

MEASUREMENTS OF PAHS, PBDES, AND PCBs IN DUST FROM CALIFORNIA FIREHOUSES

Shen B¹, Whitehead TP¹, McNeel S², Brown FR³, Das R², Israel L⁴, Park JS³, Petreas M^{3*}

¹School of Public Health, University of California, 50 University Hall, Berkeley, California, USA; ²Environmental Health Investigations Branch, California Department of Public Health, 850 Marina Bay Parkway, Richmond, California, USA; ³Environmental Chemistry Laboratory, California Department of Toxic Substances Control, 700 Heinz Avenue, Berkeley, California, USA; ⁴Center for Occupational and Environmental Health, University of California, 5201 California Avenue, Irvine, California, USA

Introduction

Indoor dust provides a useful estimate of environmental contamination and serves as a surrogate of exposure to indoor contaminants such as polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs)¹. Dust measurements have been used to assess exposure to chemicals in homes, vehicles, schools, and workplaces but not in firehouses. Firefighters are exposed to a unique profile of potentially fire-related chemical contaminants, including dioxins, antimony, and other metals, as demonstrated by bio-monitoring studies². In this pilot study, we measured concentrations of PAHs, PBDEs, and PCBs in dust from 20 California firehouses.

Materials and methods

Dust samples were collected from the vacuum cleaner bags used in the living quarters of 20 California firehouses in 2010 and in 2011. Firehouses were randomly selected from a larger bio-monitoring study of firefighters. All firehouse vacuum cleaner bags were collected during on-site surveys, resulting in a total of 27 vacuum cleaner bags. Samples were sealed in a polyurethane bag and stored at 4°C until analysis. Analytical methods have been described previously³. Briefly, the samples were sieved to remove fibers and debris larger than 150µm. The resulting fine dust was aliquotted (~0.2 g) and spiked with a mixture of labeled internal standards (1 PAH, 8 PBDEs, 15 PCBs, and 2 pesticides) and extracted by accelerated solvent extraction in an 11mL cell (Dionex) with hydromatrix as the bulking agent. The extraction used a solvent mixture of hexane:methylene chloride (95:5) with one heating and five static cycles at 100°C and 1500psi. The extracts were first cleaned using a silica gel column and then with gel permeation chromatography (Waters Corp). The extracts were finally solvent-exchanged with 40µL of tetradecane and spiked with a mixture of labeled recovery standards (1 PAH, 2 PBDEs, 4 PCBs). For PBDE analysis, the extracts were further diluted (1:5) before analysis. Extracts were analyzed for PAHs using low-resolution electron impact-gas chromatography-mass spectrometry (EI-GC-MS; Agilent Technologies). PBDEs and PCBs were analyzed using high resolution EI-GC-MS (ThermoFinnigan MAT95). We used the National Institute of Standards and Technology Standard Reference Material (NIST SRM) No. 2585 in each run for additional quality control.

Results and discussion

Tables 1 and 2 display summary statistics for concentrations of PAHs and PBDEs, respectively, in dust from the 20 firehouses. The PAH profile (Table 1) is dominated by pyrene, followed by benzo(*g,h,i*)perylene, fluoranthene, chrysene, and phenanthrene. The elevated pyrene concentrations in dust from our study population may point to a unique source of chemical contamination in the firehouses tested. Dust from a study of Northern California

Table 1. PAH concentrations (ng/g) in dust from 20 California firehouses (n=27)

Chemical	Mean	Med.	Min.	Max.
Phenanthrene	453	404	250	798
Fluoranthene	634	662	241	1,540
Pyrene	1,330	1,040	428	5,610
Benzo(a)anthracene	187	158	56.1	844
Chrysene	625	547	231	2,800
Benzo(b)fluoranthene	369	357	113	831
Benzo(k)fluoranthene	167	173	50.0	297
Benzo(a)pyrene	205	216	46.1	402
Indeno(1,2,3-c,d)pyrene	214	222	55.7	384
Dibenzo(a,h)anthracene	59.0	61.3	17.3	96.1
Benzo(g,h,i)perylene	771	688	176	1,690

residences³ showed some elevated levels of pyrene in its PAH profile, but the levels were not as prominent as seen in the firehouses.

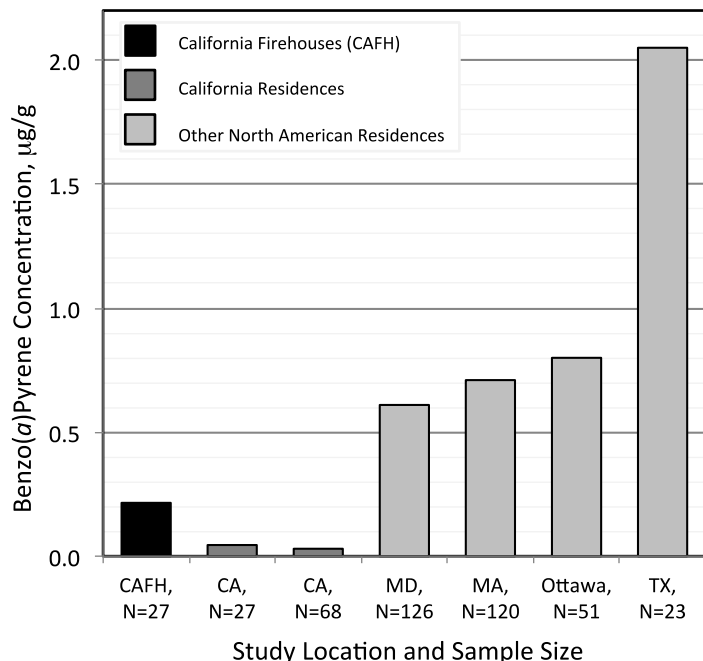


Figure 1. Comparison of median benzo(a)pyrene levels between California firehouses and North America residences

California firehouses showed higher PAH concentrations as compared to California (CA) residences³; however, they did not show the highest PAH concentrations in North America⁴⁻⁷ (Maryland [MD], Massachusetts [MA], Texas [TX]) (Figure 1). Earlier findings have suggested that lower PAH levels west of the Continental Divide are due to differences in smoking habits or pavement surface types⁷. In TX, higher total PAH concentrations were found in indoor (Figure 1) and outdoor dust from apartments that have coal-tar as a pavement sealant⁷; coal tar is used less frequently in California⁸. Likewise, one indoor source of PAH is cigarette smoking and statewide smoking rates are lower in California than in other states in the United States⁹.

As shown in Table 2, BDE-209 was the predominant PBDE congener measured in the California firehouses followed by BDE-99, BDE-47, BDE-100, BDE-153, BDE-206 and to a lesser extent, BDE-154, BDE-207, and BDE-208. The levels of BDE-209 measured in the California firehouses (maximum of 390 µg/g) are among the highest ever reported. We compared BDE-209 levels in California firehouse dust to BDE-209 concentrations in dust from homes in North America¹⁰⁻¹² and the United Kingdom (UK)¹³ (Figure 2) and to BDE-209 concentrations in dust from other occupational settings¹³⁻¹⁷ (Figure 3).

Table 2. PBDE concentrations (ng/g) in dust from 20 California firehouses (n=27)

Cong. No.	Mean	Med.	Min.	Max.
BDE-28	113	40.3	6.60	620
BDE-32	6.15	<MRL	<MRL	165
BDE-47	14,600	5,170	1,310	94,900
BDE-66	301	96.3	18.9	2,620
BDE-71	482	120	<MRL	3,310
BDE-99	31,000	9,240	2,450	201,000
BDE-100	5,430	1,720	485	36,000
BDE-153	3,990	1,220	332	23,200
BDE-154	2,860	919	250	18,100
BDE-155	167	51.1	17.3	1,160
BDE-179	13.6	<MRL	<MRL	122
BDE-183	151	77.9	16.9	644
BDE-190	13.1	8.90	<MRL	57.5
BDE-196	106	76.6	9.47	399
BDE-197	63.1	51.1	6.29	255
BDE-201	67.0	48.4	7.36	312
BDE-202	23.0	17.5	2.33	91.6
BDE-203	105	81.5	9.63	362
BDE-206	1,860	1,140	214	9,680
BDE-207	852	592	109	4,570
BDE-208	488	379	60.4	2,250
BDE-209	78,200	47,000	8,070	391,000

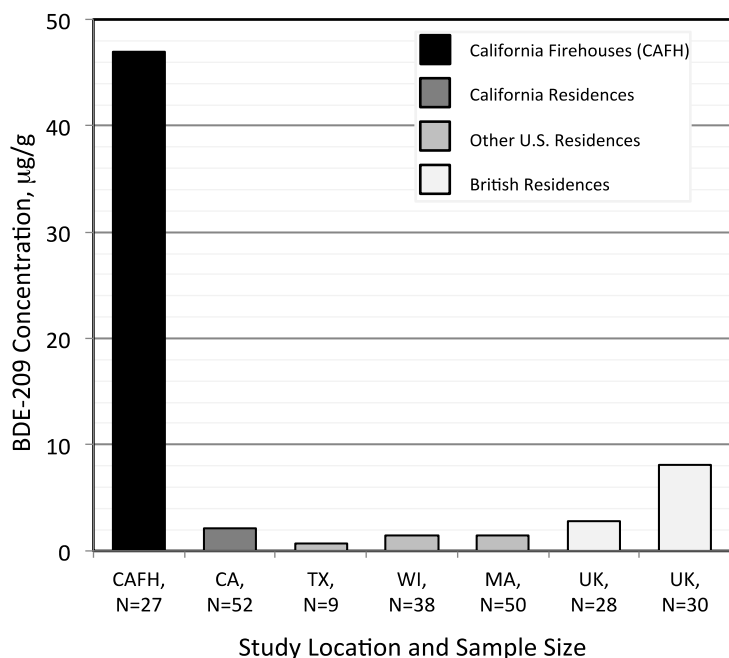


Figure 2. Comparison of median BDE-209 levels between California firehouses, North America residences, and United Kingdom residences

Generally, PBDE levels have been found to be higher in house dust from California homes than in house dust from other states in the United States¹⁸; however, the highest house-dust BDE-209 levels have been reported for homes in the United Kingdom¹³. Our California firehouse dust has higher median levels of BDE-209 than homes in California or the United Kingdom (Figure 2). It seems that firefighters may be exposed to high levels of PBDEs; the findings suggest that occupation may play an important role in exposure to environmental contaminants.

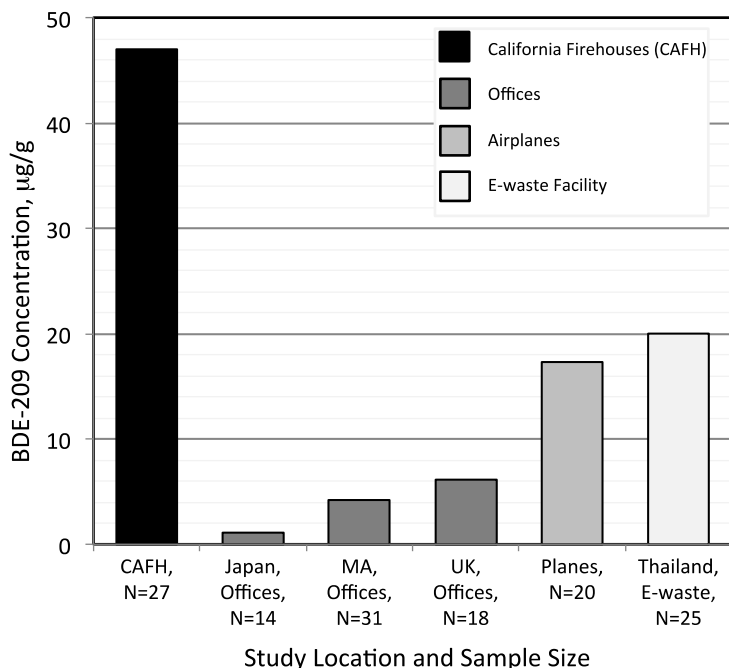


Figure 3. Comparison of median BDE-209 levels between California firehouses and other occupational settings

We also compared median BDE-209 concentrations in dust across varying occupational settings including office buildings from the United States and abroad, airplanes, and electronic waste (e-waste) sites. Again, median BDE-209 concentrations in California firehouses exceed the levels reported for other occupational settings.

PCB concentrations in California firehouses were more consistent across congeners and were dominated by 3 congeners: CB-153, CB-138, and CB-180. PCB levels in California firehouses were comparable to PCB levels seen in Northern California residences.

The implications of these findings are significant. Concentrations of PAHs and PBDEs are much higher in dust from California firehouses than in house dust from California homes, suggesting that firefighters may be exposed to unique chemical sources. Concentrations of PBDEs in dust from California firehouses were orders of magnitude higher than concentrations of PAHs and PCBs in the same samples. PBDEs are particularly pervasive in California, most likely due to the state's unique flammability standards in Technical Bulletin 117¹⁹. PBDEs have been associated with developmental effects in children²⁰ and reduced fecundability in females²¹. It is possible that firefighters carry dust contaminated with PAHs and PBDEs into their firehouses on their boots and protective clothing after extinguishing fires. As this pilot study was not designed to identify determinants of chemical contamination, future work may be warranted to investigate the possibility of track-back from fires and to identify the unique sources of chemical contaminations in firehouses.

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References:

1. Whitehead T, Metayer C, Buffler P, Rappaport SM. (2011) *J Expos Sci Environ Epidemiol.* 21(6): 549-564
2. Edelman P, Osterloh J, Pirkle J, Caudill SP, Grainger J, Jones R, Blount B, Calafat A, Turner W, Feldman D, Baron S, Bernard B, Lushniak BD, Kelly K, Prezant D. (2003) *Environ Health Perspect.* 111(16): 1906-1911
3. Whitehead T, Holden A, Odion Z, Visita P, Brown FR, Metayer C, Rappaport SR, Buffler PA, Petreas MX. (2010) *Organohalogen Compounds* 72: 181-184
4. Egeghy PP, Quackenboss JJ, Catlin S, Ryan PB. (2004) *J Expo Anal Environ Epidemiol.* 15(5): 388-397
5. Rudel RA, Camann DE, Spengler JD, Korn LR, Brody JG. (2003) *Environ Sci Technol.* 37(20): 4543-4553
6. Maertens RM, Yang X, Zhu J, Gagne RW, Douglas GR, White PA. (2008) *Environ Sci Technol.* 42(5): 1747-1753
7. Mahler BJ, Metre PC, Wilson JT, Musgrove M, Burbank TL, Ennis TE, Bashara TJ. (2010) *Environ Sci Technol.* 44(3): 894-900
8. Van Metre PC, Mahler BJ, Wilson JT. (2009) *Environ Sci Technol.* 43(1): 20-25
9. Centers for Disease Control and Prevention. (2009) *MMWR Morb Mortal Wkly Rep.* 58(9) : 221-226
10. Schecter A, Pöpke O, Joseph JE, Tung KC. (2005) *J Toxicol Environ Health A.* 68(7): 501-513
11. Imm P, Knobeloch L, Buelow C, Anderson HA. (2009) *Environ Health Perspect.* 117(12): 1890-1895
12. Johnson PI, Stapleton HM, Sjödin A, Meeker, JD. (2010) *Environ Sci Technol.* 44(14): 5627-5632
13. Harrad S, Ibarra C, Diamond M, Melymuk L, Robson M, Douwes J, Roosens L, Dirtu AC, Covaci A. (2008) *Environ Int.* 34(2): 232-238
14. Suzuki G, Nose K, Takigami H, Takahashi S, Sakai SI. (2006) *Organohalogen Compounds.* 68: 1843-1846
15. Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, Webster TF. (2011) *Environ Health Perspect.* 119(9): 1247-1252
16. Christiansson A, Hovander L, Athanassiadis I, Jakobsson K, Bergman Å. (2008) *Chemosphere.* 73(10): 1654-1660
17. Muenhor D, Harrad S, Ali N, Covaci A. (2010) *Environ Int.* 36(7): 690-698
18. Zota AR, Rudel RA, Morello-Frosch RA, Brody JG. (2008) *Environ Sci Technol.* 42(21): 8158-8164
19. State of California. (2000) Department of Consumer Affairs Bureau of Home Furnishings and Thermal Insulation.
20. Herbstman JB, Sjödin A, Kurzon M, Lederman SA, Jones RS, Rauh V, Needham LL, Tang D, Niedzwiecki M, Wang RY, Perera F. (2010) *Environ Health Perspect.* 118(5) : 712-719
21. Harley KG, Marks AR, Chevrier J, Bradman A, Sjödin A, Eskenazi B. (2010) *Environ Health Perspect* 118(5): 699-704