Fire Literacy - The Effects of Smoke

F.I.R.E. 2013
Firefighting. Instruction. Research. Engineering

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OTTAWA FIRE SERVICES
SERVICE DES INCENDIES D'OTTAWA
Protecting Our Nation's Capital With Pride
Protéger notre capitale nationale avec fierté

What is Industrial Hygiene?

- Industrial hygiene is the science of anticipating, recognizing, evaluating, and controlling workplace conditions that may cause workers' injury, illness or death.
- Industrial hygienists use environmental monitoring and analytical methods to detect the extent of worker exposure and employ engineering, work practice controls, and other methods to control potential health hazards.

Percivall Pott

F.R.S., 1714 – 1788

English surgeon, one of the founders of orthopedy, and the first scientist to demonstrate that a cancer may be caused by an environmental carcinogen.

"Every body is acquainted with the disorders to which painters, plumbers, glaziers and the workers in white lead are liable; but there is a disease as peculiar to a certain set of people which has not, at least to my knowledge, been publickly noticed; I mean chimney sweeper's cancer"…

Young boys with testicular cancer as early as twelve years old due to soot (creosote) exposures!

300 Years Later
What Have We Learned?

- Chimney sweeps in England were young children and rarely bathed due to the association of water with water borne diseases
- Whereas in France bathing was more common and chimney sweeps did not develop scrotal cancer
- In Germany sweeps wore thick tight-fitting pants & shirts which prevented contact of the soot to the skin
- PPE & Bathing are basic industrial hygiene measures !

What is SMOKE?

The airborne solid and liquid particulates and gases evolved when a material undergoes pyrolysis or combustion, together with the quantity of air that is entrained or otherwise mixed into the mass.

SOLID & LIQU ES & GASES

Particles
Solids & Liquids

- A particle may refer to an atom, part of an atom, a molecule or an ion
- Particulates are a suspension of particles and are also known as Particulate Matter or PM
- The size of particles is directly linked to their potential for causing health problems

Particles
Solids & Liquids

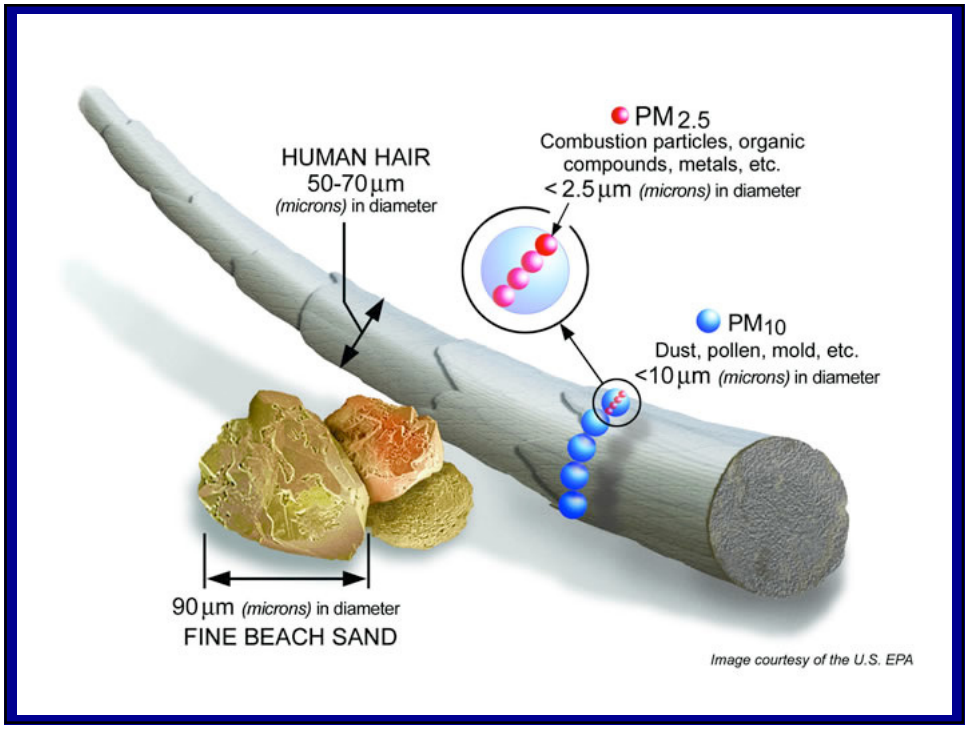
- Exposure to such particles can affect both your lungs and your heart
- Small particles of concern include
  - "inhalable coarse particles" - 2.5 to 10 micrometres in diameter
  - "fine particles" - 2.5 micrometres in diameter and smaller.
  - **NOTE: 2.5 *U*m = 2500 nano metres (nm)**

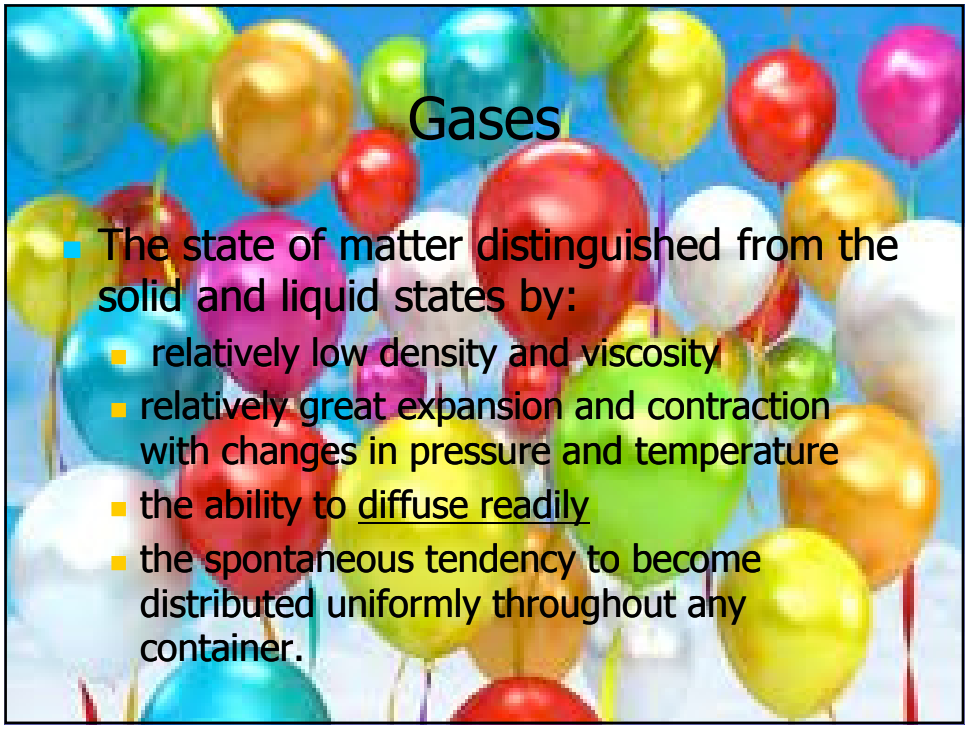
Particulates
Solids & Liquids

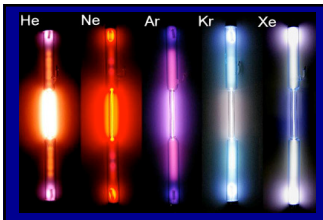
- Smoke particulates may be solids (ash, soot, fibres and dust) or liquids (tar, water)
- Smoke particulates have three modes of particle size distribution:
  - nuclei mode, with geometric mean radius between 2.5–20 nm
  - accumulation mode, ranging between 75–250 nm and formed by coagulation of nuclei mode particles
  - coarse mode, with particles in micrometer range

Nano Names

- In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties
- Particles further classified to size in terms of diameter:
  - Coarse particles range between 10,000 and 2,500 nanometres
  - Fine particles range between 2,500 and 100 nanometres
  - Ultrafine particles, or nanoparticles range between 100 and 1 nanometres.
  - Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution
  - Nanopowders are agglomerates of ultrafine particles/nanoparticles, or nanoclusters
  - Nanocrystals are nanometer-sized single crystals, or single-domain ultrafine particles


HUMAN HAIR
50-70 µm
(microns) in diameter
PM2.5
Combustion particles, organic compounds, metals, etc.
< 2.5 µm (microns) in diameter
PM10
Dust, pollen, mold, etc.
<10 µm (microns) in diameter
90 µm (microns) in diameter
FINE BEACH SAND
Image courtesy of the U.S. EPA


Gases
The state of matter distinguished from the solid and liquid states by:
relatively low density and viscosity
relatively great expansion and contraction with changes in pressure and temperature
the ability to diffuse readily
the spontaneous tendency to become distributed uniformly throughout any container.



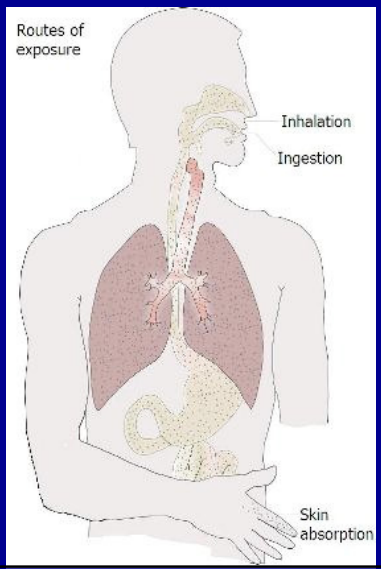
Gases

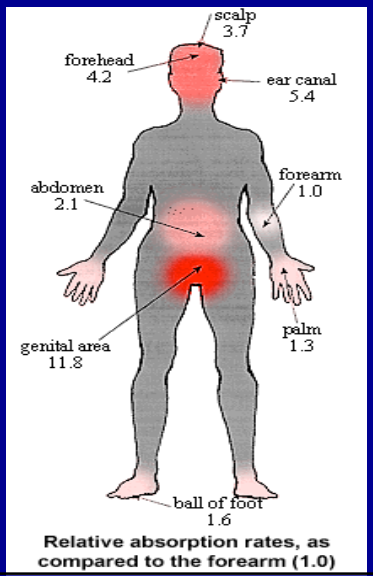
- A pure gas may be made up of individual atoms, elemental molecules made from one type of atom (e.g. oxygen), or compound molecules made from a variety of atoms (e.g. carbon dioxide).
- A gas mixture would contain a variety of pure gases much like the air.
- What distinguishes a gas from liquids and solids is the vast separation of the individual gas particles.

Gases – Wood Smoke

- ***carbon monoxide***, 66methane, volatile organic compounds (C2-C7), aldehydes: formaldehyde, 72acrolein, propionaldehyde, butyraldehyde, acetaldehyde, furfural; substituted furans, benzene, alkyl benzenes: Otoluene, acetic acid, formic acid; nitrogen oxides (NO, NO2), sulfur dioxide, methyl chloride,naphthalene, substituted naphthalenes, oxygenated monoaromatics: guaiacol (and derivatives), phenol (and derivatives), syringol (and derivatives), catechol (and derivatives); particulate organic carbon, oxygenated polycyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons: fluorene, phenanthrene, anthracene, methylanthracenes, fluoranthene, pyrene,benzo(a)anthracene, chrysene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, perylene, pyrene, benzo(ghi)perylene, coronene, Odibenzo(a,h)pyrene, retene, dibenz(a,h)anthracene; trace elements: Sodium, Magnesium, Aluminum, Silicon, Sulfur, Chlorine, Potassium, Calcium, Titanium, Vanadium, OChromium, Manganese, Iron, Nickel, Copper, Zinc, Bromine, Lead; particulate elemental carbon, normal alkanes (C24-C30), cyclic di-and triterpenoids, dehydroabietic acid, isopimaric acid, lupenone, friedelin, Ochlorinated dioxins

Smoke & The Routes of Entry

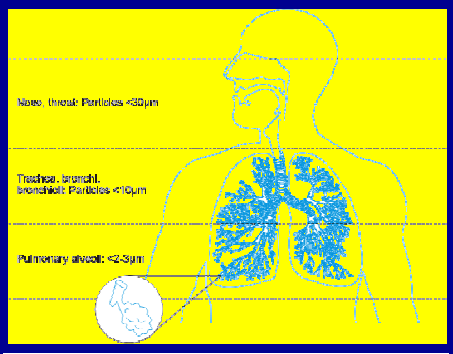




Routes of Exposure: Inhalation

Inhalation has been a major focus of the nanotoxicology community; NP penetration into the lung depends on its aggregation state

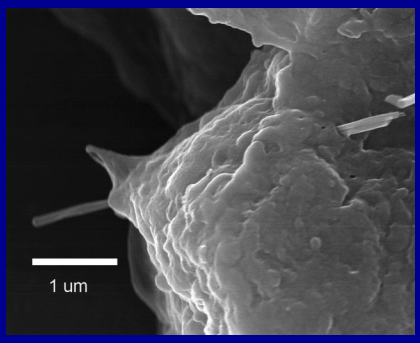
- Airborne NPs can be inhaled and deposit in the respiratory tract
- Inhaled NPs may enter the blood stream and translocate to other organs



Inhalation Hazards

Certain nanomaterials can

- Induce cancers, including mesothelioma
- Cause rapid and persistent pulmonary fibrosis
- Cause cardiovascular dysfunction
- Migrate along the olfactory nerve into the brain



Alveolar Epithelial Penetration by Multi-walled Carbon Nanotube

Courtesy of R. Mercer, NIOSH

Different Types of Nanomaterials

Naturally Occurring	Human Origin (Incidental)	Human Origin (Engineered)
Forest fires	Cooking smoke	Metals
Sea spray	Diesel exhaust	Quantum dots
Mineral composites	Welding fumes	Buckyballs/Nanotubes
Volcanic ash	Industrial effluents	Sunscreen pigments
Viruses	Sandblasting	Nanocapsules

Nanotechnology

Incidental Nanoparticles' Health Effects

Human Origin (Incidental	Health Impacts
Cooking smoke	Pneumonia; chronic respiratory disease; lung cancer
Diesel exhaust	Cancer; respiratory disease
Welding fumes	Metal fume fever; infertility; benign pneumoconiosis
Industrial emissions/effluents	Asthma, atherosclerosis, chronic obstructive pulmonary disease
Sandblasting	Silicosis

Ultrafine Particle Exposure During Fire Suppression
Is It an Important Contributory Factor for Coronary Heart Disease in Firefighters?

C. Stuart Baxter, PhD, Clara Sue Ross, MD, JD, Thomas Fabian, PhD, Jacob L. Borgerson, PhD, Jamila Shawon, MS, Pravinray D. Gandhi, PhD, James M. Dalton, MArch, and James E. Lockey, MD, MS

- Conclusions: Exposure to ultrafine particles during fire suppression should be considered a potential contributing factor for CHD in firefighters.
- Of major significance is their predominance during overhaul, where firefighters frequently remove respiratory protection.
-

NIOSH Mice Study Finds Nanotubes Lung Cancer Risk

- Can exposure to mulyi-walled carbon nanotubes promote lung cancer ?
  - Preliminary answer: YES!
  - 1.3 tumors in 50% of the control saline mine
  - 3.3 tumors in 90% of the **Methylcholanthrene exposed mice**
- *http://nanotech.lawbc.com/2013/03/articles/united-states/federal/niosh-announces-new-findings-on-lung-tumor-formation-in-laboratory-mice-exposed-to-multiwalled-carbon-nanotubes/*

Routes of Exposure: Ingestion

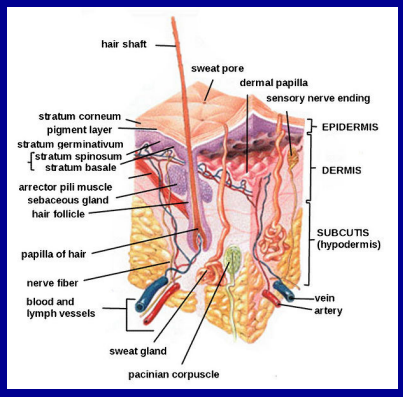
Ingestion is a viable route of exposure;
Ingested nanoparticles can translocate throughout the body

- Ingestion may occur after inhalation exposure when mucus is brought up the respiratory tract and swallowed
- Poor work practice can result in hand-to-mouth transfer
- Ingested nanoparticles do translocate to other organ systems
  - **SWCNT delivered into gut for treating Alzheimer's disease were found in liver, brain and heart**
  - **Ingestion of colloidal silver can result in permanent discoloration of skin, nails and eyes**

Routes of Exposure: Dermal

Available data are limited and often conflict;
Skin cannot be ruled out as a potential route of exposure

- Several studies show little to no penetration of nanoscale oxides beyond surface skin layers
- Polysaccharide and metal nanoparticles have been shown to penetrate flexed, damaged or diseased skin
- Quantum dots were found to penetrate intact pig skin within 8-24 hours at occupationally relevant doses



Routes of Exposure: Dermal

- Skin does act as a protective barrier against some chemicals
- Chemicals via gases and particles are being absorbed through the skin into the blood vessels
- Some chemicals can penetrate the skin causing damage to the skin/tissue
  - Dermatitis

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

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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 skin sites.

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

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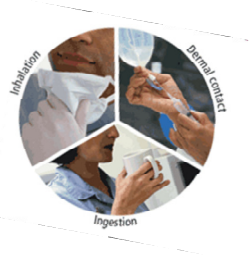
Routes of Chemical Exposures

- **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.



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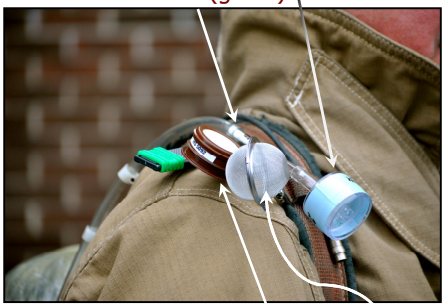
Personal Air Sampling Equipment and Skin Sampling Sites on Fire Fighters

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

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Skin Sampling of Ottawa Fire Fighters
Back
Forearm
Neck
Fingers
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Take-home Messages

- 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.

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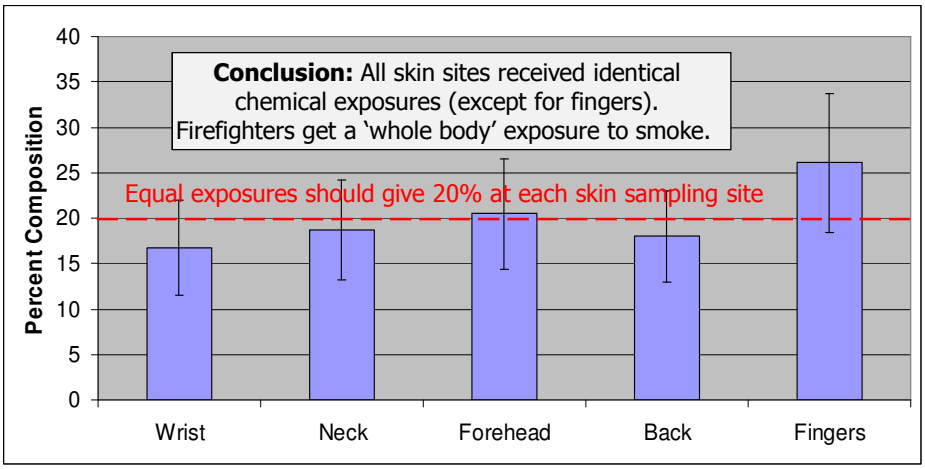
Percentage Compositions of PAH and Methoxyphenols on Skin (28 Fire Fighters)



T-test (p values)	0.05	0.34		0.18	**0.02**

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Take-home Messages

- 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 uniform & underwear home.

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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

Take-home Messages

- 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.

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Part 5: Identification of New Markers of Smoke Exposures

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

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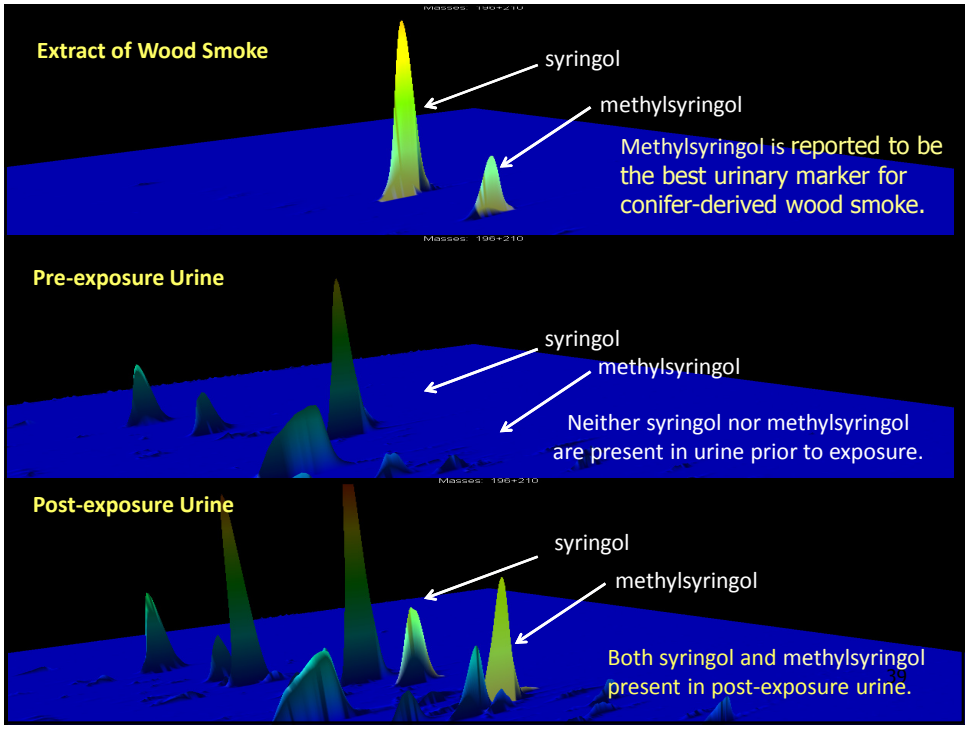
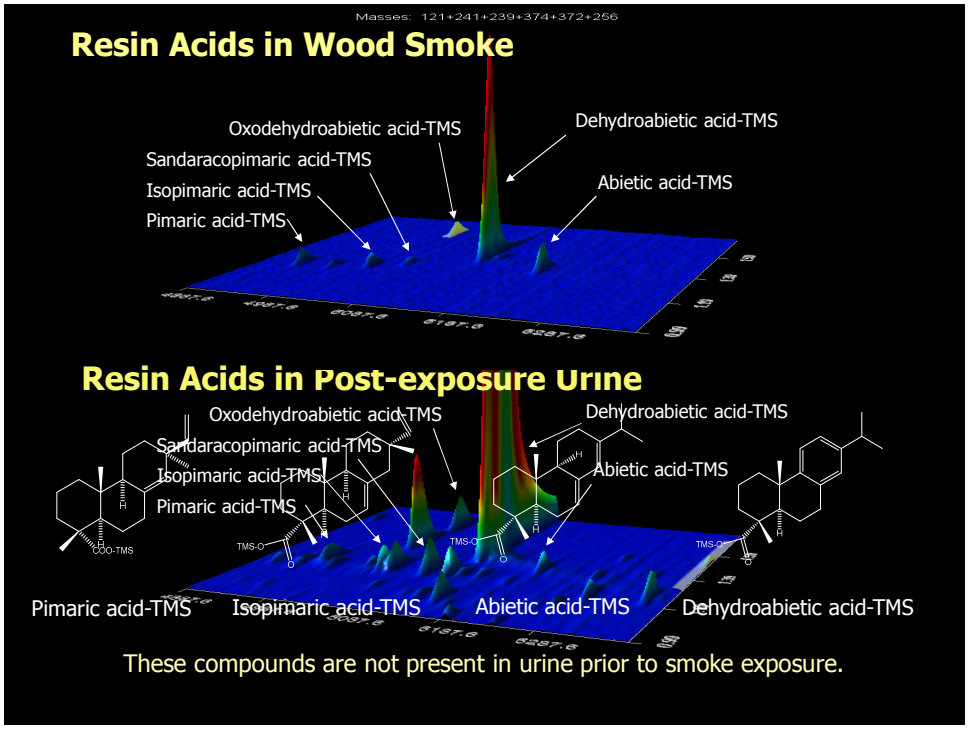

Extract of Wood Smoke
syringol
methylsyringol
Methylsyringol is reported to be the best urinary marker for conifer-derived wood smoke.
Masses: 196+210
Pre-exposure Urine
syringol
methylsyringol
Neither syringol nor methylsyringol are present in urine prior to exposure.
Masses: 196+210
Post-exposure Urine
syringol
methylsyringol
Both syringol and methylsyringol present in post-exposure urine.


Masses: 121+241+239+374+372+256
Resin Acids in Wood Smoke
Oxodehydroabietic acid-TMS
Sandaracopimaric acid-TMS
Isopimaric acid-TMS
Pimaric acid-TMS
Dehydroabietic acid-TMS
Abietic acid-TMS
Resin Acids in Post-exposure Urine
Oxodehydroabietic acid-TMS
Sandaracopimaric acid-TMS
Isopimaric acid-TMS
Pimaric acid-TMS
Dehydroabietic acid-TMS
Abietic 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.

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.

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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.

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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.

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.

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Conclusions

- Much of the early nanoEHS research has focused on simple systems of limited relevance to human health (e.g., cytotoxicity)
- Some nanoparticles can translocate throughout the body after exposure via inhalation, ingestion or contact with skin
- Some nanoparticles can induce unwanted health effects in animals or cell cultures
- WSIB study indicates firefighters are receiving a whole body exposure to the skin and particles and chemicals are being absorbed into the body

It makes sense to control exposure to those nanomaterials for which preliminary hazard data show unwanted health effects or hazards are unknown

F.I.R.E. in the Mind

UN Declaration

INTERNATIONAL YEAR OF THE FIRE FIGHTER

- Objectives
  - Focus passion and the committed human mind on:
    - Fire Fighting (Anticipation, Prevention, Intervention, Recovery)
    - Instruction
    - Research
    - Engineering

International Partnerships

Urgent, Significant

Build Connections

Share, Store Data

Expand FIRE Community

Outreach Programmes

Expressions of Interest → Coordination Proposals → Endorsed Projects

"International Year of the F.I.R.E. Fighter "

"Progress Inspired by Tradition"

Fire Literacy - The Effects of Smoke

F.I.R.E. 2013
Firefighting. Instruction. Research. Engineering

Peter McBride
Division Chief – Safety & Innovation
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