Exposures of Fire Fighters during Training Exercises

Dr. Brian E. McCarry, Lorraine Shaw, Don Shaw and Sujan Fernando

Department of Chemistry and Chemical Biology
McMaster University

Ontario Professional Fire Fighters Association, Health & Safety 2013
Delta Chelsea Hotel, Toronto
February 7, 2013

Fire Fighter Exposure Study: Research Goals

1. Overall Goal of Study:

To assess exposures of fire fighters to chemicals during fires, both gas-phase and particle phase chemicals.

2. Exposures of Concern:

Gases: carbon monoxide, formaldehyde

Volatile Organic Compounds: benzene, hydrocarbons, etc.

Semi-volatile Compounds: polycyclic aromatic hydrocarbons (PAH).

Particulate Material: particles and chemicals bound to particles

3. How to Assess Exposures?

Air Exposures: active and passive air samplers.

Dermal Exposures: samples from various sites.

Internal Exposures: analysis of smoke-derived chemicals in urine.

Routes of Chemical Exposures

- **Inhalation Exposures** – Should be low, except when not wearing SCBA (e.g., during knockdown and overhaul).
- **Ingestion Exposures** - Should be minimal for fire fighters.
- **Dermal (Skin) Exposures** – Surprisingly little is known about skin exposures to fire chemicals.

Part 1: Air Sampling, Skin Sampling and Analysis of Smoke Samples

Personal Air Sampling Equipment

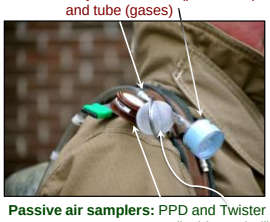
Air Sampling:

- **Active air samplers:** Filters and tubes use pumps.
- **Passive air samplers:** Personal Passive Dosimeters (PPDs) and Twisters® do not use pumps.

Gas sampling tube | Particulate filter attached to an air pump. | Twister® and 3M Personal Passive Dosimeter (PPD)

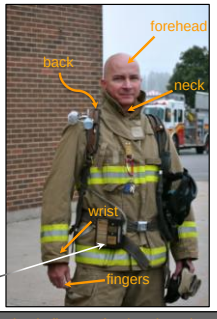
Personal Air Sampling Equipment and Skin Sampling Sites on Fire Fighters

Active Samplers: Air filter (particulate) and tube (gases)



Passive air samplers: PPD and Twister (inside tea ball)

Air pump for air filter and tube sampler



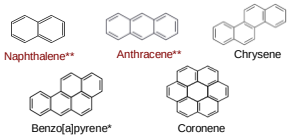
Skin sampling sites: back, fingers, forehead, neck, wrist

PAH Primer

Polycyclic Aromatic Hydrocarbons (PAH) are by-products of incomplete combustion of carbon-based fuels (wood, plastic, coal, gasoline, diesel fuel, etc.).

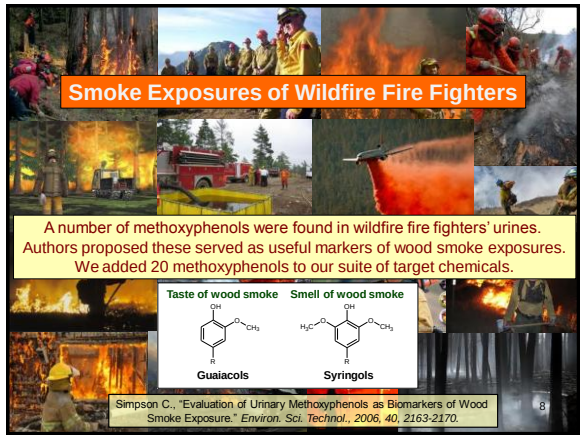
Some PAH are carcinogens*, hence concerns about getting cancer from smoke. PAH are metabolized and excreted as hydroxyPAH derivatives in urine and feces.

The levels of hydroxy-PAH in urine are considered to be an excellent measure of human PAH exposures whether *via* inhalation, ingestion or dermal routes.



** indicates compound exists primarily in gas phase

Smoke Exposures of Wildfire Fire Fighters



A number of methoxyphenols were found in wildfire fire fighters' urines. Authors proposed these served as useful markers of wood smoke exposures. We added 20 methoxyphenols to our suite of target chemicals.

Taste of wood smoke

Guaiacols

Smell of wood smoke

Syringols

Simpson C., "Evaluation of Urinary Methoxyphenols as Biomarkers of Wood Smoke Exposure." *Environ. Sci. Technol., 2006, 40, 2163-2170.*

Burn House Training Exercises

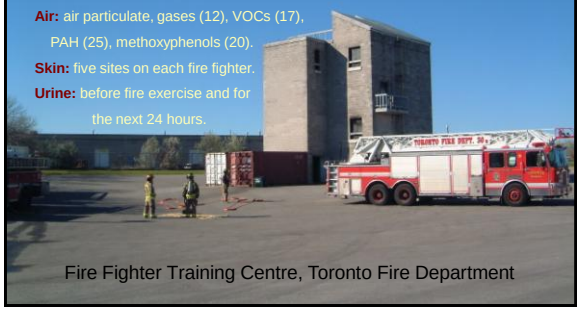
Burlington, Hamilton (2x), Ottawa, Toronto Fire Services

Sampling and Analysis:

Air: air particulate, gases (12), VOCs (17), PAH (25), methoxyphenols (20).

Skin: five sites on each fire fighter.

Urine: before fire exercise and for the next 24 hours.



Fire Fighter Training Centre, Toronto Fire Department

Analytical Instrumentation

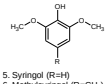
Agilent 6890N Gas Chromatograph coupled to an Agilent 5973N MSD Mass Spectrometer

Analysis of Particle Board Wood Smoke

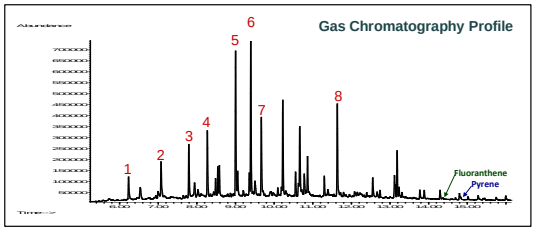
Taste of wood smoke

1. Guaiacol (R=H)
2. Methylguaiacol (R=CH_3)
3. Ethylguaiacol (R=CH_2CH_3)
4. Propylguaiacol (R=$CH_2CH_2CH_3$)

Smell of wood smoke



5. Syringol (R=H)
6. Methylsyringol (R=CH_3)
7. Ethylsyringol (R=CH_2CH_3)
8. Propylsyringol (R=$CH_2CH_2CH_3$)



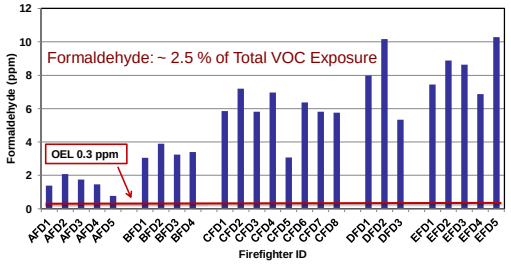
Part 2: Assessing Fire Fighter Exposures in Fire Training Exercises:

Particulate and Gases

Toronto Fire Service Burn House Training Exercise

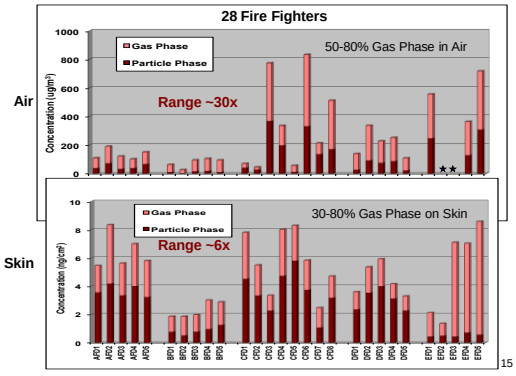
13

Formaldehyde Concentrations in Air



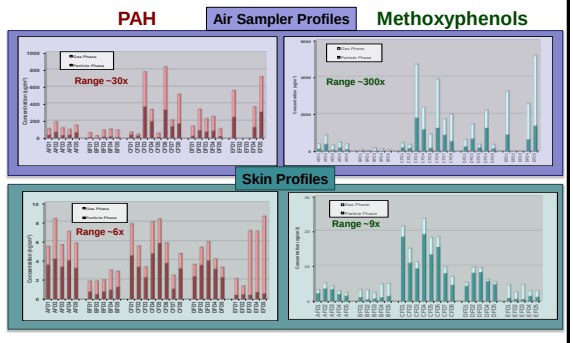
14

Comparison: Gas and Particle Phase PAH - Air vs. Skin



15

Air Sample and Fire Fighter Skin Profiles



16

Take-home Messages – Part 2

- Exposures to particles and gas–phase chemicals in fire training exercises exceed Occupational Exposure Limits.
- Skin vs. air exposures:
  - Skin exposures correlate roughly with air concentrations.
  - Particle-phase chemicals more predominant on skin than in air.
  - Even rather low concentrations of chemicals in air can result in significant skin exposures.

17

Part 3: Skin Sampling:

Evaluation of Body Exposures to Smoke

18

Skin Sampling

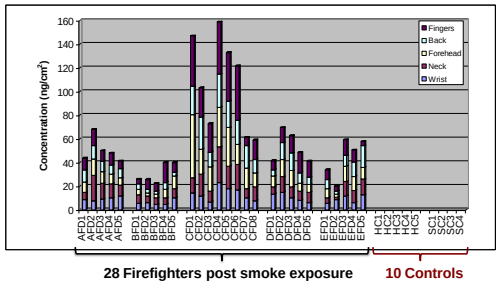
Skin Sampling Protocol:

- There are no standard methods for sampling chemicals on skin.
- We have used a filter paper wipe method with rubbing alcohol (isopropanol).
- Fire fighters were sampled **before** and **after** exercise in training facility at 5 body sites:

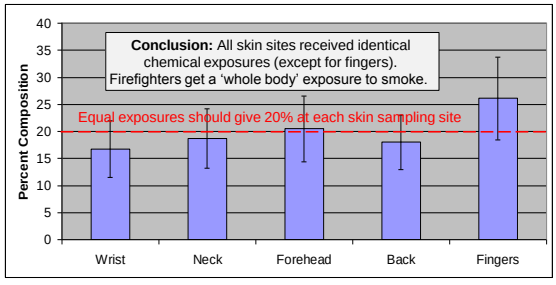
Back, fingers, forehead, neck and wrist.

Skin Sampling of Ottawa Fire Fighters

PAH and Methoxyphenol Concentrations at 5 Skin Sites



Percentage Compositions of PAH and Methoxyphenols on Skin (28 Fire Fighters)



	Wrist	Neck	Forehead	Back	Fingers
T-test (p values)	0.05	0.34		0.18	0.02

Take-home Messages – Part 3

- Exposures at 5 sites essentially identical.
- Result: a 'whole body' exposure.
- Finger exposures higher due to post-fire handling of sooty gear.

- Recommendations:
  - Shower thoroughly at fire hall after a fire.
  - Change into clean clothes to go home.
  - Don't wear Nomex undergear home.

Part 4: Urine Sampling:

Analysis of PAH Metabolites and Methoxyphenols in Urine

HydroxyPAH and Methoxyphenols as Exposure Indicators

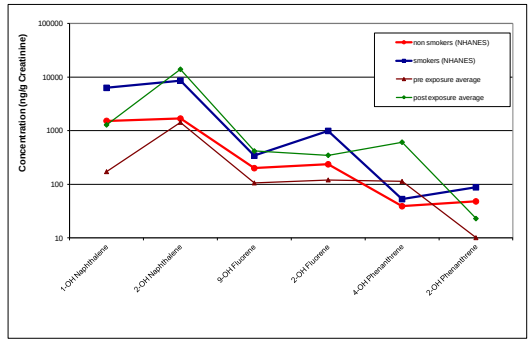
- The determination of hydroxyPAH in urine is considered to be the best measure of PAH exposures in humans.
- For many years, **1-hydroxypyrene** was the only compound used as a PAH exposure marker. Today, a **suite of hydroxyPAH** is advocated as the new measure of PAH exposure (as used in NHANES Study).
- Selected methoxyphenols are good indicators of wood smoke exposures.

Urine Sample

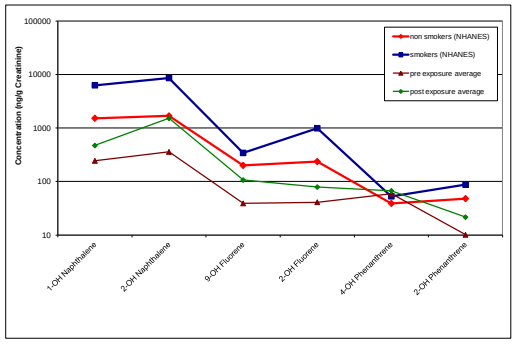
Step 1:

Provide a Urine Sample

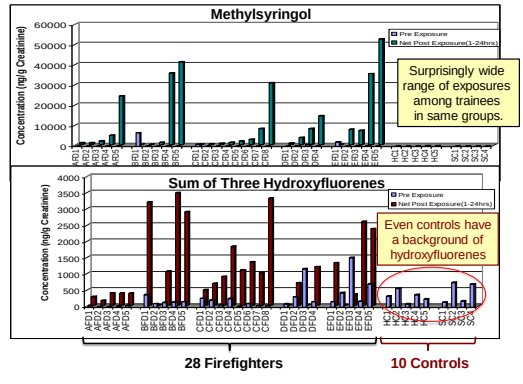
HydroxyPAH Urine Profiles of 'Top 5' Firefighters



HydroxyPAH Urine Profiles of 'Low 5' Firefighters

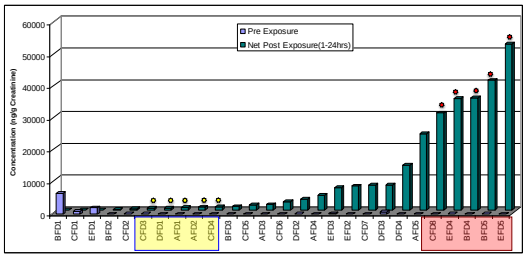


Methylsyringol and Hydroxyfluorene Levels in FF Urines



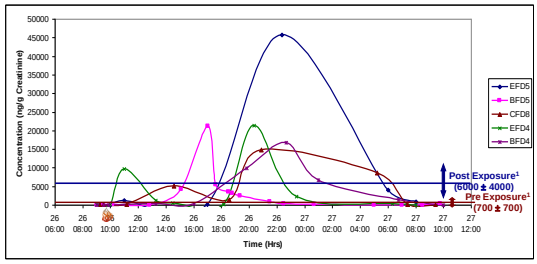
Net Methylsyringol Levels in All Fire Fighters

Sorted by methylsyringol levels: 'Top 5' and 'Low 5' highlighted



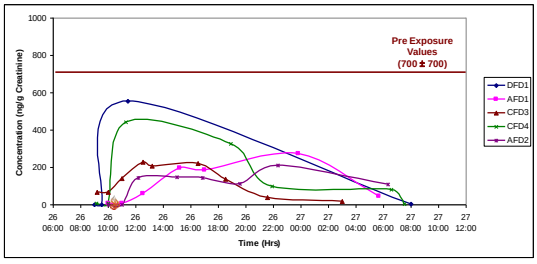
Low 5 Top 5

Urinary Methylsyringol Profiles of 'Top 5' Fire Fighters over 24 Hours



Methylsyringol shown to be the "best" marker of wood smoke exposures. Methylsyringol levels very low before exposure and return to low levels within 24 hours. Simpson C., "Evaluation of Urinary Methoxyphenols as Biomarkers of Wood Smoke Exposure." *Environ. Sci. Technol., 2006, 40, 2163-2170.*

Urinary Methylsyringol Profiles of 'Low 5' Fire Fighters over 24 Hours



Note: Scale on this graph is **140 times** less than previous "Top 5 Fire Fighters" plot.

Take-home Messages – Part 4

- Reliable urinary markers of wood smoke exposures (hydroxyPAH and methoxyphenols) confirmed.
- Exposures to smoke chemicals varied greatly.
- In highest exposures, hydroxyPAH levels equaled levels found in average US smoker.
- After 24 hours hydroxyPAH and methoxyphenols in urine returned to pre-exposure levels.

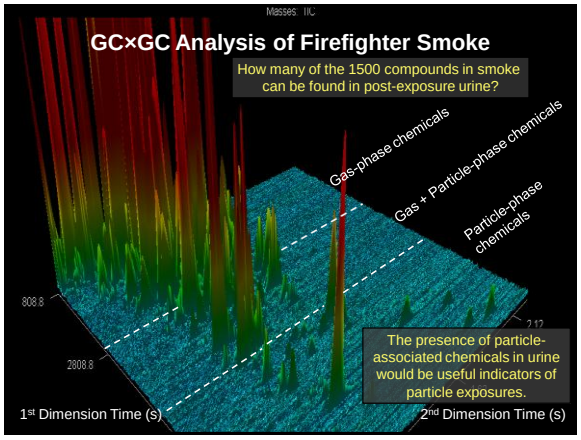
- Recommendations:
  - ➢ Make sure SCBAs are properly fitted on fire fighters.
  - ➢ Drink lots of fluids after fire.

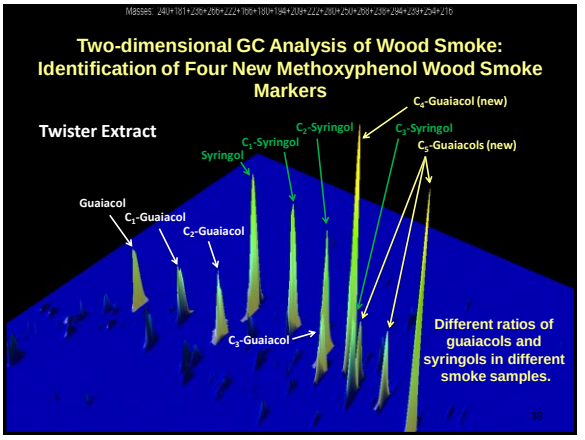
34

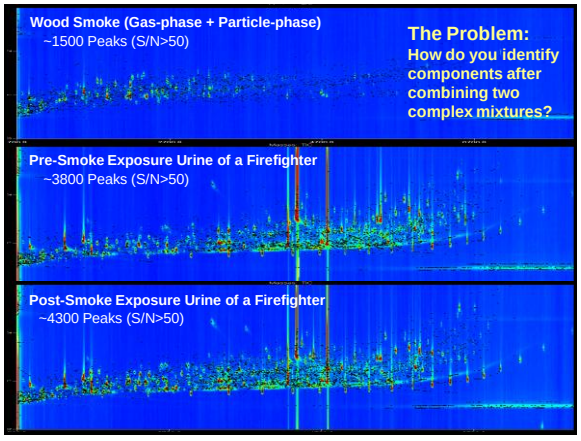
Part 5: Identification of New Markers of Smoke Exposures

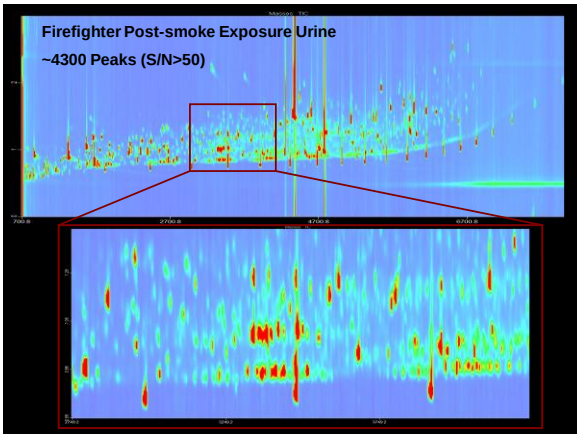
Analysis of Smoke and Urine Samples to Identify New Chemical Indicators of Smoke Exposures

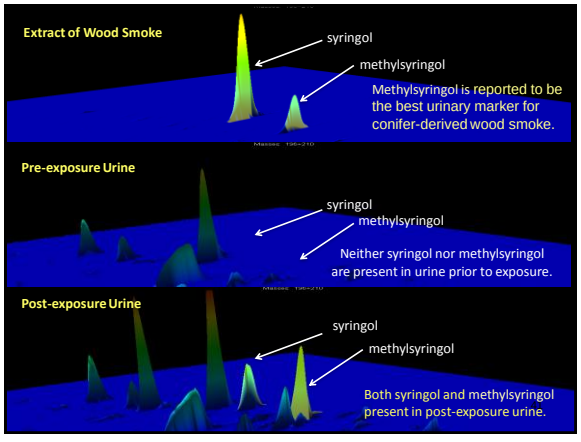
35

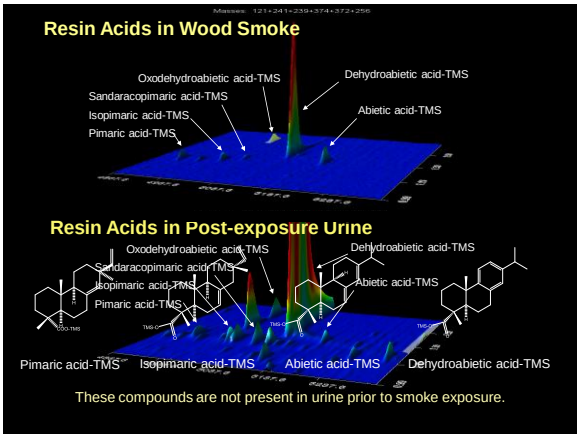

GC×GC Analysis of Firefighter Smoke
How many of the 1500 compounds in smoke can be found in post-exposure urine?
Gas-phase chemicals
Gas + Particle-phase chemicals
Particle-phase chemicals
The presence of particle-associated chemicals in urine would be useful indicators of particle exposures.
1st Dimension Time (s)
2nd Dimension Time (s)


Two-dimensional GC Analysis of Wood Smoke: Identification of Four New Methoxyphenol Wood Smoke Markers
Twister Extract
Guaiacol
C1-Guaiacol
C2-Guaiacol
C3-Guaiacol
Syringol
C1-Syringol
C2-Syringol
C3-Syringol
C4-Guaiacol (new)
C4-Guaiacols (new)
Different ratios of guaiacols and syringols in different smoke samples.


Wood Smoke (Gas-phase + Particle-phase)
~1500 Peaks (S/N>50)
The Problem:
How do you identify components after combining two complex mixtures?
Pre-Smoke Exposure Urine of a Firefighter
~3800 Peaks (S/N>50)
Post-Smoke Exposure Urine of a Firefighter
~4300 Peaks (S/N>50)

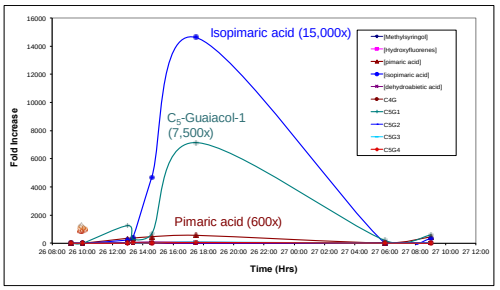

Firefighter Post-smoke Exposure Urine
~4300 Peaks (S/N>50)


Extract of Wood Smoke
syringol
methylsyringol
Methylsyringol is reported to be the best urinary marker for conifer-derived wood smoke.
Pre-exposure Urine
syringol
methylsyringol
Neither syringol nor methylsyringol are present in urine prior to exposure.
Post-exposure Urine
syringol
methylsyringol
Both syringol and methylsyringol present in post-exposure urine.


Resin Acids in Wood Smoke
Oxodehydroabietic acid-TMS
Dehydroabietic acid-TMS
Sandaracopimaric acid-TMS
Isopimaric acid-TMS
Abietic acid-TMS
Pimaric acid-TMS
Resin Acids in Post-exposure Urine
Oxodehydroabietic acid-TMS
Dehydroabietic acid-TMS
Sandaracopimaric acid-TMS
Isopimaric acid-TMS
Abietic acid-TMS
Pimaric acid-TMS
Pimaric acid-TMS
Isopimaric acid-TMS
Abietic acid-TMS
Dehydroabietic acid-TMS
These compounds are not present in urine prior to smoke exposure.

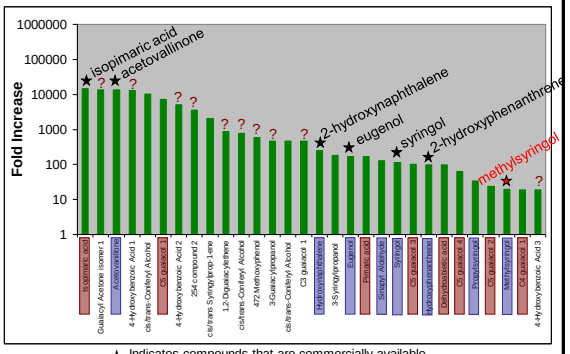
GC-MS/MS Analyses of Urine Samples

Fold increase in post-exposure urine of selected smoke marker compounds in the urines of exposed firefighter compared to pre-exposure levels.



Fire training exercise from 10-10:30 a.m.

Fold Increase in Post-exposure Urine (log scale)



★ Indicates compounds that are commercially available

? Indicates compounds that are unknowns

Take-home Messages – Part 5

- New chemical markers of particulate smoke exposure identified.
- No chemical markers of particulate exposure exist.
- Additional urinary smoke markers also identified.
- Ten chemicals identified in urine which showed more than 1000x increases following smoke exposure.

- Recommendations:
  - These new markers should be investigated in detail so see how useful they are as measures of smoke and particulate exposures.

Conclusions: Fire Fighter Smoke Exposures

- Fire fighters in fire-training exercises experience wide range of exposures to over 1500 fire-generated chemicals.
- Skin analyses of fire fighter trainees showed they received similar exposures to smoke chemicals at five body sites. Fire fighters likely receive a "whole-body exposure" to smoke.
- Methylsyringol and three hydroxyfluorenes are excellent urinary markers of smoke exposure.
- Ten new wood smoke chemicals identified in urine which show huge changes (>1000-fold) pre-exposure versus post-exposure.
- Smoke chemicals are substantially cleared from the body within 24 hours.

Recommendations to Reduce Smoke Exposures

- Fire fighters should shower at the fire station.
- Fire fighters should wear clean clothes home after a fire.
- Fire fighters should make sure that their SCBA mask fits properly on their face.
- The reasons for the variability of smoke markers in urine needs to be sorted out.

The Future

- WSIB grant has ended.
- We are in the process of arranging meetings with the 28 fire fighters who participated in this study.
- Interviews will be conducted by Lorraine Shaw (CIH), Don Shaw (CIH) and Dr. Ron House, an occupational health physician.
- We have applied for provincial funding to follow up on this study.

Acknowledgements

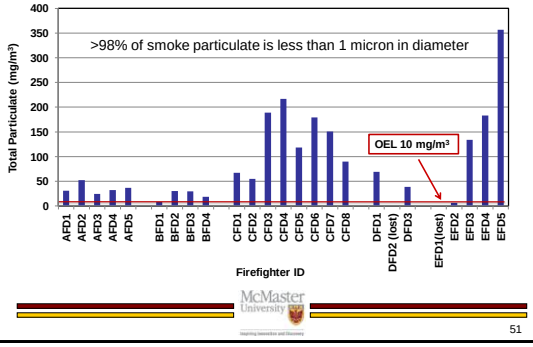
We would like to thank:

- The Ontario WSIB for funding this study.
- Fire Services in Burlington, Hamilton, Ottawa and Toronto for all their cooperation and assistance.
- The Ontario Professional Fire Fighters Association for their kind invitation to speak at this conference.

McMaster University

49

Airborne Particulate Concentrations



McMaster University

51

California Wildfires: October 24, 2007

Many wildfire fire fighters are exposed to high levels of smoke when fighting these fires. There are serious concerns about smoke exposures of these fire fighters.

Conclusions

GC×GC-TOF-MS and GC-MS-MS Analyses of Wood Smoke and Urine Samples

- GC×GC analyses of smoky air and urine samples of exposed firefighters resulted in the identification of a number of new wood smoke markers.
- New urinary markers for smoke particulate exposure identified.
- Identification of >200 wood smoke markers in the smoky air and in urine samples using a user-built library and the NIST 2008 library.
- GC-MS-MS analyses have been developed for quantitative analysis of wood smoke markers in air, on skin and in urine.

53