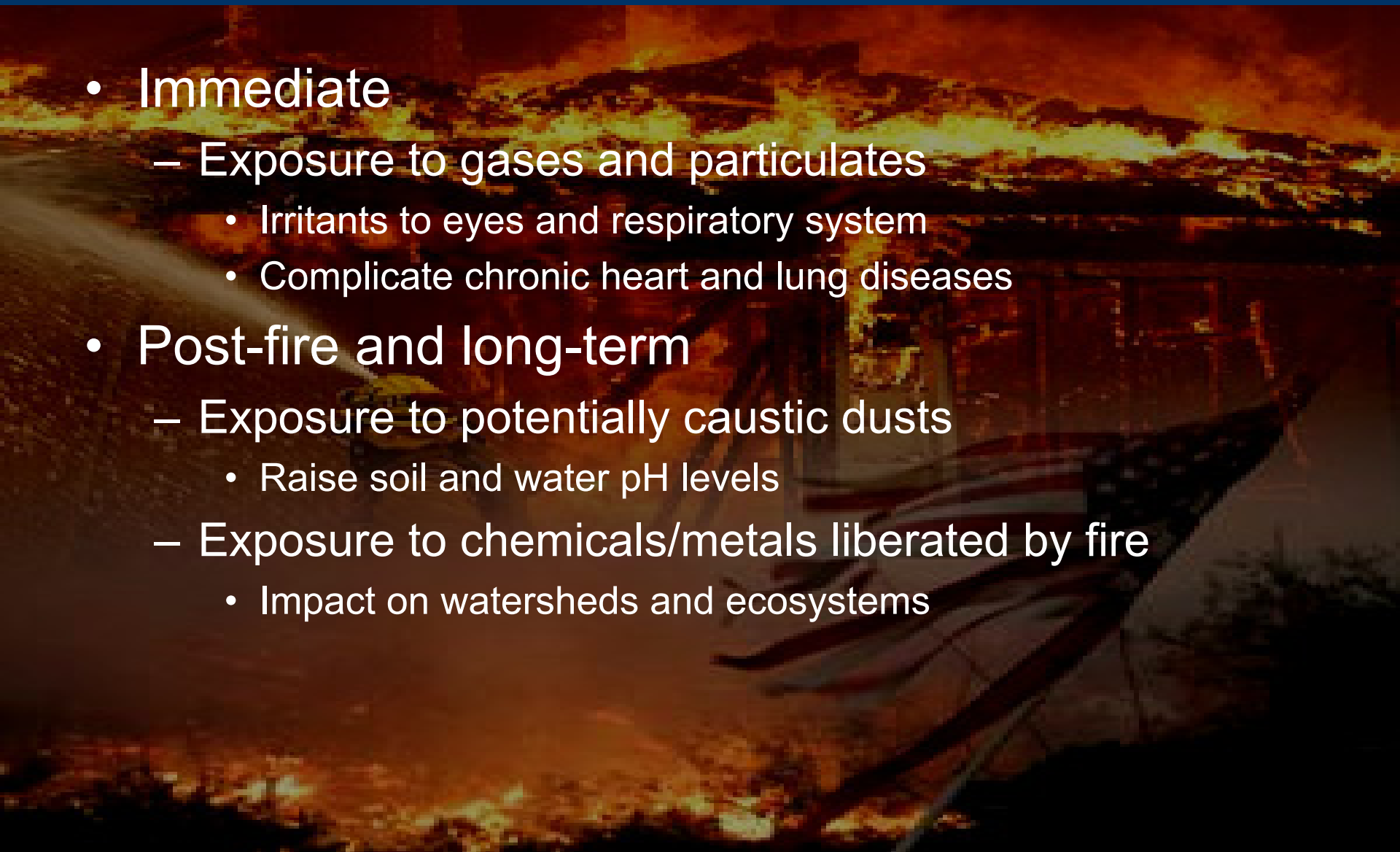
Effects of Fires on Health



- 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

Wildfire Health Advisories Issued

Huge Montana wildfire grows

Bees complicate firefighting efforts; blazes continue in Washington state

James Woodcock / Billings Gazette

ht a backfire Wednesday near McLeod, Mont., as crews try to contain the Derby
now estimate 5,000 acres in size.

10A» SUNDAY, JUNE 29, 2008

NationBriefs

CALIFORNIANS FIND WILDFIRES BURN LUNGS, TOO

SACRAMENTO, CALIF.» Hundreds of lightning-sparked wildfires have turned the air of northern California into an unhealthy stew of smoke and ash, forcing the cancellation of athletic events and other outdoor activities.

Health advisories urging residents to stay indoors to limit exposure to the smoky air were issued Saturday from Bakersfield north to Redding, a distance of nearly 450 miles.

On Saturday, President Bush issued an emergency declaration for California and ordered federal agencies to assist in firefighting efforts.

Areas hardest hit include Butte County, where 31 fires have burned 19 square miles; Mendocino County, where 121 fires have burned 45 square miles; and Shasta and Trinity counties, where about 160 fires have burned 58 square miles.

The wildfire south of the tourist town of Big Sur was 80 percent contained Saturday.

Eastern N.C. under highest air-quality warning

Posted: Jun. 13, 2008

The state Division of Air Quality issued a Code Purple alert – the most extreme warning possible – for part of northeast North Carolina because of lingering smoke from a wildfire that has been burning for almost two weeks.

The Code Purple alert, which signals very unhealthy air, was issued for Friday and Saturday for areas east of Interstate 95 and north of U.S. Highway 70 and included the cities of Edenton, Elizabeth City, Greenville, Roanoke Rapids, Rocky Mount, Tarboro, Washington and Wilson.

Rocky Mount Fire Chief Keith Harris said his department has seen a spike in the number of emergency runs related to respiratory ailments – since the smoke settled over the city.

JOINT PRESS RELEASE

EL DORADO COUNTY
Public Health Department
Air Quality Management District

PUBLIC HEALTH DEPARTMENT • El Dorado County

FOR IMMEDIATE RELEASE
September 10, 2007

Contact: Margaret Williams
Public Health Department
(530) 621-6243

Health Advisory Continues For Wildfire Smoke

Health officials from the El Dorado County Air Quality Management District and Public Health Department are extending a health advisory issued last week due to smoky air from wildfires in the region. As of September 10, the wildfire in Plumas National Forest continues to burn and create smoky conditions intermittently in parts of El Dorado County. Weather forecasts are predicting that could move more smoke into and out of the county over the next several days.

Smoke From Wildfires Could Damage Lake Tahoe

RENO (AP) — Studies are under way to determine the effect of thick smoke from California wildfires on Lake Tahoe's environment.

Scientists fear the lingering smoke could deposit loads of nitrogen into Tahoe's waters and diminish its famed clarity by fueling algae growth.

Last summer's Angora Fire on Lake Tahoe's south shore caused a brief bloom of algae at Tahoe, but researchers say the impacts of the current wildfires are unclear.

Researchers next week plan to install a state-of-the-art air sampler to help measure possible toxins being sent to Tahoe by the wildfires.

Fire Ash Studies – 2007 CA Fires

- Samples from burned wild land 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/

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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

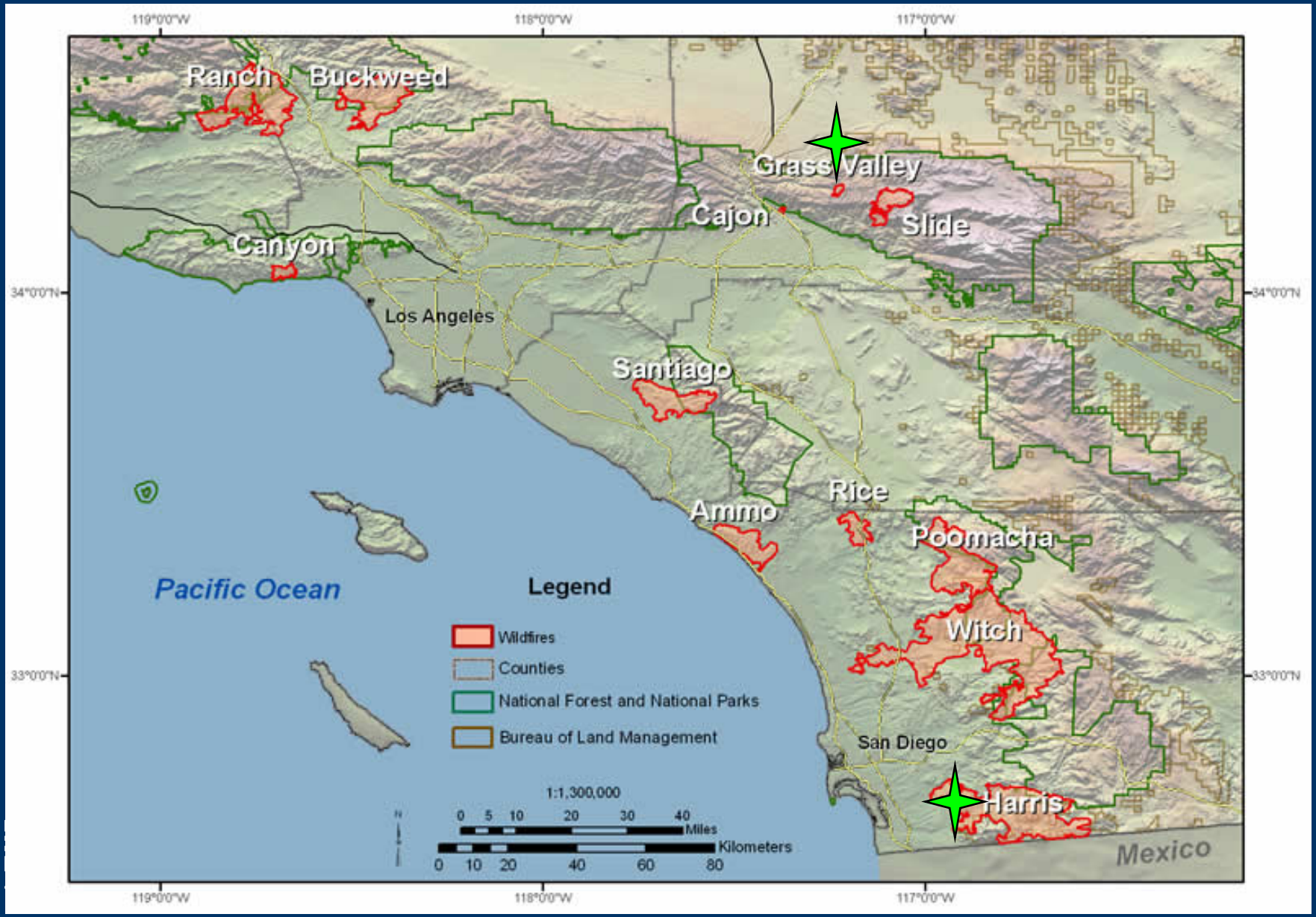
Ash from last month's southern California fires may pose problems to health and the environment, according to preliminary results from a U.S. Geological Survey (USGS) study released to the Multi-Agency State and Federal Task Force.

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.

2007 California Burn Areas



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 (e.g. 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 3100 mg/kg
  - Zn (2,800 mg/kg), EPA PRG 23000 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

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Element Content in DI-Leaches

- Total elemental analysis in 5 minute DI-water leach
  - Limited information on actual potential for toxicity or impacts on human health and environment
- Toxicity depends of chemical form of element
  - Cr(VI) >> Cr(III), Cr(VI) a known carcinogen (lung)
  - As(III) > As(V), aquatic species
  - Can we determine what form these elements are in?

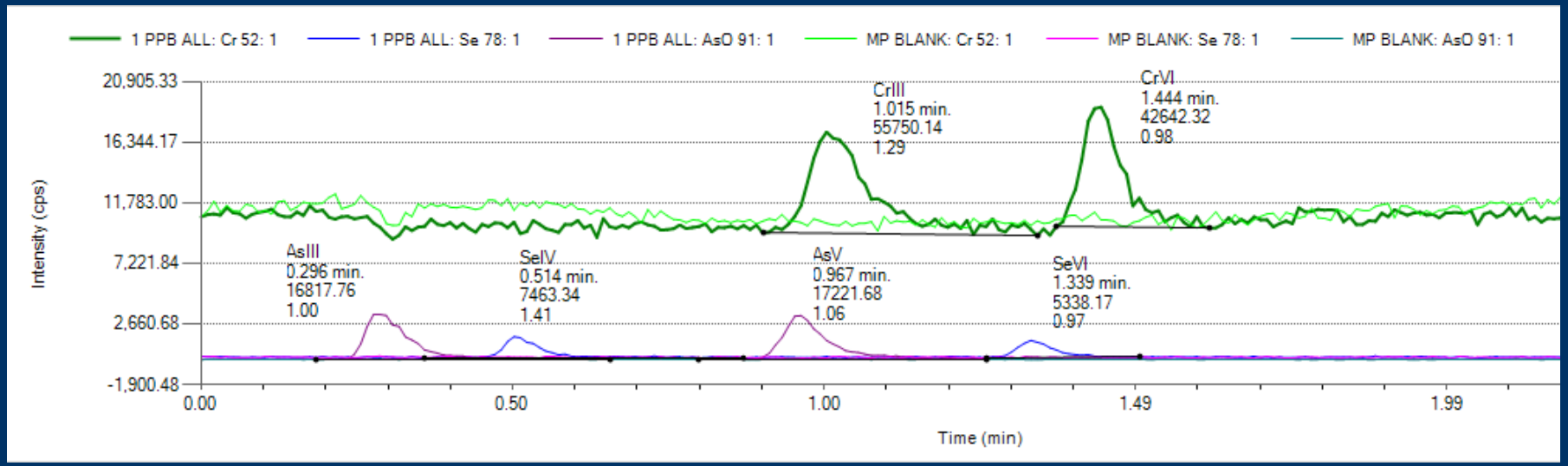
Sample	Location Description	pH	As (µg/L)	Cr (µg/L)	Se (µg/L)
Harris 06 Ash	Steep hillside	10.9	1	1.5	7.2
Grass Valley 02 Soil	Hillside	8.2	1	<1	<1
Grass Valley 02 Ash	Hillside	9.8	1	1.4	3.1
Grass Valley 01 Soil	Modern Homes	10.9	2	7.7	1.6
Grass Valley 01 Ash	Modern Homes	12.7	2	31.9	3.6
Harris 07 Soil	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

Alternative Leach Method

- Simulated lung fluid
  - 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
    - 150mM Na, 0.2mM Ca, 10 mM NH_4^+, 6mM glycine, 67mM formaldehyde, 20mM methanol, 126mM chloride, 0.5mM sulfate, 27mM hydrogen carbonate, 1.2 mM phosphate, 0.2mM citrate, adjusted to pH 7.4

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 (modified version - JAAS, 2007, 22, 1051-1060)
  - Rapid method < 2 minutes (allows stability/time studies)
  - Detection limits ~50-100 ppt in aqueous samples
- Tested in waters, soil leaches, air filter extracts, simulated bio-fluid leaches
- Sample collection/storage protocols being evaluated



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

Method Validation

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

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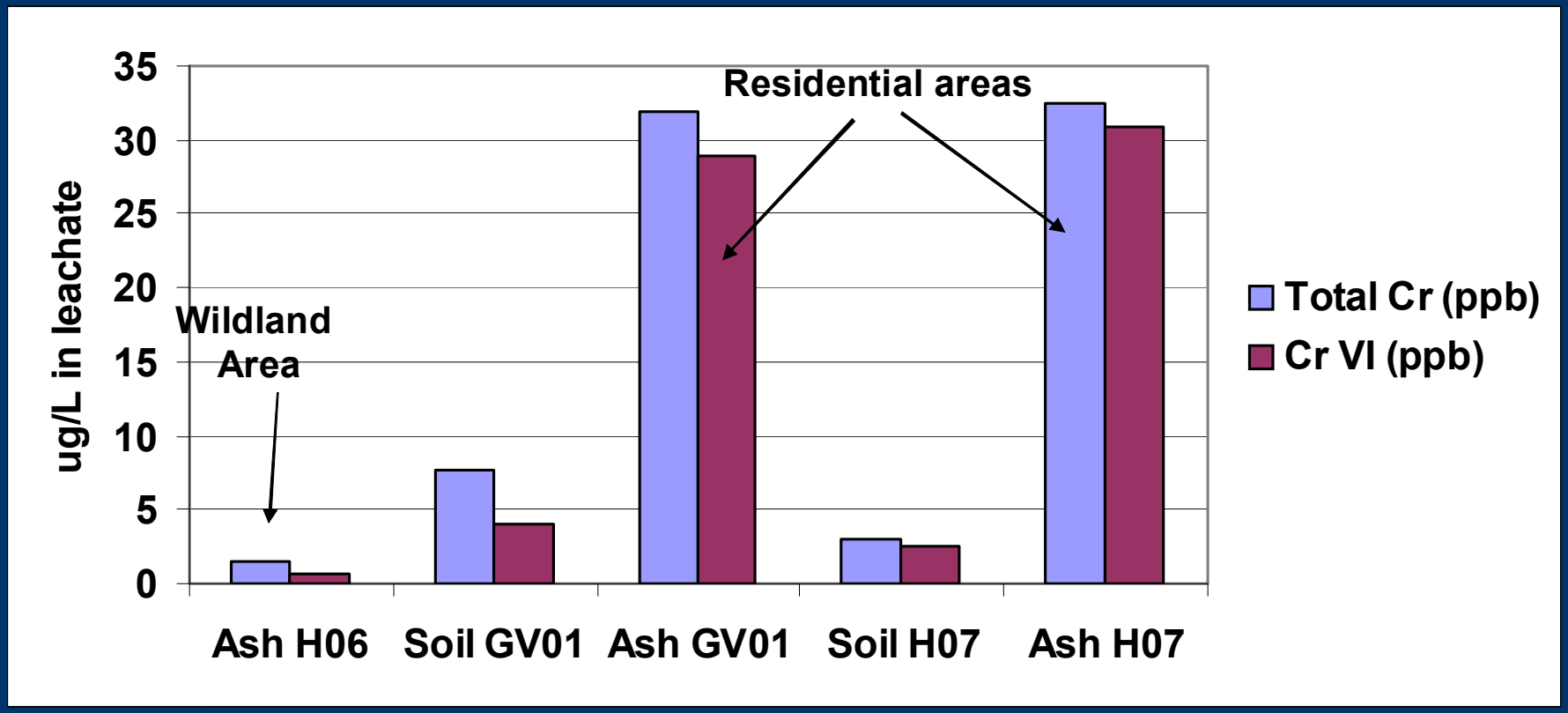
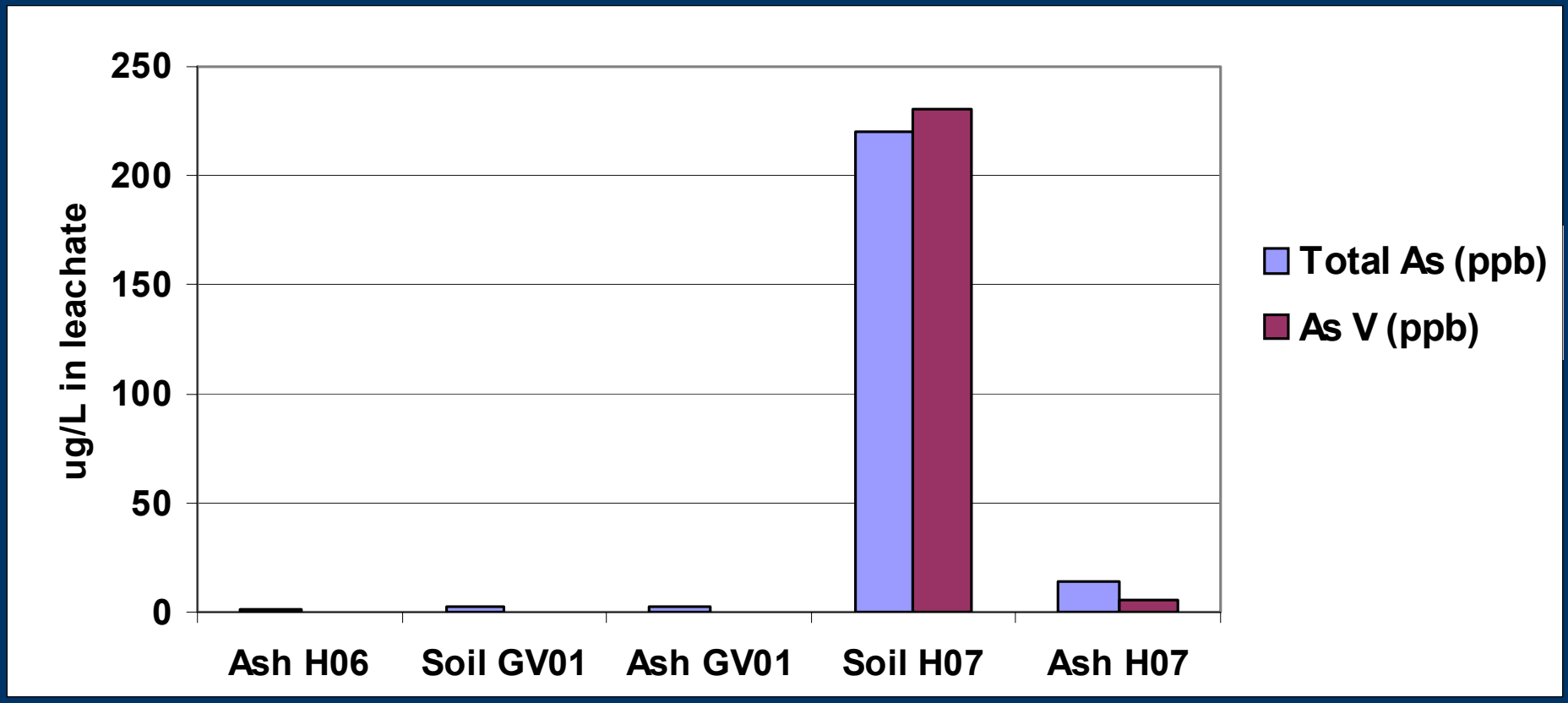
Total Cr vs. Cr(VI)

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



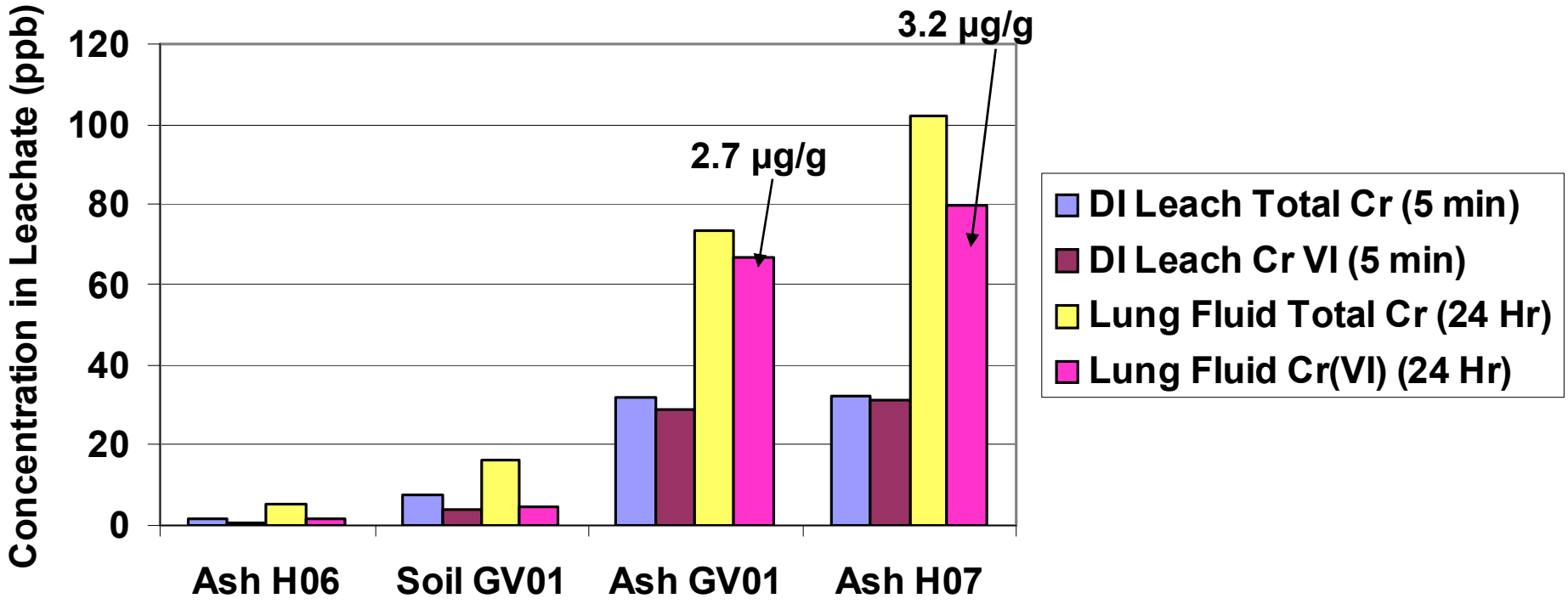
Total As vs. As(V)

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



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

- Predominant form of Cr found in fire-impacted soil and ash samples is Cr(VI)
- Soils and ashes from residential areas have higher Cr(VI) levels than wild land area
- 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
  - Air monitoring data during fire clean-up/recovery operations would be useful to assess potential exposure to Cr(VI) per OSHA PELs

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References Cited

Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service, Toxicological Profile for Chromium—Draft for Public Comment, September 2008, 610 p., *http://www.atsdr.cdc.gov/toxprofiles/tp7.html*

Hageman, P.L., 2007, U.S. Geological Survey field leach test for assessing water reactivity and leaching potential of mine wastes, soils, and other geologic and environmental materials: U.S. Geological Survey Techniques and Methods, book 5, chap. D3, 14 p.

Plumlee, Geoffrey S., Morman, Suzette A., and Ziegler, Thomas L., 2006, The toxicological geochemistry of earth materials—An overview of processes and the interdisciplinary methods used to understand them: Reviews in Mineral Geochemistry, v. 64, chap. 2, p 5–57.

Plumlee, G.S., Martin, D.A., Hoefen, T., Kokaly, R., Hageman, P., Eckberg, A., Meeker, G.P., Adams, M., Anthony, M., and Lamothe, P.J., 2007, Preliminary analytical results for ash and burned soils from the October 2007 southern California Wildfires: U.S. Geological Survey Open-File Report 2007–1407.

Wolf, Ruth E., Morrison, Jean M., and Goldhaber, Martin B., 2007, Simultaneous determination of Cr(III) and Cr(VI) using reversed-phased ion-pairing liquid chromatography with dynamic reaction cell inductively coupled plasma mass spectrometry, Journal of Analytical Atmospheric Spectrometry, v. 22, p. 1051–1060.