Journal of Exposure Analysis and Environmental Epidemiology (2004) 14, 164–172
© 2004 Nature Publishing Group All rights reserved 1053-4245/04/$25.00
www.nature.com/jea

Persistent organic pollutants in dusts that settled indoors in lower Manhattan after September 11, 2001

JOHN H. OFFENBERG,[a] STEVEN J. EISENREICH,[a,b] CARI L. GIGLIOTTI,[a] LUNG CHI CHEN,[c] JUDY Q. XIONG,[c] CHUNLI QUAN,[c] XIAOPENG LOU,[c] MIANHUA ZHONG,[c] JOHN GORCZYNSKI,[c] LIH-MING YIIN,[d] VITO ILLACQUA[d] AND PAUL J. LIOY[d,e]

[a]*Department of Environmental Science, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901, USA*
[b]*Institute for Environment and Sustainability, Joint Research Centre, Ispra, Italy*
[c]*Nelson Institute of Environmental Medicine, NYU School of Medicine, Tuxedo, New York 10987, USA*
[d]*Environmental and Occupational Health Sciences Institute, Piscataway, New Jersey 08854, USA*
[e]*University of Medicine and Dentistry of New Jersey - Robert Wood Johnson Medical School, Piscataway, New Jersey 08854, USA*

The explosion and collapse of the World Trade Center (WTC) was a catastrophic event that produced an aerosol impacting many residents, workers, and commuters after September 11, 2001. In all, 12 bulk samples of the settled dust were collected at indoor locations surrounding the epicenter of the disaster, including one sample from a residence that had been cleansed and was once again occupied. Additionally, one sample was collected from just outside a fifth story window on the sill. These samples were analyzed for many components, including inorganic and organic constituents as well as morphology of the various particles. The results of the analyses for persistent organic pollutants on dusts that settled at indoor locations are described herein, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and select organo-chlorine pesticides. The Σ_{86}-PCB concentrations, comprising less than one part per million by mass of the bulk in the two samples analyzed, indicated that PCBs were of limited significance in the dust that settled at indoor locations across lower Manhattan. Likewise, organo-chlorine pesticides, Hexachlorobenzene, Heptachlor, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT and Mirex were found at even lower concentrations in the bulk samples. Conversely, Σ_{37}-PAHs comprised up to 0.04% (<0.005–0.036%) by mass of the bulk indoor dust in the 11 WTC impacted bulk indoor samples. Analysis of one sample of indoor dusts collected from a vacuum cleaner of a rehabilitated home shows markedly lower PAH concentrations (<0.0005 mass%), as well as differing relative contributions for individual compounds. In addition to similar concentrations, comparison of PAH concentration patterns (i.e. chemical fingerprints) shows that dusts that settled indoors are chemically similar to previously measured WTC dusts found at outdoor locations and that these PAH analyses may be used in identifying dusts of WTC origin at indoor locations, along with ascertaining further needs for cleaning.
Journal of Exposure Analysis and Environmental Epidemiology (2004) **14,** 164–172. doi:10.1038/sj.jea.7500310

Keywords: *World Trade Center, aerosol, organic analysis, PAH, PCB.*

Introduction

The September 11, 2001 attack on the World Trade Center (WTC) resulted in an intense fire and the subsequent complete collapse of both tower structures, as well as the collapse of and damage to adjacent buildings. A consequence of the burning and pulverization of buildings was the development of a large plume of smoke that released both gases and particles into the ambient atmosphere of Lower Manhattan. The dust cloud was initially dispersed in all directions from ground zero and later to many outdoor and indoor locations downwind. For the first 12–18 h after the collapse, the winds transported the plume to the east and then to the southeast toward, and across Brooklyn (Lioy et al., 2002).

To assess the possible impacts of the dust and smoke on indoor locations in Lower Manhattan, 13 samples of smoke and dusts that had settled indoors were taken from five locations around the WTC site. The purpose of collecting the samples was to determine the chemical and physical characteristics of the material that were present in dusts that settled indoors, and to determine if contaminants were present in indoor dusts that could potentially affect acute or long-term human health. The compounds and materials present in the dusts, which were caused by the WTC collapse and fires, and which settled indoors, would be similar to those found in building fires or collapsed buildings. The primary

1. Address all correspondence to: Dr. J.H. Offenberg Department of Environmental Science, Rutgers, the State University of New Jersey, 14 College Farm Road, New Brunswick, NJ 08901, USA. Tel.: +1-732-932-3097. Fax: +1-732-932-8644.
E-mail: jho@envsci.rutgers.edu
Received 16 February 2003; accepted 28 July 2003.

differences from these more typical situations are (1) the intensity of the fire (as compared with normal building fires), (2) the occurrence of a building collapse in conjunction with such extreme fires, and (3) the extremely large mass of material ($\sim 1 \times 10^6$ tons) reduced to dust and smoke (Claudio, 2001). A summary of the potential hazards Landrigan, 2001) as well as a list of initial steps taken to assess human health exposure during and after the disaster are outlined elsewhere (Manuel, 2001).

Previously reported measurements have focused on the general composition of the dusts and smoke that settled outdoors (Lioy et al., 2002). The organic analysis of indoor dusts described herein parallels the battery of measurements on the outdoor settled dusts, which also focused on organic components of the mass, as well as soluble ions, and trace metals, and general and morphological characterization of the percent distribution of various materials present in each sample. Results of the analyses of outdoor settled smoke and dust samples, including morphological, inorganic, and organic analyses are reported elsewhere (Lioy et al., 2002; Offenberg et al., 2003). The concentrations of organic compounds found in dusts collected indoors are discussed in this manuscript, and placed into context of the organic measurements of dusts that settled in outdoor locations. Furthermore, the results of the indoor dust analyses were used to demonstrate that the chemical profiles of the indoor dust could identify whether or not an indoor location was impacted by dusts that were generated by the WTC disaster.

Methods

Sample Collection

In all, 11 bulk, settled dust samples were collected on November 19, 2001, by investigators from New York University (NYU) and The Environmental and Occupational Health Sciences Institute (EOHSI); two from 90 and 100 Liberty Street and nine from within 114 Liberty Street. All of these 11 samples were collected in an effort organized and completed by EOHSI & NYU investigators. A resident of 55 Liberty Street collected, from windowsills at that location, a single sample within a film canister sometime between September 2001 and June 2002, when it was delivered to EOHSI. Finally, on April, 22 2002, a resident of 395 South End Avenue sampled the dusts collected within their home vacuum cleaner, which had been operated only after restoration of the residence following the WTC disaster (Table 1). For all samples collected by NYU or EOHSI personnel, samples were collected using the protocols established for surface soil collection in studies of the dispersal of Cr laden hazardous waste in Jersey City, New Jersey (Kitsa et al., 1992), and the National Human Exposure Assessment Survey (Pellizzari et al., 1995). After collection, all samples were stored at 4°C prior to delivery of sub-fractions to collaborators' laboratories for analysis.

Quantitative Chemical Analysis

The analyses conducted on each settled dust sample were based upon the nature of the sources of the particles that were generated on September 11, 2001 and the results of outdoor samples (Lioy et al., 2002; Offenberg et al., 2003). The organic chemical analyses for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), select organo-chlorine pesticides of indoor dusts are presented in detail here. A summary of the results of chemical analyses of dusts that settled outdoors including inorganic analyses, organic analyses, as well as asbestos, alpha and beta radionuclide activity, and morphology of outdoor settled dusts are presented elsewhere (Lioy et al., 2002; Offenberg et al., 2003). The limited quantity of each sample required that the analyses of these indoor samples focus on only those species that had the potential for the greatest human exposure and health concern, as well as potential for use as an indicator of WTC dusts found at indoor locations.

(a) *Polychlorinated Biphenyl and OC Pesticides* Replicate aliquots ($n = 3$ and 5) of ~ 0.7 g of indoor dust samples from two locations (see Table 1) were ultrasonically extracted twice in 30 ml dichloromethane, then reduced in volume under a gentle stream of clean dry nitrogen and fractionated on a column of 3% water deactivated alumina. After final reduction in volume to 0.5 ml, samples were injected with a solution containing 50 ng of PCB congeners 30 and 204 (2,4,6-trichlorobiphenyl and 2,2′,3,4,4′,5,6,6′octachlorobiphenyl, respectively), as internal standards prior to analysis by gas chromatography/electron capture detection on a Hewlett Packard 6890 equipped with a ^{63}Ni Electron Capture Detector for quantification of 68 polychlorinated biphenyl congeners, hexachlorobenzene, DDTs (4,4′-DDE, 2,4′-DDT, and 4,4′-DDT) and Mirex according to the procedures of Brunciak et al. (2001). All compounds were identified and quantified against known concentrations of authentic standards as described by Mullins (1985). For comparison and verification of results, NIST Standard Reference Material 1649a — Urban Dust, Organics (Wise et al., 2000), was processed in parallel with each sample. Procedural blank samples (i.e. 0 g of dust) were also processed in parallel with samples in order to quantify the overall operational limits of detection for the procedures. This PCB/Organo-chlorine pesticide analysis was identical to that performed in the analyses of outdoor settled dusts described elsewhere (Lioy et al., 2002; Offenberg et al., 2003).

(b) *Polycyclic Aromatic Hydrocarbons* Additional triplicate aliquots of ~ 0.7 g of each settled dust sample were weighed, ultrasonically extracted twice in 30 ml

dichloromethane, reduced in volume to ~0.5 ml under a gentle stream of clean, dry nitrogen and injected with a solution containing 100 ng each of four per-deuterated internal standards. These samples were analyzed by gas chromatography/mass selective detection on a Hewlett Packard 6890/5973 for 37 individual PAHs and six chlordane species utilizing well-established methods (Offenberg and Baker, 1999; Naumova et al., 2002). The mass selective detector was operated in selective ion monitoring mode with an electron impact ionization energy of 70 eV. The 37 PAHs reported herein are as follows: naphthalene, acenapthylene, acenapthene, fluorene, 1-methylfluorene dibenzothiophene, phenanthrene, anthracene, methylphenanthrenes + methylanthracenes (the sum of 1-methylphenanthrene, 2-methylphenanthrene, 1-methylanthracene, 2-methylanthracene, and 9-methylanthracene), 4,5-methylenephenanthrene, 3,6-dimethylphenanthrene, 9,10-dimethylanthracene, fluoranthene, pyrene, benzo[*a*]flourene, retene, benzo[*b*]fluorene, cyclopenta[*cd*]pyrene, benz[a] anthracene, chrysene + triphenylene, naphthacene, benzo[*b*] naptho[2,1-d]thiophene, benzo[*b*]fluoranthene + benzo[*k*] fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, dibenzo[*ah*]anthracene + dibenzo[*ac*] anthracene, benzo[*g,h,i*]perylene, and coronene. All compounds were identified and quantified against standard solutions containing known concentrations of authentic compounds and where possible, compared to NIST Standard Reference Material 1649a — Urban Dust, Organics (Wise et al., 2000), which was processed in parallel with each sample for comparison and verification of results. Procedural blank samples (i.e. 0 g of dust) were also processed in parallel with samples in order to quantify the overall operational limits of detection for the procedures. This GC/MS procedure for quantifying PAHs was identical to that utilized for analysis of both bulk and size-segregated outdoor settled dust samples as described elsewhere (Lioy et al., 2002; Offenberg et al., 2003).

Quality Assurance

Surrogates Average percent recoveries of 50 ng of four PCB congeners, not found in commercial Aroclor mixtures, added to each of the samples analyzed were: 108 ± 16%, 105 ± 16%, 106 ± 15%, and 102 ± 15% for IUPAC congener numbers 14, 23, 65, and 166, (3,5-dicholorbiphenyl, 2,3,5-tricholorbiphenyl, 2,3,5,6-tetracholorbiphenyl, and 2,3,4,4′,5,6-hexachlorobiphenyl, respectively) in the PCB sample extractions. Similarly, average percent recoveries of per-deuterated PAHs utilized as surrogate standards (± 1 SD) added to each sample were: 76 ± 11%, 83 ± 7%, 70 ± 10%, and 74 ± 8% for *d*10-acenapthene, *d*10-anthracene, *d*10-fluorene, and *d*12-pyrene, respectively. These surrogate recoveries indicate that there were limited sample losses during processing and handling. The concentrations reported herein have not been corrected to account for the minimal losses indicated by the recoveries of surrogate compounds that differed from 100%.

Blanks Chemical analysis of procedural and laboratory blanks indicated that background levels of Σ_{68}-PCBs were 0.33 ng ($n = 1$) and Σ_{37}-PAHs were 23 ± 26 ng ($n = 3$) in the measurements reported here. This translates into limits of detection (as three times the average) for analysis of 1 g of dust equal to 0.99 ng/g for Σ_{68}-PCBs and 69 ng/g for Σ_{37}-PAHs. The concentrations measured in the samples are several orders of magnitude greater than those observed in the procedural blanks for PCB congners and individual PAHs (a factor of 152–18,350 for PCB congeners and a factor of 832–48,560 for individual PAHs), thereby indicating that the contribution of sample handling and preparation to the measured values was negligible. Blank-based limits of detection for 4,4′-DDT, 2,4′-DDT, and 4,4′-DDE are approximately 0.006, 0.018, and 0.048 ng/g, respectively. Finally, using the methods described here, blank based limits of detection for heptachlor, hexachlorobenzene, and mirex are approximately 0.006, 0.012, and 0.009 ng/g, respectively.

Comparisons to Standard Reference Materials Chemical analyses of standard reference materials (SRMs) in parallel with samples allows for direct assessment of extraction, handling, and quantitative methods utilized in this work. Of the 68 PCB congeners measured here, there are 27 for which certified concentrations have been determined in NIST SRM 1649a (Wise et al., 2000). A linear correlation of the average concentrations measured via the methods described above ($n = 3$) vs. the certified values results in a significant correlation ($P < 0.0001$; $R^2 = 0.954$). The resulting slope of this correlation (with both expressed as ng/g) was equal to 0.93 ± 0.05 ($P < 0.0001$) and the intercept was not different than zero (−1.63 ± 1.88; $P = 0.40$). The concentrations measured in SRM 1649a generally fall within the reported uncertainties for the certified concentrations (Wise et al., 2000).

Of the 37 PAH compounds measured here, there are 16 for which certified concentrations have been determined in SRM 1649a (Wise et al., 2000). A linear correlation of the average concentrations measured via the methods described above ($n = 3$) vs. the certified values results in a significant correlation ($P < 0.001$; $R^2 = 0.833$). The resulting slope of this correlation (with both expressed as ng/g) was equal to 0.89 ± 0.16 ($P < 0.001$) and the intercept was not different than zero (−151 ± 632; $P = 0.82$). The concentrations measured in SRM 1649a generally fall within the reported uncertainties for the certified concentrations (Wise et al., 2000). Thus, based upon these analyses of SRM 1649a, we conclude that the sample handling and analysis techniques used here represent accurate measurements of the concentra-

tions in the indoor dusts, and furthermore do not introduce significant biases into the reported results.

Results and discussion

Analysis of Indoor Bulk Dust Samples

Results of analysis of the 13 bulk indoor dust samples for PCBs, PAHs, and organo-chlorine pesticides are shown in Table 1. Concentrations of the sum of 68 polychlorinated biphenyl congeners (Σ_{68}-PCBs) in the two bulk samples collected at 114 Liberty Street and 90 and 100 Trinity Place (samples 8 and 10, respectively) averaged 537 ± 35 and 662 ± 33 ng/g, respectively. These concentrations are not different from the measured concentrations of PCBs on dusts that settled at outdoor locations immediately following the WTC disaster (Offenberg et al., 2003), which averaged 667 ± 113 ng/g ($n = 9$, representing triplicate analysis of three outdoor locations). Furthermore, these concentrations on WTC-related dusts that settled at indoor locations are not different from the measured concentrations of PCBs on ambient aerosols in Jersey City, New Jersey, which averaged 890 ± 760 ng/g ($n = 78$) over the period of 7/5/98 to 1/19/01. These measurements taken at a station located in Liberty State Park, 3.5 km west/southwest of the WTC, were made as part of the New Jersey Atmospheric Deposition Network (NJADN), and are summarized elsewhere (Brunciak et al., 2001). PCB congener patterns in these two indoor bulk dust samples were dominated by congeners 163 + 138, 153 + 132, 180 and 149 + 123 + 107 (Figure 1). This congener pattern is in contrast to that found on ambient aerosols in Jersey City, NJ (Brunciak et al., 2001), which were dominated by congeners 163 + 138, 66 + 95, 52 + 43, and 180, generally representing a lighter mixture of PCB congeners than was seen in the two dust samples presented here. However, the patterns of congeners in these two indoor dust samples match the pattern of congeners measured on outdoor dust samples (Lioy et al., 2002; Offenberg et al., 2003).

Concentrations of hexachlorobenzene in the two bulk indoor samples analyzed were 2.14 ± 2.03 ng/g ($n = 5$) at site 10 and 2.66 ± 3.69 ng/g ($n = 3$) at site 8. These concentrations were higher than those on outdoor WTC-related dusts, which averaged 1.3 ± 0.4 ng/g. This increase in concentration of indoor dusts over outdoor dusts may be related to particle size fractionation leading to smaller aerosols that may have been enriched relative to larger particles that penetrated indoors less efficiently. This remains a hypothesis as no samples were size segregated and analyzed as part of this work. Alternatively, there was a longer period of time between the aerosol generation and sample collection for the indoor dusts as compared with the outdoor dusts. This extended period of time may have allowed for greater sorption to the WTC dusts that were relatively clean with respect to HCB. Interestingly, the concentrations measured on indoor dusts were lower than those on ambient aerosols in Jersey City, NJ, which averaged 8.1 ± 10.0 ng/g ($n = 74$ over

Table 1. List of samples by date collected

Date collected	Label	Address	Floor	Location of dusts collected	Analysis performed[a]	[Σ_{36}PAH] (ng/g)	[Σ_{68}PCB] (ng/g)
19 Nov. 01	1	114 Liberty Street	5A	Library under bookshelves	PAHs[a]	285,000 ± 102,000 n=3	NA
19 Nov. 01	2	114 Liberty Street	5A	Hall shelf	PAHs	21,0000 ± 13,000 n=3	NA
19 Nov. 01	3	114 Liberty Street	5A	Baseboard	PAHs	264,000 ± 26,000 n=3	NA
19 Nov. 01	4	114 Liberty Street	4A	Floor	PAHs	281,000 ± 49,000 n=3	NA
19 Nov. 01	5	114 Liberty Street	4A	Hall and room baseboard	PAHs	302,000 ± 25,000 n=3	NA
19 Nov. 01	6	114 Liberty Street	4A	Infant's highchair	PAHs	357,000 ± 7800 n=3	NA
19 Nov. 01	7	114 Liberty Street	2A	Front room atop three boxes	PAHs	14,0000 ± 30,000 n=3	NA
19 Nov. 01	8	114 Liberty Street	2A	Entryway — edge of elevator door	PAH, PCB, OCP	297,000 ± 88,000 n=3	537 ± 35 n=3
19 Nov. 01	9	90 and 100 Trinity Place	7	Walkway radiator	PAHs	217,000 ± 35,000 n=3	NA
19 Nov. 01	10	90 and 100 Trinity Place	10	Office facing WTC — window left open, not blown out	PAH, PCB, OCP	59,000 ± 9400 n=3	662 ± 33 n=5
19 Nov. 01	11	114 Liberty Street	8A	Living room light switch and baseboards	PAH	111,000 ± 12,000 n=3	NA
22 April 02	12	395 South End Avenue	Apt 22F	Contents of vacuum cleaner	PAH	2370 ± 380 n=3	NA
Unknown Sampled by Resident	13	55 Liberty Street	5B	Outdoor windowsills	PAH	189,000 ± 23,000 n=3	NA
Outdoor Dusts	—	Various Locations[a]	—	Six bulk dusts from various locations around WTC site	PAH, PCB, OCP	42,000–383,000 n=6	477–843

[a] See Lioy et al. (2002) and Offenberg et al. (2003) for further analyses of outdoor settled dust samples. NA denotes that this sample was not analyzed for these contaminants.

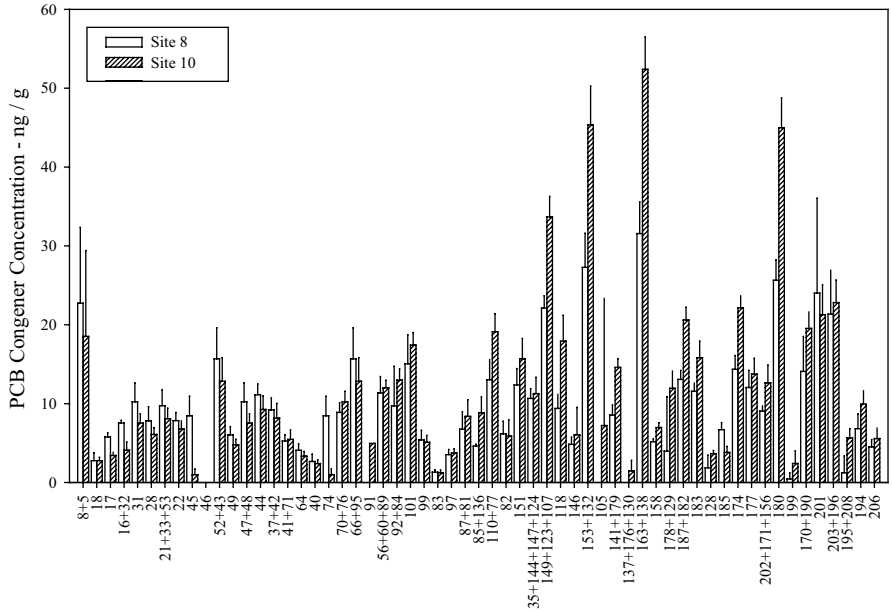

Figure 1. Concentrations of PCB congeners (± 1 SD) in two bulk settled dust samples collected at indoor locations in lower Manhattan.

the period of 7/5/98 through 1/19/01). Concentrations of heptachlor in the two bulk indoor samples analyzed were 1.34 ± 1.12 ng/g ($n = 5$) at site 10 and 1.09 ± 3.11 ng/g ($n = 3$) at site 8. These concentrations were higher than those measured on outdoor WTC-related dusts, which were below the blank-based limit of detection of ~ 0.5 ng/g. Similar to the case of HCB above, the increase in concentration of indoor dusts over outdoor dusts may be related to particle size fractionation during aerosol penetration or sorption during the several weeks that the dusts were exposed to ambient indoor air prior to sampling; however, we have no direct evidence for either of these explanations. Alternatively, there may also be some indoor sources of heptachlor. However, the concentrations of heptachlor measured on indoor dusts were lower than those on ambient aerosols in Jersey City NJ, which averaged 9.7 ± 8.9 ng/g ($n = 74$ over the period of 7/5/98 through 1/19/01). Concentrations of 4,4′-DDT, 2,4′-DDT, 4,4′-DDE as well as mirex, in these two bulk indoor samples were below the levels measured in laboratory blanks processed in parallel with these samples. Thus, the concentrations of these four compounds measured on indoor dusts were lower than 0.006, 0.018, 0.048, and 0.009 ng/g, respectively. Concentrations of 4,4′-DDT and 2,4′-DDT in three bulk outdoor samples were also below the levels measured in laboratory blanks processed in parallel with those samples. Mirex was measured at a concentration of 0.8 ng/g in a single outdoor dust sample and was below blank based limits of detection in two other instances. Only 4,4′-DDE was found at concentrations above limits of detection in all outdoor dust analyses, averaging 2.2 ± 0.9 ng/g and ranging from 1.3 ± 0.8 to 3.0 ± 0.5 ng/g. All WTC-related dust measurements of DDT/DDE and mirex were much lower than those on ambient aerosols in Jersey City, NJ, which averaged 38.3 ± 66.4, 17.3 ± 19.2, 21.5 ± 18.3, and 1.5 ± 7.0 ng/g, (4,4′-DDT, 2,4′-DDT, 4,4′-DDE, mirex, respectively; $n = 74$ over the period of 7/5/98 through 1/19/01).

Concentrations of the sum of 37 individual polycyclic aromatic hydrocarbons (Σ_{37}-PAHs) ranged from $357{,}000 \pm 25{,}000$ ng/g (site 6) to $59{,}000 \pm 9400$ ng/g (site 10) in the 11 indoor bulk dust samples (sites 1–11; Figure 2). The lone dust sample that represents postrehabilitation conditions, and was analyzed as part of this work (site 12), contained an average concentration of 2390 ± 380 ng/g, nearly a factor of 25 lower than the lowest concentration

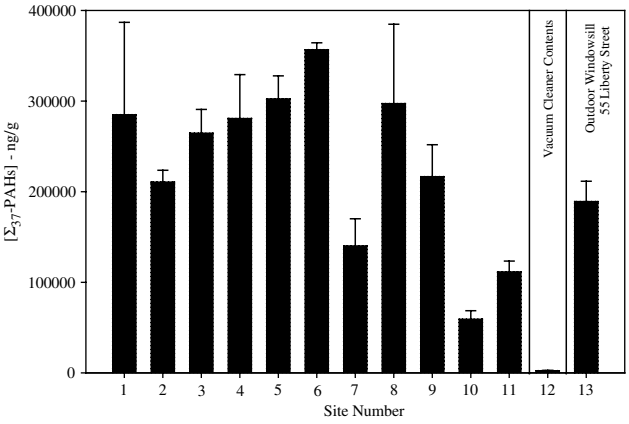

Figure 2. Σ_{37}-PAH concentrations (± 1 SD) measured in bulk settled dust samples collected at indoor locations in lower Manhattan. Note sample 12 represents dusts collected from a vacuum cleaner operated in a home after rehabilitation and reoccupation. Sample 13 represents dusts collected on a fifth floor outdoor windowsill at 55 Liberty Street.

measured from WTC impacted indoor dust samples. A single sample of dusts collected from a fifth story outdoor windowsill (site 13) contained an average concentration of 189,000 ± 23,000 ng/g, For comparison, the concentrations of these same PAH species in bulk dusts that settled at outdoor locations surrounding the WTC site ranged from 42,000 to 383,000 g/g (Offenberg et al., 2003). Thus, there is a wide range in PAH content in both indoor and outdoor settled dusts. In contrast, concentrations of the same PAH species on airborne particulate matter at a long term monitoring site in Jersey City, NJ average 107,000 ± 112,000 ng/g of total suspended particulate matter (TSP) over the period spanning from 7/5/98 to 1/19/01 (Gigliotti et al., 2000). For a complete discussion of all methods and results pertaining to the outdoor dust samples, we refer the reader to Lioy et al. (2002) and Offenberg et al. (2003).

The similarity in both concentrations and relative contributions of the several compounds analyzed is indicative of the direct linkage between the dusts generated outdoors and those that were carried into indoor locations. PAHs associated with the bulk dusts that settled indoors were dominated by phenanthrene, fluoranthene, pyrene benz[*a*]anthracene and benzo[*b* + *k*]fluoranthene (Figures 3 and 4). The observed pattern is nearly identical to that observed on dusts that were collected from outdoor locations. In contrast, PAH fingerprints in ambient air over Jersey City, NJ were dominated by benzo[*b* + *k*]fluoranthene, methylphenanthrenes, indeno[123,*cd*]pyrene, chrysene + triphenylene, benzo[*ghi*]perylene, and coronene.

The total concentrations of 37 individual PAHs represented up to nearly 0.04% by mass of the bulk settled dusts measured at indoor locations. The levels of individual PAH ranged from hundreds of pg/g to $> 50\,\mu$g/g. Of the indoor bulk samples analyzed as part of this work, the highest concentrations of the 37 individual PAHs were found in the 114 Liberty Street sample, collected from atop a child's highchair. Concentrations in samples from within the same building varied by almost a factor of three, while the two samples from 90 and 100 Trinity Street varied by almost a factor of four. The large variety of concentrations in dusts generated by the disaster may be a result of the wide variety of unburned and partially burned hydrocarbons derived from the diverse mix of plastics, metals, woods, and other synthetic products in the collapsed buildings. Additionally, varying levels of penetration of the outdoor dusts into the numerous areas of each building may have also influenced composition and thus the observed concentrations on the indoor dusts.

Particle size distributions of the contaminants measured in these dusts that settled indoors have not been measured as

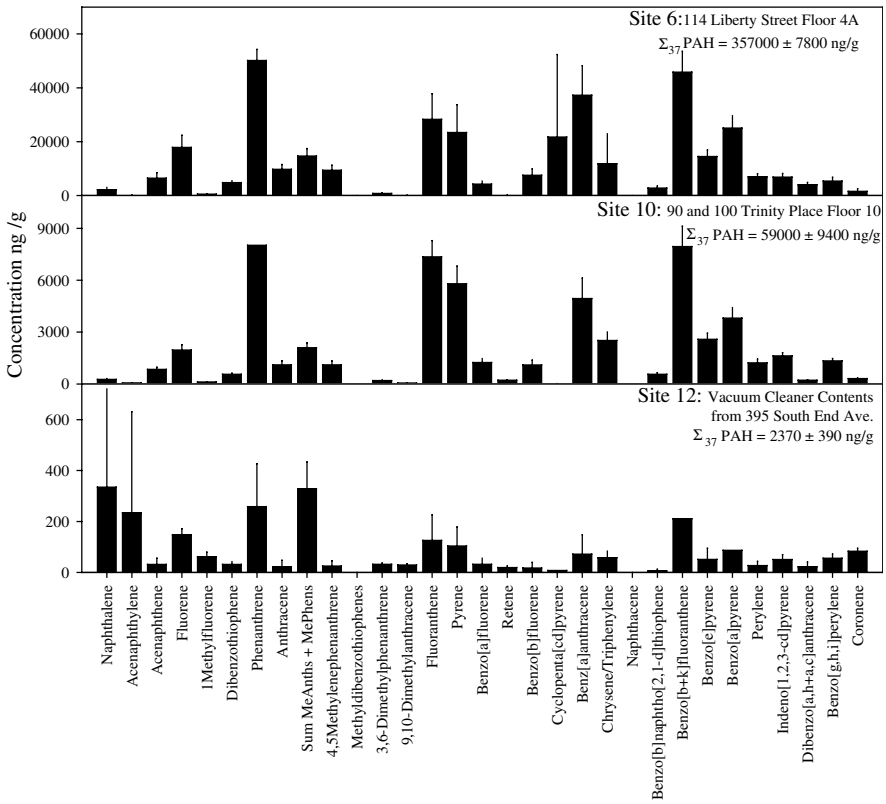

Figure 3. Concentrations of individual PAHs (ng/g) in three, bulk representative settled dust samples collected at indoor locations in lower Manhattan. Error bars represent 1 SD of triplicate analyses of each dust sample. Note the differences in *y*-axis scaling.

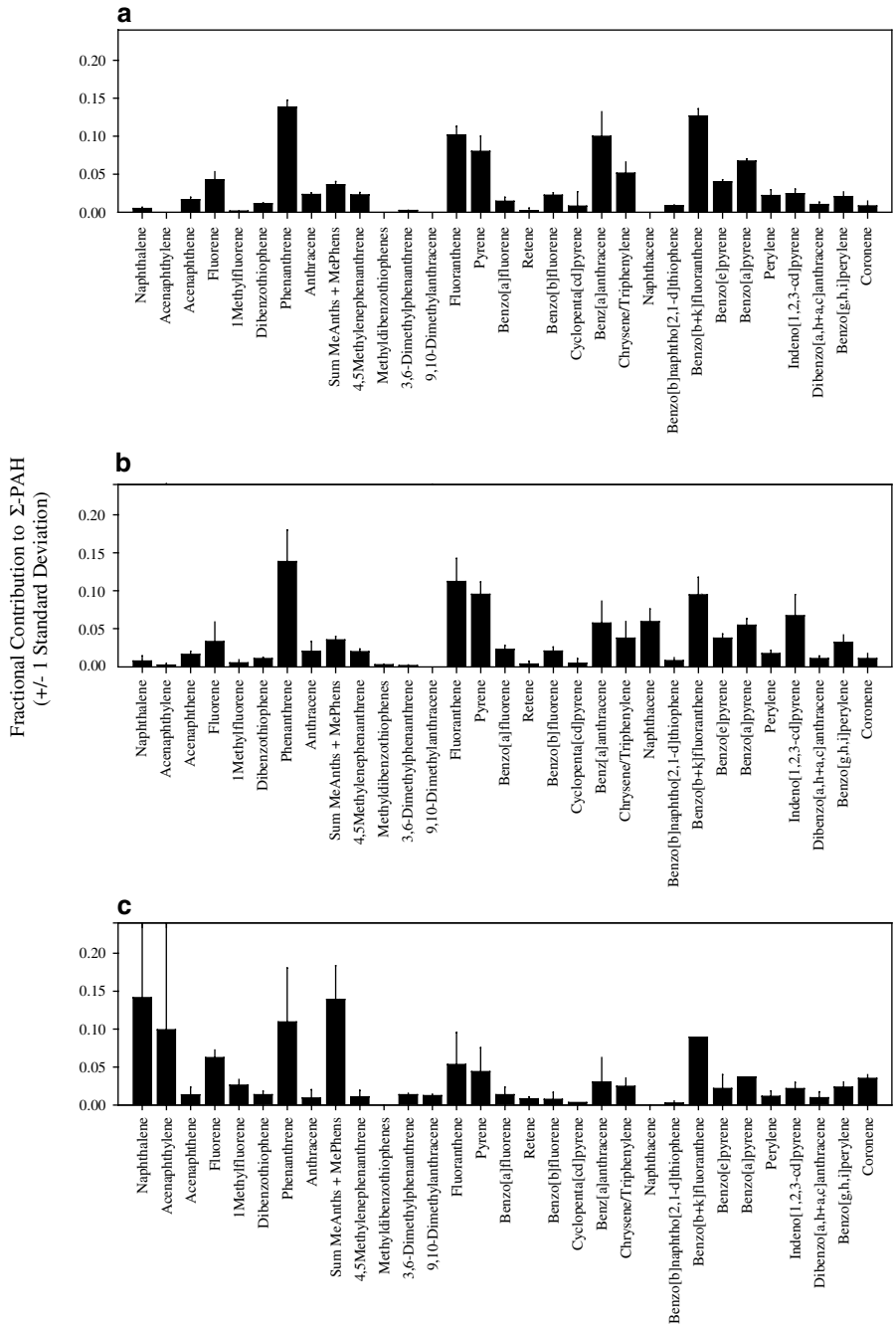

Figure 4. PAH compound fingerprints representing average fractional contribution to (a) indoor WTC-related settled dusts ($n = 12$; 11 from this work and one from Offenberg et al., 2003), (b) outdoor WTC-related settled dusts ($n = 7$; 1 one from this work and six from Offenberg et al., 2003) and (c) postrehabilitation dust from a vacuum cleaner at in an indoor location (triplicate analysis of one sample).

part of this work. However, a single distribution of PAH concentration according to particle sizes was previously reported by Offenberg et al. (2003). A sample from inside 120 Broadway was comprised of more than 96% by weight of particles larger than 10 μm aerodynamic equivalent diameter (a.e.d.), with only 8% of the total mass being greater than 53 μm diameter. This single size distribution of indoor dusts is in contrast to that measured for several outdoor settled dust samples that exhibited a greater mass percentage in the largest size fraction, $> 53\,\mu$m, than did the indoor dusts. Not unlike outdoor settled dusts, the concentrations of the same 37 PAHs were higher on larger particles (10–53 μm) than on small particles ($< 2.5\,\mu$m) in this single indoor sample. Owing to the limited quantity of sample available, and the very low mass concentrations of particles in the 2.5–10 μm a.e.d. size range, no attempt was

made to quantify the concentrations of these Σ_{37}PAHs in this size range. However, the concentration of the same 37 PAHs on this previously reported sample was 40,700 ng/g for particles less than 2.5 μm in diameter and 233,000 ng/g for larger particles (10–53 μm), agreeing quite favorably with the bulk indoor samples reported here.

In individual samples of dusts that settled at indoor locations in Lower Manhattan Σ_{37}-PAH concentrations represent up to 0.04% of the mass. Although total concentrations of PAHs varied considerably among the collected samples, the relative concentration profile varied little indicating that the PAHs in settled dusts, which spread into many indoor locations across lower Manhattan, originated from a common source. The lone sample that represents dusts collected from a home after rehabilitation (vacuum cleaner contents; sample 13) shows a fingerprint that differs from the others (Figure 4). Greater relative proportions of naphthalene, acenaphthene, methylphenanthrenes + methylanthracenes, and coronene occur in the vacuum cleaner contents as compared with both the WTC impacted indoor and outdoor samples. These differences can easily be seen the fractional contribution to total PAH concentration of indoor and post rehabilitation samples are each plotted against the same compound contribution to total outdoor PAH composition (Figure 5). Relatively small deviations from the 1:1 line are seen for WTC impacted indoor dusts suggesting a strong linkage between the indoor dusts and the outdoor WTC dusts. Conversely, relatively large deviations, both positive and negative, exist for the post-rehabilitation vacuum cleaner sample suggesting looser linkages between the postrehabilitation sample and WTC-generated dusts. In combination with significantly lower concentrations, these differences in fingerprint patterns will be helpful in determining the extent of cleaning completed, or whether further cleaning of dusts that were generated during the WTC disaster is necessary prior to reoccupation.

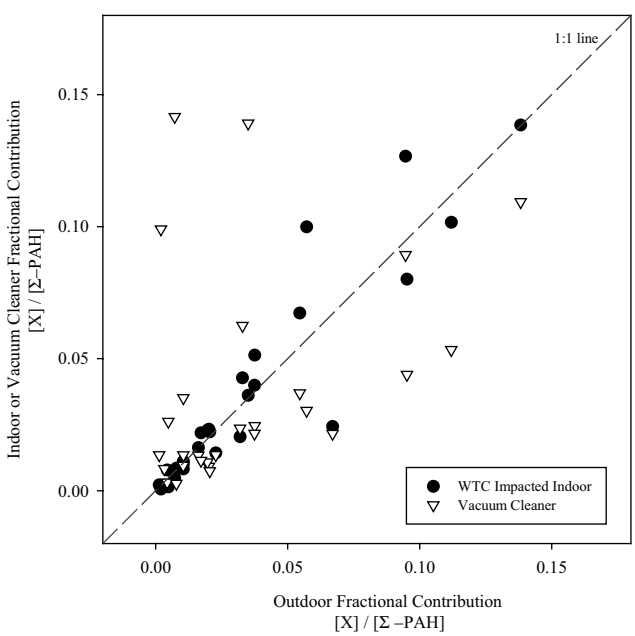

Figure 5. Relative fractional contribution of individual PAHs in the average of indoor WTC-impacted bulk dust samples ($n = 11$; solid circles) and postrehabilitation bulk vacuum cleaner sample (sample #13; open triangles) plotted against the relative contribution of that compound in WTC-impacted outdoor bulk dust samples. Note relatively large deviations from the 1:1 line for the postrehabilitation vacuum cleaner sample and relatively small deviations for WTC-impacted indoor dusts. Error bars removed for clarity.

The sets of dust/smoke samples from indoor locations around lower Manhattan provide valuable information on the composition, and the human and ecosystem health concerns arising from the WTC disaster. The dusts that settled in indoor locations appear to be of similar composition and concentration to the previously reported outdoor dusts. The levels of PCBs are similar to those found in the unaffected local environment, while select organo-chlorine pesticide concentrations were found to be well below average ambient concentrations. The explosion, collapse and subsequent fires produced aerosol particles from pulverized building debris, which included various products of incomplete combustion. This is not unexpected due to the variety of plastics, woods, furnishings, and business machines, and computers. Semivolatile organic contaminants with significant concentrations or surface loadings included polycyclic aromatic hydrocarbons. In addition to the material of concern for acute effects as well as those for asbestos, these results indicate that the PAH levels detected in these samples support ongoing effort to clean homes and to reduce the potential for longer term consequences of indoor human exposure to byproducts of incomplete combustion caused by the collapse and fires at the WTC. The relative concentration profiles in indoor settled dusts were useful in resolving the origins of the dusts in lower Manhattan homes. Moreover, the PAH concentration profiles may be used to determine the need for, and effectiveness of, cleaning residences and workplaces contaminated by dusts derived from the collapse of the WTC complex.

Acknowledgments

We thank the NIEHS and Dr. Ken Olden for the supplemental funds provided to the NIEHS Centers at EOHSI (ES05022-12), and at the NYU Institute of Environmental Medicine (ES00260) to complete these analyses, as well as the EPA University Partnership with the National Exposure Research Laboratory (CR827033), which supports Dr. Lioy. We also thank Dr. Dan Vallero, US EPA, NERL, for obtaining the necessary approvals to gain access to the sampling sites surrounding ground zero. Additionally, we thank The Henry and Camille Dreyfus Foundation for financial support during the completion of

this work. Furthermore, we thank Daryl Van Ry and Shahnaz Alimokhtari for assistance in the expedient completion of the sample preparation and analyses of the samples described here. This is a contribution of the NJ Agricultural Experiment Station of Rutgers University. The complete dataset of compound specific concentrations is available online at the following web-address: http://www.eohsi.rutgers.edu/WTC/eohsiresearch.shtml. Finally, express our sympathy and continuing concern for the survivors and for the families of the victims of September 11, 2001.

References

Brunciak P.A., Dachs J., Gigliotti C.L., Nelson E.D., and Eisenreich S.J. Atmospheric polychlorinated biphenyl concentrations and apparent degradation in coastal New Jersey. *Atmos Environ* 2001: 35: 3325–3339.

Claudio L. Environmental aftermath. *Environ Health Perspect* 2001: 109: A528–A537.

Gigliotti C.L., Dachs J., Nelson E.D., Brunciak P.A., and Eisenreich S.J. Polycyclic aromatic hydrocarbons in the New Jersey coastal atmosphere. *Environ Sci Technol*, 2000: 34: 3547–3554.

Kitsa V., Lioy P.J., Chow J.C., Watson J.G., Shupack S., Howell T., and Sanders P. *Aerosol Sci Technol* 1992: 17: 213–229.

Landrigan P.K. Health Consequences of the 11 September 2001 attacks. *Environ Health Perspect* 2001: 109(11): A514–A515.

Lioy P.J., Chen L.C., Weisel C., Millette J., Vallero D., Eisenreich S., Offenberg J., Buckley B., Turpin B., Zhong M., Cohen M.D., Yang I., Stiles R., Johnson W., and Alimokhtari S. Characterization of the dust/smoke aerosol that settled east of the World Trade Center (WTC) in Lower Manhattan after the collapse of the WTC 11 September 2001. *Environ Health Perspect* 2002: 110: 703–714.

Manuel J.S. NIEHS responds to the World Trade Center Attacks. *Environ Health Perspect* 2001: 109(11): A526–A527.

Mullins M.D., PCB workshop. US EPA Large Lakes Research Station, Gross Ile, MI, 1985.

Naumova Y.Y., Eisenreich S.J., Turpin B.J., Weisel C.P., Morandi M.T., Colome S.D., Totten L.A., Stock T.H., Winer A.M., Alimokhtari S., Kwon J., Shendell D., Jones J., Maberti S., and Wall S.J. Polycyclic aromatic hydrocarbons in the indoor and outdoor air of three cities in the U.S. *Environ Sci Technol* 2002: 36: 2552–2559.

Offenberg J.H., and Baker J.E. Aerosol size distributions of polycyclic aromatic hydrocarbons in urban and over-water atmospheres. *Environ Sci Technol* 1999: 33: 3324–3331.

Offenberg J.H., Eisenreich S.J., Chen L.C., Cohen M.D., Chee G., Prophete C., Weisel C., and Lioy P.J. Persistent organic pollutants in the dusts that settled across lower Manhattan after September 11, 2001. *Environ Sci Technol* 2003: 37: 502–508.

Pellizzari E., Lioy P.J., Quackenboss J., Whitmore R., Clayton A., Freeman N., Waldman J., Thomas K., Rodes C., Wilcosky T. The design and implementation of Phase I National Human Exposure Study in EPA Region V. *J. Expos Anal Environ Epidemiol* 1995: 5: 327–358.

Wise S.A., Sander L.C., Schantz M.M., Hays M.J., Benner B.A. Recent developments in the NIST standard reference materials for polycyclic aromatic hydrocarbons in environmental matricies. *Polycyclic Aromatic Comp* 2000: 13: 419–456.