POLYCHLORINATED DIOXIN AND FURANS (PCDD/F) IN ORGANIC WINDOW FILMS AFTER SEPTEMBER 11TH

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Introduction

The terrorist attacks at the World Trade Center (WTC) on September 11th, 2001, resulted in an unprecedented release and deposition of contaminants in lower Manhattan and adjacent boroughs of New York City (NYC). In addition to the collapse of the Twin Towers, which dispersed more than 1.2 million tons of building material [1], contaminants were released into the environment during the combustion processes in the initial explosions and ensuing fires in the wreckage pile. Whereas pre-collapse fires were estimated to burn at 750-800 °C [2], much lower temperature fires persisted in the wreckage for 3 months.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are known to be produced as combustion byproducts from a wide range of natural and anthropogenic products. The unknown tons of plastics in the WTC buildings, contained in PVC piping and coated copper wires, as well as the ~130,000 gallons of PCB contaminated transformer oil underneath "7 World Trade Center" [1] provided the precursors necessary for PCDD/F formation. An additional source of PCDD/F was likely the combustion of the large quantities of paper products present in the WTC.

Organic films on window surfaces provide a convenient passive sampler for assessing the time-integrated deposition and partitioning of atmospheric contaminants [3]. Particles and particle-sorbed compounds are efficiently captured on organic films, which initially form due to the condensation of gas-phase compounds. This paper presents PCDD/F concentrations and congener profiles from organic films, collected six weeks after the September 11th terrorist attacks, along a 4 km transect extending northward from the WTC.

Methods and Materials

Organic films were collected from exterior window surfaces at eight sites in lower Manhattan and Brooklyn, New York City, between October 27-29, 2001. Three sites (Church/Warren, Park Row/Spruce and Museum) were within 0.5-0.75 km of the WTC, while the remaining Manhattan sites were located on a northward transect extending from the WTC. Brooklyn, situated 4 km south of the WTC, served as a background control site. Films were sampled by scrubbing with pre-cleaned laboratory Kimwipes, initially soaked in HPLC grade isopropanol (IPA), following methods described by Diamond *et al.* [3]. Field blanks were collected at three sites using identical methods to sample collection except that field blanks did not contact window surfaces.

Sampled Kimwipes were extracted overnight with a 80:20 toluene:acetone mixture using a Soxhlet apparatus. Details describing sample extraction, clean-up and instrumental analyses are presented in Ikonomou *et al.* [4]. Samples were analyzed using high-resolution gas chromatography with high-resolution mass spectrometry (HRGC-HRMS) in the selected ion monitoring (SIM) mode.

Results and Discussion

Window film concentrations of total (Σ) P_{4-8}CDD/F concentrations (sum of 135 PCDD/F congeners) were highest within 1 km of the WTC, ranging up to 651,000 pg/m^2, and decreased rapidly with distance, falling to levels of 1,463-5,518 pg/m^2 at sites that were >3 km from the WTC (Table 1). ΣP_{4-8}CDD/F decreased exponentially with distance from the WTC, forming a conical pattern extending from Ground Zero. These results indicate that the combustion processes resulting from the September 11th attacks released a significant quantity of PCDD/F that was deposited on the surfaces of lower Manhattan.

Aerial film concentrations (pg/m^2) were converted to mass-based concentrations using an estimated film density of 500 mg/m^2, consistent with the presence of a significantly greater film mass in Manhattan films relative to Toronto (~100-200 mg/m^2) [3]. ΣP_{4-8}CDD/F film concentrations at sites near the WTC exceeded 1,300,000 pg/g (Table 1). Such high levels have only been observed in municipal solid waste incinerator (MSWI) fly and bottom ash [5], where concentrations range from 12-7,780,000 pg/g. These results are consistent with the PCDD/F in films within 1 km of the WTC originating from combustion processes due to the September 11th attacks.

While these concentrations are very high, their time course is uncertain. The organic film integrates the atmospheric signal over time, but its minimal depth and high potential for removal renders it a dynamic reservoir with a chemical residence time of days [7]. Loss processes from the film include washoff (the region experienced rain events on 13 days between September 11th and the time of sampling), volatilization and chemical transformation (eg. photolysis), although the latter is considered minimal for P_{4-8}CDD/F.

Table 1. ΣPCDD/F window film concentrations from lower Manhattan and Brooklyn.

	ΣPCDD/F		**TEQ**	**Distance from**
	pg/m^2	pg/g	pg-TEQ/m^2	**WTC (km)**
Church/Warren	651,341	1,302,682	3,465	0.50
Museum	159,826	319,652	1,801	0.75
Park Row/Spruce	69,372	138,744	916	0.75
Worth/Broadway	230,253	460,506	5,220	1.0
Canal/Broadway	76,790	153,580	3,309	1.5
NYU	1,463	2,926	72	2.75
Union Square	39,411	78,822	732	4.0
Brooklyn	5,518	11,036	131	3.5

Lower Manhattan window films displayed homologue profiles of PCDD/Fs that were unique as compared to the reference site in Brooklyn (Figure 1). On a mass basis, lower Manhattan films were dominated by tetra-, penta- and hexa-CDDs (46-67% of ΣPCDD/F). These films had lower proportions (3-20%) of hepta- and octa-CDDs, congeners that dominated the Brooklyn profile (55%). Lower Manhattan film profiles, characterized by decreasing homologue contribution with increasing chlorination, are consistent with combustion-influenced atmospheric and particulate samples [8]. Further, the Brooklyn profile is consistent with ambient urban and rural air samples [9], indicating that this site was not influenced by the WTC fires. Therefore, our results indicate the lower Manhattan film profiles were directly influenced by the combustion events at the WTC, consistent with higher aerial film concentrations.

Toxic equivalents (TEQs) were calculated from window films concentrations using World Health Organization (WHO) TEFs for humans. TEQs near the WTC ranged up to 5,200 pg-TEQ/m^2 (~10,400 pg-TEQ/g) with declining values with distance from the WTC, following the spatial trends in film concentrations. TEQs in films situated near the WTC were within the range measured in MSWI fly ash [5] and exceeded the action level of soil requiring “consideration of action to interdict exposure” as defined by U.S. Department of Health and Human Services. The organic film is a model for atmospheric deposition onto all surfaces, and surface accumulated contaminants may be transferred by hand-to-mouth activity. These data suggest it would be prudent to monitor PCDD/F levels in films and soil as these are potential routes of human exposure.

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References

1. Nordgrén, N.D., Goldstein, E.A., Izeman, M.A. (2002), The Environmental Impacts of the World Trade Center Attacks: A Preliminary Assessment, National Resources Defense Council.
2. Eager, T.W., Musso, C. (2001), J. Metals 53, 8-11.
3. Diamond, M.L., Gingrich, S.E., Fertuck, K., McCarry, B.E., Stern, G.A., Billeck, B., Grift, B., Brooker, D., Yager, T.D. (2000), Environ. Sci. Technol. 34, 2900-2908.
4. Ikonomou, M.G., Fraser, T.L., Crewe, N.F., Fischer, M.B., Rogers, I.H., He, T., Sather, P.J., Lamb, R.F. (2001), Can. Data Rep. Fish Aquat. Sci. 2389, 1-95.
5. Sakai, S.I., Hayakawa, K., Takatsuki, H., Kawakami, I. (2001), Environ. Sci. Technol. 35, 3601-3607.
6. Shuhmacher, M., Granero, S., Rivera, J., Muller, L., Llobet, J.M., Domingo, J.L. (2000), Chemosphere, 40, 593-600.
7. Diamond, M.L., Priemer, D.A., Law, N.L. (2001), Chemosphere, 44, 1655-1667.
8. Yasuhara, A., Katami, T., Okuda, T., Ohno, N., Shibamoto, T. (2001), Environ. Sci. Technol. 35, 1373-1378.
9. Duarte-Davidson, R., Sewart, A., Alcock, R.E., Cousins, I., Jones, K.C. (1997), Environ. Sci. Technol., 31, 1-11.

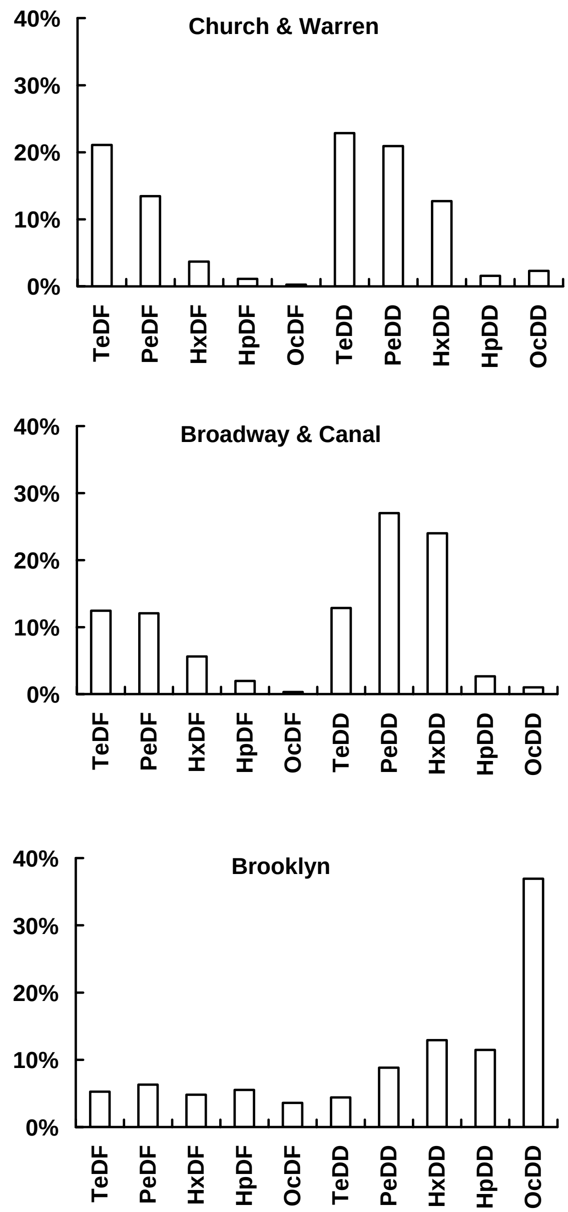

Figure 1. PCDD/F homologue profiles for window films in lower Manhattan and Brooklyn.