Assessment of Woodsmoke Exposure in Wild-land Firefighters

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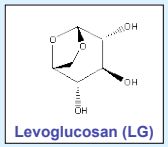
BACKGROUND

Woodsmoke is a complex mixture of particles and gaseous components. The fine particulate matter of less than 2.5 µm in diameter along with other chemicals like polycyclic aromatic hydrocarbons, nitrogen dioxide, volatile organic compounds, and carbon monoxide are of concern because of their contribution to adverse health such as asthma, COPD, impaired lung function, and lung cancer. 100,000 people annually are exposed to elevated levels of woodsmoke from wildfires, urban fires, agricultural field burning, and prescribed burns. An estimated 70,000-80,000 of these individuals are wildland firefighters. To better understand this occupational exposure, personal sampling of 12 United States Forest Service (USFS) firefighters working controlled burn activities at Savannah River Site, Georgia took place during Spring '08. Their exposures to fine particle matter ($PM_{2.5}$), carbon monoxide (CO), and levoglucosan (LG) are characterized here.



Levoglucosan (LG)

METHODS AND DESIGN

Collection and Analysis of Particulate Matter

Personal levels of $PM_{2.5}$ (µg/m³) were measured on firefighters on days they worked on a prescribed burn. They wore the $PM_{2.5}$ sampling equipment for the full work shift. Personal sampling was accomplished by an SKC Air Check Pump attached to a cyclone selective for fine particle matter by Tygon tubing. Attached to the cyclone was cassette with a PTFE membrane filter inside where the particulate matter could be collected.

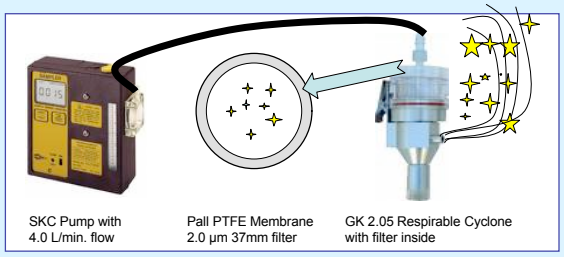


Figure 1: Sampling equipment for collection of $PM_{2.5}$ and levoglucosan

To quantify the amount of $PM_{2.5}$ on the filters, gravimetric analysis was conducted at the University of Georgia before being shipped over to the University of Washington for levoglucosan extraction analysis.

Figure 2: Draeger Pac III CO chemical Sensor

Measurement of CO

Carbon monoxide (CO) was measured using a Draeger Pac III CO chemical sensor with data logger. Measurements were taken and logged every 60 seconds. Equipment was hung at the beginning and removed at the end of each shift. Time weighted average concentrations of CO are reported here for each firefighter workshift.

Determination of LG Concentration

In the laboratory, extraction and analysis of levoglucosan from the $PM_{2.5}$ collected on the filters followed the analytical procedure below [1-2].

- Spike Teflon filters with d7-levoglucosan (recovery standard)
- Add 30 mL EtOAc with Triethylamine and sonicate 1 hour
- Reduce volume to 0.5 mL with TurboVap (N_2)
- Filter extract and add internal standard + derivatization standard
- Derivatize 50 µL with MSTFA and pyridine for 6+ hours
- Analyze levoglucosan by GC/MS

Table 1: Chemicals

Chemical	Amount	Purpose
Ethyl Acetate containing 3.6 mM triethylamine	30 ml	Extraction solvent
Deuterated levoglucosan (d7-LG)	20 µl	Recovery standard
Anhydroheptulose	20 µl	Derivatization standard
Triisopropylbenzene	20 µl	Internal standard
Methylsilyltrifluoroacetamide (MSTFA*) w/ 1 % trimethylchlorosilane + pyridine	50 µl	Derivatization agent

* MSTFA is a silylating agent that replaces the reactive alcohols in a molecule to produce a volatile and thermally stable derivative. The derivative gives better chromatographic separation and stronger detector response than the underivatized levoglucosan.

GC/MS Detection

The instrument was programmed to selectively monitor specific ions created from splitless injection of the derivatized samples. The peaks of most interest are the LG and d7-LG peaks which had *m/z* ratios of 204 and 206 respectively. The concentration of the two were then quantified by relative response to the internal standard and a calibration curve below. The calibration was set to quantify LG concentrations 0.1-100 µg/mL in the extract. Workshift LG exposures = (LG extract concentration)*(extract volume, 0.5 ml) / workshift air volume = µg/m³ LG

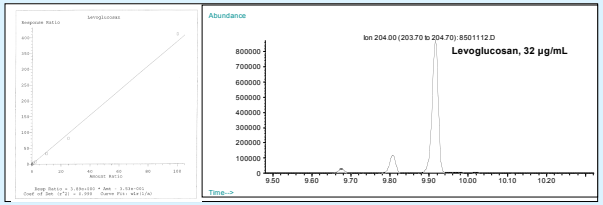


Figure 3: Calibration curve and selective ion chromatogram for levoglucosan

RESULTS

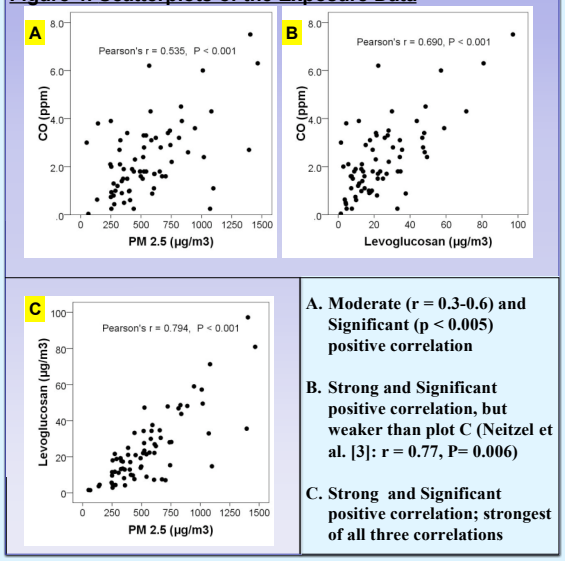
Table 2 : Workshift concentrations

Analyte	*N*	Min.	Max	Mean	SD
$PM_{2.5}$ (µg/m³)	71	50	1466	553	306
LG (µg/m³)	71	1.4	97	24	19
CO (ppm)	71	.04	7.5	2.3	1.5

Quality Control

Field blanks were analyzed for LG along with all other samples. The mean concentration of these filters is 0.16 ± 0.12 µg/mL. Five of the data points were excluded because of quality issues either with the collection of the sample or from poor recovery during extraction analysis. Instrument precision was ± 2% for duplicate injections. The recovery of d7-LG for all samples was 75% ± 10%.

Figure 4: Scatterplots of the Exposure Data



A. Moderate (r = 0.3-0.6) and Significant (p < 0.005) positive correlation

B. Strong and Significant positive correlation, but weaker than plot C (Neitzel et al. [3]: r = 0.77, P= 0.006)

C. Strong and Significant positive correlation; strongest of all three correlations

DISCUSSION

➢In general there are good correlations between all three comparisons. Concentrations of LG and $PM_{2.5}$ show the strongest relationship.

➢Outliers in scatter points could have been associated with different work activities among the firefighters on the day of the controlled burn. Future analysis could focus on dividing up data into different exposure groups.

➢***Is CO a good surrogate for woodsmoke exposure?*** Our results suggest that CO would not be the best surrogate, contrary to previous work [4].

➢***Are these exposures levels safe?*** OSHA's TWA for CO is 50 ppm and 5,000 µg/m³ for respirable matter PM_4 (no occupational standard for $PM_{2.5}$). EPA's annual average NAAQS for $PM_{2.5}$ should not exceed 35 µg/m³.

CONCLUSIONS

1. Levoglucosan is a better surrogate than CO for woodsmoke exposure.
2. Exposure levels are not exceeding occupational limits, but far exceed EPA's limits for personal exposure.

Acknowledgements

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References **1.** Simpson C.D. et al. (2004) J Air Waste Manage Assoc 54:689-694. **2.** Ward T.J. et al (2006) Atmos Environ 40:7005-7017 **3.** Neitzel R. et al. (2008) J Expos Sci Environ Epidemiol (*in press*). **4.** Reinhardt T.E. and Ottmar R.D. (Oct 2000) USDA Research Paper PNW-RP-526.