PBDE, PCB, PCN AND PAH IN WINDOW FILMS FROM LOWER MANHATTAN AFTER SEPTEMBER 11th, 2001

Craig M. Butt[1], Miriam L. Diamond[1], Jennifer Truong[1], Michael G. Ikonomou[2], Paul A. Helm[3], Gary A. Stern[3]

[1] Department of Geography, University of Toronto, Toronto, Ontario, Canada, M5S 3G3
[2] Marine Environment and Habitat Science Division, Institute of Ocean Sciences, Department of Fisheries and Oceans Canada, Sidney, British Columbia, Canada V8L 4B2
[3] Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, MB, Canada R3T 2N6

Introduction

The September 11th terrorist attacks on the World Trade Center (WTC) initiated events that resulted in the massive release of contaminants to New York City (NYC) area. The initial fires and explosions, estimated to reach temperatures of 750-800 ^{o}C[1], were followed by lower temperature fires in the wreckage pile which continued to burn until December 14th, 2001. Combustion processes are known to generate polychlorinated biphenyls (PCB), polychlorinated naphthalenes (PCN) and polycyclic aromatic hydrocarbons (PAH).

PCBs, PCNs and polybrominated diphenyl ethers (PBDE) are also emitted to the atmosphere through evaporation from past and, in the case of PBDEs, current usages. Two electrical substations, located under "7 World Trade Center", were destroyed likely releasing PCBs and PCNs[2]. The WTC contained tons of PBDE sources such as office equipment, furnishing and building materials; including an estimated 50,000 personal and 300 mainframe computers[2].

This paper presents PBDE, PCB, PCN and PAH concentrations in organic films from exterior window surfaces in NYC, collected 6 weeks after September 11th. Window films, formed by the condensation of gas-phase species and deposition of particulate-associated compounds, provide a convenient passive sampler of ambient air quality[3]. Contaminant profiles in films provide information on likely sources as well as an integrated sample reflective of atmospheric deposition and partitioning.

Methods and Materials

Organic film samples were collected from exterior window surfaces by wiping with pre-cleaned laboratory Kimwipes, initially wetted with HLPC grade isopropanol (IPA), using methods described by Diamond *et al.*[3]. Split samples, one for PBDE and the other for PCB, PAH and PCN, of identical surface area were collected at each site due to differences in extraction, clean-up and analytical methods. Field blanks were prepared at three sites by soaking 10 pre-cleaned Kimwipes with IPA and air drying.

Eight samples were collected from seven sites in lower Manhattan and one in Brooklyn between October 27-29, 2001. Three sites (Church/Warren, Park Row/Spruce and the paired Museum-North and Museum-South) were located within 0.5-0.75 km of the WTC. Remaining Manhattan

sites were located transect extending northward from the WTC and the Brooklyn site, located ~4 km south of the WTC, served as a control.

Sampled Kimwipes analyzed for PBDEs were Soxhlet extracted overnight with a 80:20 toluene:acetone mixture, cleaned-up and analyzed using methods outlined by Ikonomou *et al.*[4]. Samples for PCB, PAH and PCN analysis were Soxhlet extracted overnight with dichloromethane (DCM). Details describing the clean-up and instrumental analysis are presented elsewhere for PAH/PCB[3] and coplanar PCB/PCN[5]. Data were blank corrected for each congener using the method detection limit (MDL=mean blank value plus three times blank standard deviation) and the MDLs were typically less than 5% of the sample signal.

Results and Discussion

Six weeks after September 11th total (Σ) PBDE, PCB, PCN and PAH film concentrations were greatest within 1 km of the WTC and levels declined rapidly to near background by 3.5 km (Table 1). The geometric mean concentration at the three sites within 1 km of the WTC was 3282 ng/m^2 for ΣPBDE, 898 ng/m^2 for ΣPCB, 33 ng/m^2 for ΣPCN and 77122 ng/m^2 for ΣPAH. Compared to the two sites located >3.5 km from the WTC, Union Square and Brooklyn, film concentrations near the WTC were ~3, ~10, ~8 and ~8 times greater for ΣPBDE, ΣPCB, ΣPCN and ΣPAH, respectively. Elevated concentrations measured near the WTC indicate that the events resulting from the September 11th attacks released a significant amount of contaminants that was subsequently deposited within lower Manhattan. The rapid decline in film concentration with distance from the WTC indicates that most of the plume was spatially constrained to within 1 km of the WTC.

Table 1. Total contaminant concentrations (ng/m^2) in window films from lower Manhattan.

	ΣPBDE	ΣPCB	ΣPCN	ΣPAH	Distance from WTC (km)
Church/Warren	5910	407	14	27850	0.50
Museum-North	2410	1409	65	154050	0.75
Museum-South	2490	1265	40	106910	0.75
Park Row/Spruce	398	107	6.4	10340	0.75
Worth/Broadway	603	515	19	19860	1.0
Canal/Broadway	295	109	9.3	9630	1.5
NYU	70	9.9	0.5	1780	2.75
Union Square	638	90	6.8	10840	4.0
Brooklyn	1690	83	2.8	7710	3.5

Coplanar PCBs, and particularly CB-126, have been suggested to preferentially form during combustion[6] and are used as combustion markers. In general, ratios of CB-126 ("combustion" PCB) to congeners predominant in Aroclor mixtures ("Aroclor" PCBs: CB-110, -138, -153, -180) were higher in organic films sampled near the WTC, consistent with the WTC fires influencing PCB profiles in these films. For example, combustion:Aroclor congener ratios for Church/Warren

and Brooklyn sites, respectively, were 0.11 and 0.02 for CB-126:CB-110, 0.04 and 0.01 for CB-126:CB-136, 0.05 and 0.02 for CB-126:CB-153, and 0.02 and 0.05 for CB-126:CB-180.

Toxic equivalents (TEQs) were calculated from measured film concentrations and literature toxic equivalency factors (TEFs), determined for PCNs[7] and non-/mono-*ortho* PCBs[8] using H4IIE enzyme induction assays. TEQ calculations used 7 coplanar PCB and 9 PCN congeners measured in this study. Spatial trends in TEQ values followed that of film concentrations with the geometric mean total PCN and PCB TEQ at near WTC sites ~16x greater, 56.6 pg/m^2, than background NYC sites, 3.6 pg/m^2 (Figure 1). Relative to total PCN and PCB TEQ, contributions of PCNs, mono-*ortho*, and non-*ortho* PCBs were 27%, 0.3% and 73% for near WTC sites, whereas, the background NYC contributions were 41%, 0.6%, 52%. The WTC fires resulted in an enhancement of non-*ortho* PCB TEQ contribution in near WTC films, a trend that has been observed in combustion-influenced air samples in Toronto, Ontario[9]. However, compared to chlorinated dioxin and furan (PCDD/F) TEQ, total PCB and PCB TEQ accounted for only 0.5%-5% of total TEQ.

Gas-phase air concentrations were back-calculated using the measured film concentrations, literature octanol-air partition coefficients (K_{OA})[10-13] and the theoretical film-air partition coefficient (K_{FA}), $K_{FA} = f_{OC} * K_{OA}$, where f_{OC} is the fraction of organic carbon in the film (Butt *et al.*, *in prep.*). K_{OA} values were temperature corrected to 17 ^{o}C (mean air temperature from Sept. 11th-October 29, 2001), assuming a film thickness of 100 nm and f_{OC} of 0.10 at all sites. Calculated gas-phase air concentrations followed spatial trends observed in film concentrations with near WTC air concentrations up to 10x greater than background NYC. Calculated PCB air concentrations were within the range measured by the U.S. EPA (www.epa.gov/wtc).

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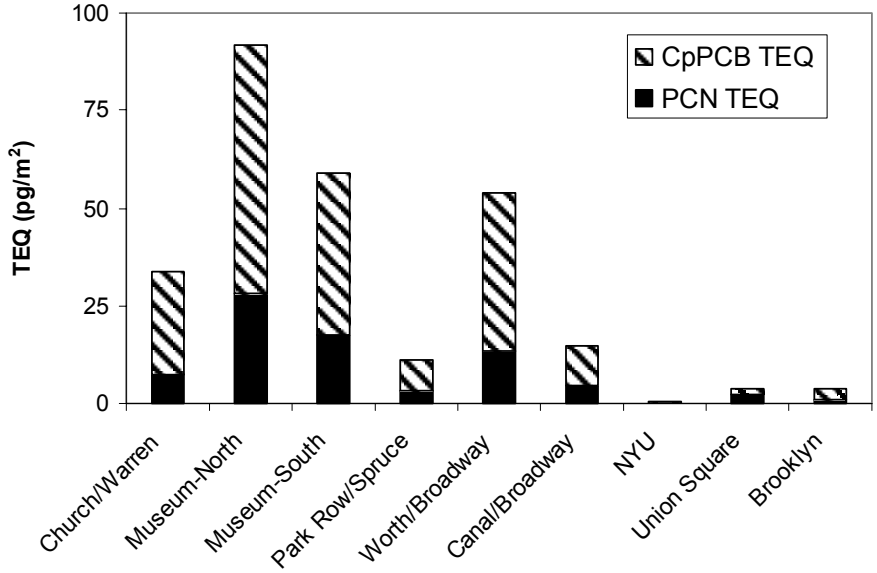

Figure 1. Toxic Equivalents (TEQ) for ΣPCN and ΣCoplanar PCB (pg/m^2) from NYC window films.

Table 2. Calculated gas-phase air concentrations (pg/m^3).

	ΣPBDE	ΣPCB	ΣPCN
Church/Warren	2020	1320	969
Museum-North	860	7050	3148
Museum-South	496	6520	1880
Park Row/Spruce	103	509	384
Worth/Broadway	256	2480	684
Canal/Broadway	104	567	424
NYU	10.5	80.1	29.9
Union Square	165	363	311
Brooklyn	41	475	229