

Aerosol Contamination at Fire Scenes



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Firefighter Health

- Sudden cardiac death is the number one cause of on-duty death. ¹
- An elevated risk of several cancers is recognized: ²
 - Testicular
 - Prostate
 - Non-Hodgkins lymphoma
 - Multiple myeloma

1. Fahy, R.F., LeBlanc, P.R., and Molis,, J.L.: *Firefighter Fatalities in the United States-2012*. Available at <http://www.nfpa.org/~media/Files/Research/NFPA%20reports/Fire%20service%20statistics/osfff.pdf> (accessed September 23, 2013).

2. LeMasters GK et al., Cancer risk among firefighters: A review and Meta-analysis of 32 studies, *Journal of Occupational and Environmental Medicine*, 48(11), 1189-1202 (2006).



Possible Causes of Chronic Diseases

- Chemical exposures
- Overexertion
- Shift work/sleep disturbance
- Lifestyles



Phases of Firefighting

- Knockdown phase
 - Self-Contained Breathing Apparatus (SCBA) worn
 - Heavy gear
 - High temperatures
- Overhaul phase
 - Often no SCBA
 - Lower temperatures
 - High humidity

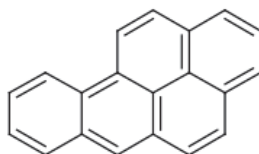
What contaminants are present?

- Toxic gases
- Fibers
- Heavy metals
- Particulate matter
- Semi-volatiles



Semi-Volatile Contaminants

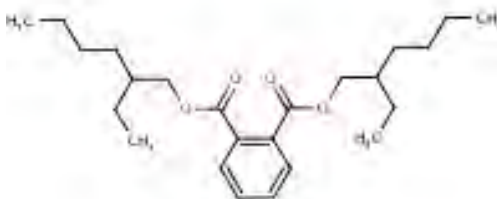
- Polycyclic Aromatic Hydrocarbons



Benzo(a)pyrene

<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~68aHmN:1>

- Phthalates



Di-(2-ethylhexyl) phthalate

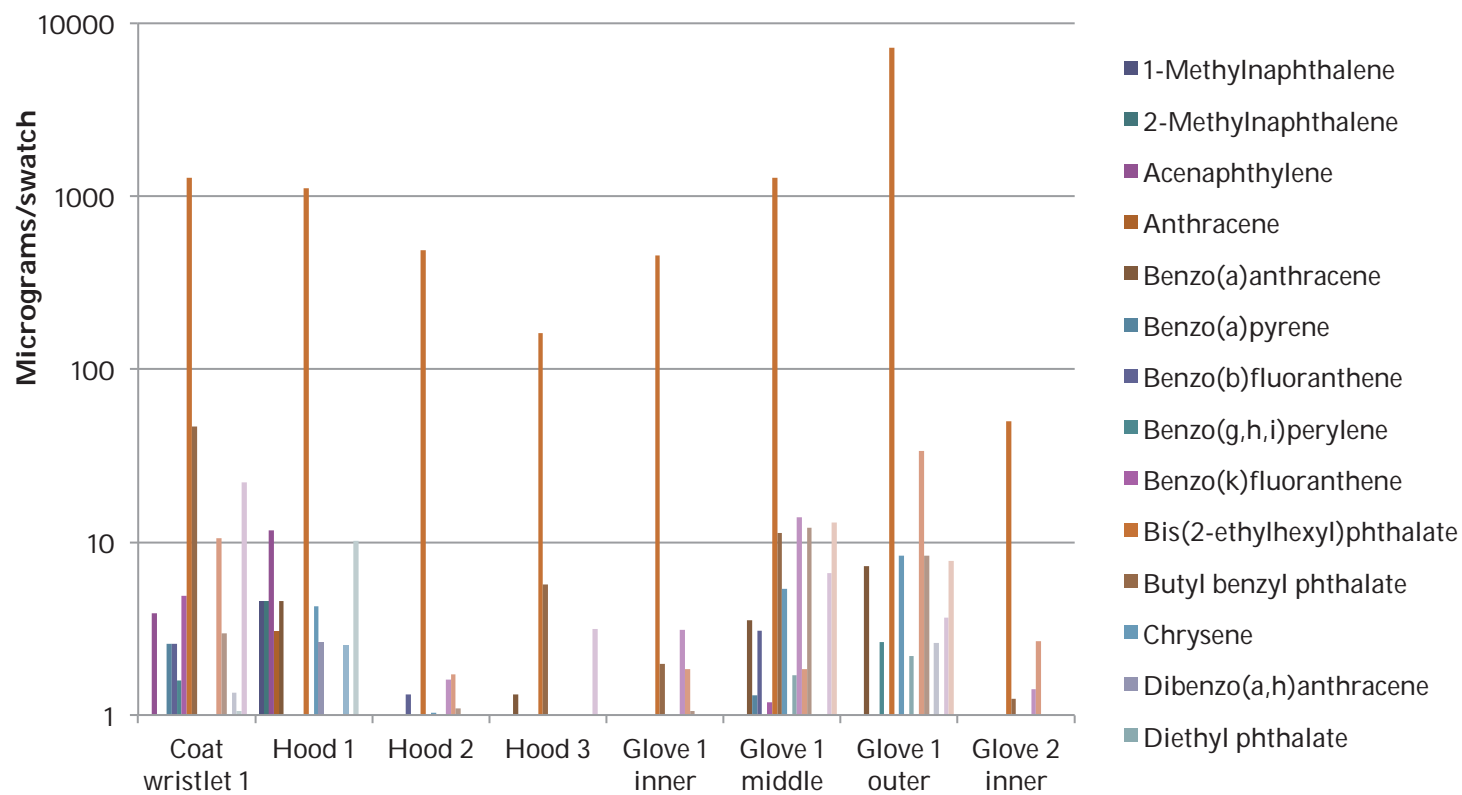
<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~dt2cvk:1>

Preliminary Results



Preliminary Results

Contaminants on Protective Gear



What is Di-(2-ethylhexyl)phthalate (DEHP)?

- Plasticizer
 - Added to polyvinyl chloride (PVC) to make it more flexible.
- Found in items such as:
 - Vinyl flooring and wall covering
 - Toys
 - Wire insulation
 - Upholstery
 - Vinyl siding
 - Pipe



DEHP Adverse Health Effects



- US EPA classifies it as Group B2, probable human carcinogen.
- NTP classifies it as “reasonably anticipated to be a human carcinogen”.
- Male reproductive effects in animal studies.
- Suspected of causing cardiac arrhythmias.



Difficulties of Research at Fire Scenes

- Frequency of fires is low
- Unpredictable times
- Inconvenient hours
- High temperatures during knockdown
- High humidity during overhaul



Difficulties of Research at Fire Scenes

- Diversity of conditions
- Lack of control over the situation
- Things get lost
- Things break
- Multiple crews
- Changing operating procedures



Difficulties of Research at Training Events

- Fire may not be involved
- If live-fire, materials burning are often not typical

Our Method

- Firefighters were trained to collect a personal particulate sample during overhaul
- Four preliminary air samples were collected – no deterioration due to humidity
- No DEHP above the limit of detection



Results of Air Sampling

- Samples obtained at 4 fires:

Date	Run time (mins)	Notes
3/24/2013	21	
4/2/2013	51	Furniture, upholstery, flooring, TV burned - smoldered due to a mattress on the floor.
4/3/2013	32	Furniture (nasty smoke, old-style filter cassette)
4/8/2013	13	Flooring, furniture, upholstery, etc.



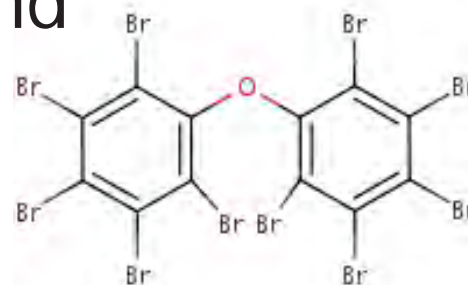
Results of Air Sampling

- No air samples above the limit of detection.
- Maximum potentially inhaled by firefighters at a fire overhaul event was 0.077 mg/m³, or a total of 100 micrograms.
- For comparison:
 - PEL, REL and TLV: 5 mg/m³
 - EPA Reference Dose (RfD) for Ingestion: 1360 micrograms per day for a 150 pound person.

Polybrominated Diphenyl Ethers (PBDEs)

- Flame-retardant chemicals
- Persistent in the environment
- Adverse health effects include neurotoxicity and endocrine disruption
- Suspected of thyroid toxicity and carcinogenicity.

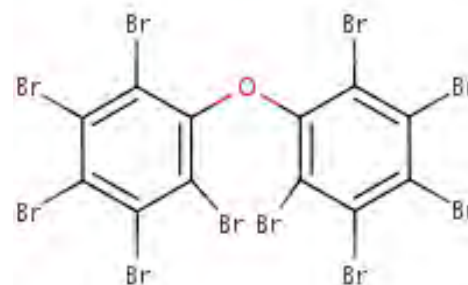
Siddiqi, M.A., Laessig, R.H. and Reed, K.D., Polybrominated Diphenyl Ethers (PBDEs): New Pollutants-Old Diseases, Clin. Med.Res. 1(4), 281-290 (2003).



<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~9i4x4C:3>

Polybrominated Diphenyl Ethers (PBDEs)

- Congeners (209) – numbered according to the number and location of bromine atoms.
- Mixtures used as flame retardants.



<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~9i4x4C:3>

PentaBDE

- Made up of:
 - 50 – 60% penta-brominated (largely PBDE-99)
 - 24 – 38% tetra-brominated (largely PBDE-47)
 - 4 – 8% hexa-brominated (largely PBDE-153)
- Used in polyurethane foam.
- Banned in California in 2003, EU in 2004, and no longer manufactured in the US by 2005.

Stapleton, H.M., Klosterhaus, S., Keller, A., Ferguson, P.L., van Bergen, S., Cooper, E., Webster, T.F., and Blum, A., Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products, *Environmental Science & Technology*, 45, 5323-5331 (2011).

Key, P.B., Chung, K.W., Hoguet, J., Shaddrix, B., Fulton, M. H., Toxicity and physiological effects of brominated flame retardant PBDE-47 on two life stages of grass shrimp, *Palaemonetes pugio*, *Science of the Total Environment* 399, 28-32 (2008).

OctaBDE

- Made up of:
 - $\leq 0.5\%$ pentabrominated
 - $\leq 12\%$ hexabrominated
 - $\leq 45\%$ heptabrominated
 - $\leq 33\%$ octabrominated
 - $\leq 10\%$ nonabrominated
 - $\leq 0.7\%$ decabrominated
- Used in plastic housings for office equipment.
- Banned in the EU in 2004, no longer manufactured in the US, EU or Pacific Rim since 2004.

Stockholm Convention on Persistent Organic Pollutants, Persistent Organic Pollutants Review Committee, Draft Risk Profile for Commercial Octabromodiphenyl Ether, http://www.pops.int/documents/meetings/poprc/drprofile/drpf/DraftRiskProfile_OctaBDE.pdf, accessed 10/2/13.

Birnbaum, L.S., and Staskal, D.F., Brominated Flame Retardants: Cause for Concern?, Environmental Health Perspectives, 112(1), 9-17 (2004).

DecaBDE

- > 97% PBDE-209.
- Used in electrical and electronic equipment, and as a backing in textiles.
- In late 2009, the two US producers of decaBDE agreed to phase out production, importation and sales.
- All US uses of decaBDE will end at the end of 2013.

Birnbaum, L.S., and Staskal, D.F., Brominated Flame Retardants: Cause for Concern?, Environmental Health Perspectives, 112(1), 9-17 (2004).

US Environmental Protection Agency, DecaBDE Phase-out Initiative, available at

<http://www.epa.gov/opptintr/existingchemicals/pubs/actionplans/deccadbe.html>, accessed August 1, 2013.

California Firefighter Study

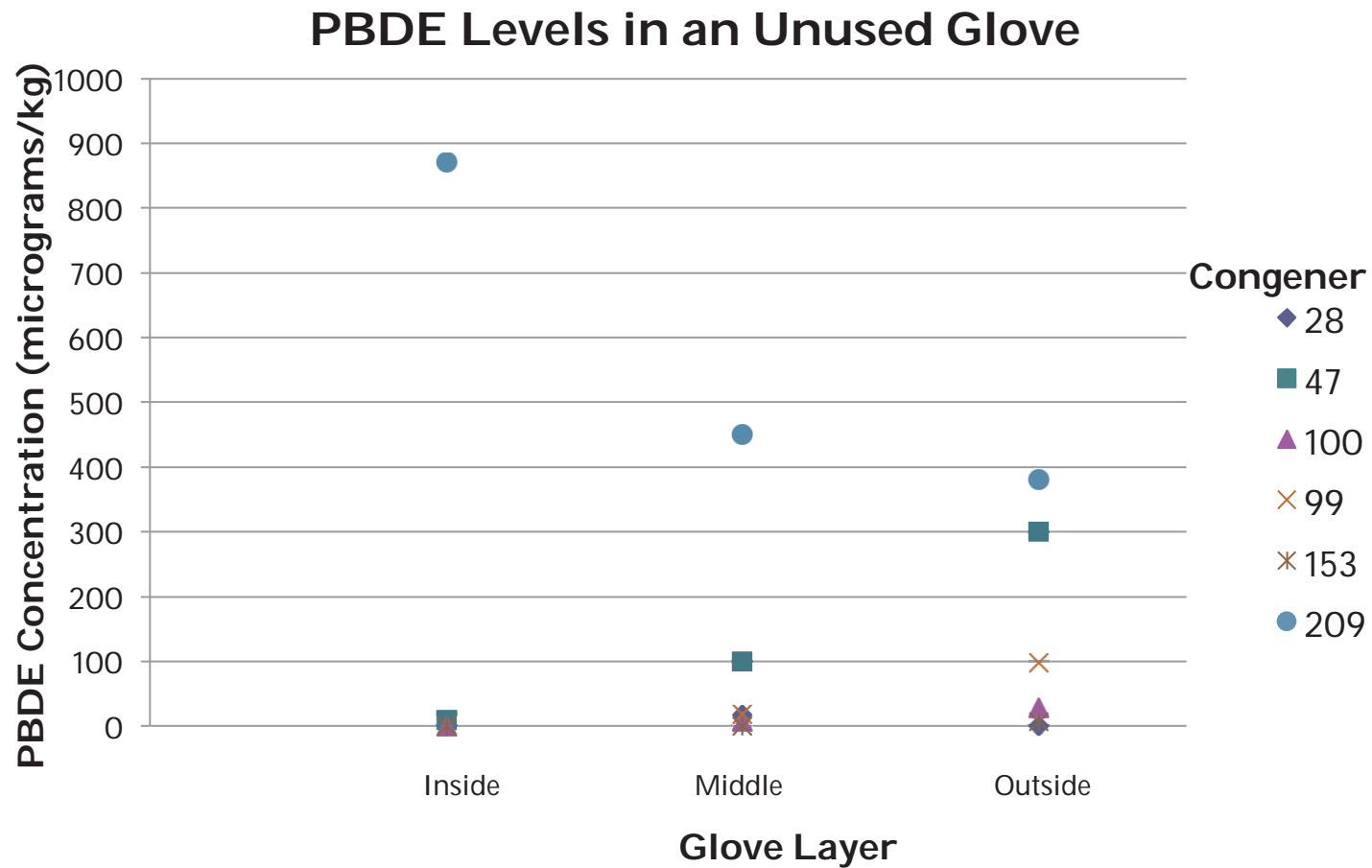
- Included 12 San Francisco firefighters.
- Had responded to a fire within the previous 24 hours.
- Blood serum samples obtained.
- PBDE levels 2 to 3 times the level in the general US population measured.
- PBDE-28, -47, -100 and -153 in 100% of samples.
- PBDE-99 in 92% of samples.
- PBDE-209 in 67% of samples.

Shaw, S.D., Berger, M.L., Harris, J.H., Yun, S.H., Wu, Q., Liao, C., Blum, A., Stefani, A., Kurunthachalam, K., Persistent Organic Pollutants Including Polychlorinated and Polybrominated Dibenzo-p-dioxins and Dibenzofurans in Firefighters from Northern California, *Chemosphere*, 91(10), 1386-1394 (2013).

Analysis for PBDEs

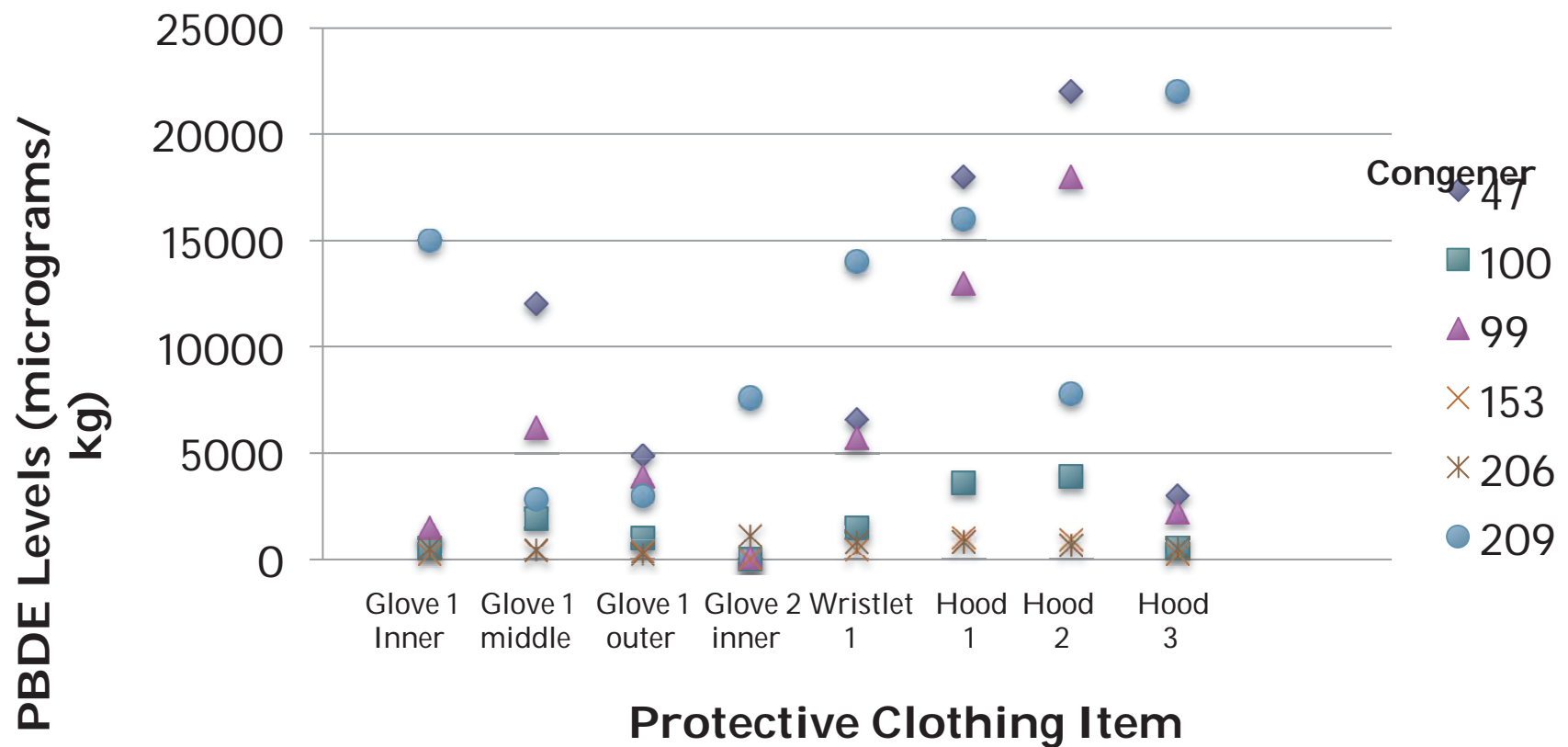


PBDEs in an Unused Glove



PBDEs in Used Protective Clothing

PBDE Congeners in Firefighter Protective Clothing

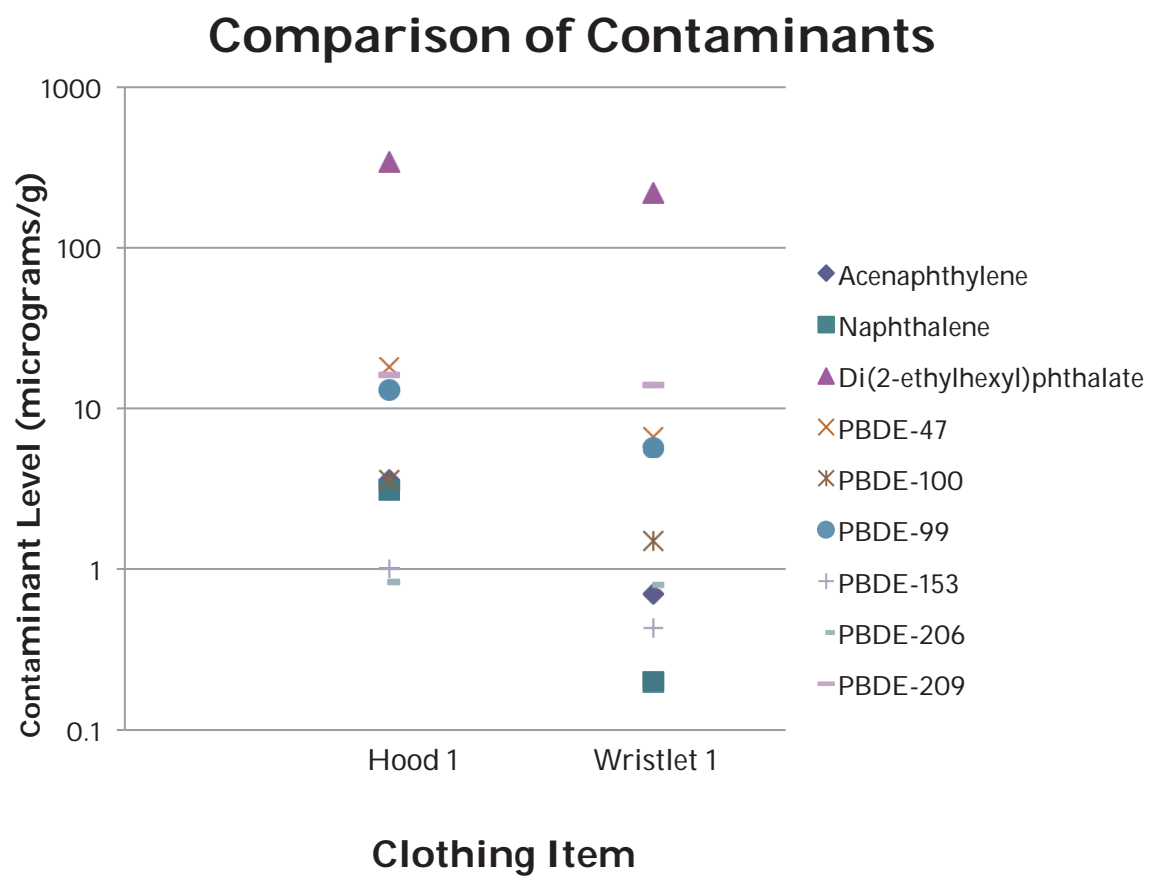




Congeners Detected

- 15 of 17 congeners were detected.
- Every layer of the unused glove held at least 2 detectable congeners.
- PBDE-47, -99 and -209 were most abundant.
- PBDE-209 was detected in every sample.
- PBDE-47 was in all but inner layer of one used glove.
- PBDE-99 was in all but inner layer of unused glove.

Contaminant Comparison





Conclusions

- Significant amounts of PBDEs were found on used firefighter protective clothing.
- Detectable quantities of PBDEs were found in every layer of an unused firefighter glove.
- Levels of DEHP were much higher than PBDEs on items analyzed for both.



Future Research

- PBDE contamination in unused firefighter hoods should be measured.
- Biological samples from firefighters should be tested for the presence of DEHP metabolites.
- The contribution of dermal exposure should be evaluated.



Acknowledgements

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- I wish to thank Dr. Stuart Baxter for his help and support with this research.
- I am grateful to the firefighters of the Cincinnati Fire Department for their cooperation and interest in this study.

Table II. Polybrominated diphenyl ether (PBDE) Congeners Detected on Firefighter Glove Samples (micrograms/g)

Congener	Unused Glove			Glove 1			Glove 2
	Inner	Middle	Outer	Inner	Middle	Outer	Inner
17					0.060		
28		0.017			0.180	0.067	
71		a		0.150	e	0.370	0.130
47	0.009	0.100	0.300	0.890	12.000	4.900	
66		a			0.210	0.067	
100		0.006	0.029	0.540	1.900	1.000	0.037
99		0.019	0.097	1.500	6.200	3.900	0.110
85		a		0.110	0.420	0.230	
154		a		0.150	0.360	0.280	0.015
153		a	0.007	0.240	0.410	0.370	0.012
138		a			0.067	0.062	
128		a					
183		a			0.028	0.013	
190		a					
203		a		0.043	0.028	0.012	0.081
206	b	c	b	0.510	0.430	0.230	1.100
209	0.870	0.450	0.380	15.000	2.800	3.000	7.600
Weight (g)	1.57	0.93	6.51	1.74	1.12	6.99	2

Blank cells indicate measurements below the limit of detection of 0.005 micrograms/g.

a - Below the limit of detection of 0.0054 micrograms/g.

b - Below the limit of detection of 0.05 micrograms/g.

c - Below the limit of detection of 0.054 micrograms/g.

d - Below the limit of detection of 0.34 micrograms/g.

e - Below the limit of detection of 0.5 micrograms/g.

f - Below the limit of detection of 1 microgram/g.

Table III. Polybrominated diphenyl ether (PBDE) Congeners Detected on Firefighter Hoods and Coat (micrograms/g)

Congener	Coat Wristlet 1*	Hood 1*	Hood 2	Hood 3
17	0.010	0.290	0.079	d
28	0.045	0.350	0.071	0.040
71	0.540	0.350	0.740	0.280
47	6.600	18.000	22.000	3.000
66	0.094	0.240	0.310	0.025
100	1.500	3.600	3.900	0.550
99	5.700	13.000	18.000	2.200
85	0.280	0.630	0.640	0.120
154	0.380	0.420	0.540	0.160
153	0.430	1.000	0.920	0.230
138	0.064		0.035	0.036
128				
183	0.015			
190				
203	0.054		b	
206	0.800	0.830	0.680	f
209	14.000	16.000	7.800	22.000
Weight (g)	4.68	3.24	3.23	3.04

*Another sample of the same clothing previously analyzed for phthalates and PAHs.

Blank cells indicate measurements below the limit of detection, 0.005 micrograms/g.

a - Below the limit of detection of 0.0054 micrograms/g.

b - Below the limit of detection of 0.05 micrograms/g.

c - Below the limit of detection of 0.054 micrograms/g.

d - Below the limit of detection of 0.34 micrograms/g.

e - Below the limit of detection of 0.5 micrograms/g.

f - Below the limit of detection of 1 microgram/g.

Table V. Hood and Wristlet 1 - Total Contaminants (micrograms per gram)			
	Congener	Hood 1	Coat wristlet 1
1-Methylnaphthalene		1.4	
2-Methylnaphthalene		1.4	
Acenaphthylene		3.6	0.7
Anthracene		0.9	
Benzo(a)anthracene		1.4	
Benzo(a)pyrene			0.4
Benzo(b)fluoranthene			0.4
Benzo(g,h,i)perylene			0.3
Benzo(k)fluoranthene			0.8
Chrysene		1.3	
Dibenzo(a,h)anthracene		0.8	
Fluoranthene			0.5
Fluorene		0.8	
Indeno(1,2,3-cd)pyrene			0.2
Naphthalene		3.1	0.2
Phenanthrene			3.8
Pyrene			
Butyl benzyl phthalate			8.0
Di(2-ethylhexyl)phthalate		340.0	220.0
Di-n-octyl phthalate			1.8
2,2',3-tribromodiphenyl ether	17	0.29	0.01
2,4,4'-tribromodiphenyl ether	28	0.35	0.045
2,3',4',6-tetrabromodiphenyl ether	71	0.35	0.54
2,2',4'4'-tetrabromodiphenyl ether	47	18	6.6
2,3',4,4'-tetrabromodiphenyl ether	66	0.24	0.094
2,2',4,4',6-pentabromodiphenyl ether	100	3.6	1.5
2,2',4,4',5-pentabromodiphenyl ether	99	13	5.7
2,2',3,4,4'-pentabromodiphenyl ether	85	0.63	0.28
2,2',4,4',5,6'-hexabromodiphenyl ether	154	0.42	0.38
2,2',4,4',5,5'-hexabromodiphenyl ether	153	1	0.43
2,2',3,4,4',5'-hexabromodiphenyl ether	138		0.064
2,2',3,3',4,4'-hexabromodiphenyl ether	128		
2,2',3,4,4',5',6-heptabromodiphenyl ether	183		0.015
2,3,3',4,4',5,6-heptabromodiphenyl ether	190		
2,2',3,4,4',5,5',6-octabromodiphenyl ether	203		0.054
2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether	206	0.83	0.8
2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether	209	16	14



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