A Congener Profile Analysis of Dioxin Emissions and Environmental Fate from the World Trade Center Fires of 2001. Part 2: Settled Dust Profiles

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Introduction

Congener profile analysis has proven to be a valuable tool in studying sources of dioxin contamination, and impacts to exposed populations. Emission sources often have a characteristic profile, which is then reflected in the media into which the emission occurs. In this two-part paper, ambient air and settled dust profiles of dioxins that result from the World Trade Center (WTC) fires are studied for trend analysis. The first paper looks at WTC emissions into the air as characterized by on-site air monitors at "Ground Zero" (GZ), and then air profiles downwind as characterized by air monitors and window films. This paper compares settled dust profiles that have been measured off-site of GZ to the emission profile, to air profiles and other profiles. By showing key similarities with data from other building fire locations, it is seen that the trends examined for the WTC site are, in reality, trends for building fires in general. A congener profile is generated by summing the concentrations of the 17 dioxin and furan congeners (dioxin-like PCBs are not examined here), and then determining the percent each congener contributes to the sum total. In the profiles shown in these two papers, the x-axis contains numbers 1-17, denoting first the seven dioxin congeners and then the 10 furan congeners, and the y-axis is the percent of total.

Unique Dust Profiles

Figure 1 shows a typical background soil profile and a profile from dust collected at the Binghamton office transformer fire. A typical indoor air profile from this building was shown in Part 1.

WTC Emission and Dust Profiles

Figure 2 shows four representative profiles that describe WTC emissions and nearby dust impacts: a) the "emission" profile into air as measured by the ambient on-site monitor (from Part 1), b) an undisturbed settled dust sample collected on Sep. 16, 2001, from Market Street, 0.7 km from GZ.¹ c) a settled dust sample collected by EPA at GZ on Sep. 22, 2001, and d) a settled dust sample from a window ledge collected from an highly impacted apartment 2 blocks east of GZ on Sep 18, 2001.²

Congener Profiles from 130 Liberty Street

A building at 130 Liberty Street, located directly across the street from GZ, was heavily impacted by the collapse of the towers. A portion of the building facing GZ was severely damaged, and over 1500 windows were shattered throughout the building. The ongoing fires resulted in depositions directly into the interior of the building. Extensive monitoring studies have taken place within the building to determine whether it can be rehabilitated and reused. To evaluate the data³, sampling locations were grouped into 5 sectors, termed: 1) "below gash": the basement through floor 7; 2) "gash": the north side facing GZ of floors 8 through 23; 3) "opposite gash"; the remaining, less impacted, portions of floors 8 through 23, 4) "above gash": floors 24 through 39, and 5) the "top": floors 40 and 41. The most heavily impacted areas, based on broken windows, obvious visual inspection, and plume incursion included the "gash" and "below gash" areas. For the five locations, interior dioxin wipe samples averaged, in ng TEQ/m²: gash (n=118) – 11.1; below gash (n=383) – 13.4; opposite gash (n=423) – 3.9; above gash (n=738) – 1.7, and top (n=57) – 5.6. Figure 3 shows representative dioxin congener profiles from the impacted "gash" and "below gash" sectors, and from the less impacted "above gash" and "opposite gash" sectors.

Congener Profiles from a Building Fire in Pennsylvania

EMV - General – Environmental Levels

On February 23, 1991, a commercial office building in Philadelphia sustained a fire that destroyed eight floors (floors 22-29) of the 38-story structure⁴. Ancillary fire damage included visible surface deposits of combustion soot that covered essentially every vertical and horizontal surface on floors 22-38. In addition, the fire consumed equipment (e.g., fluorescent light ballasts) and materials (e.g., caulking between exterior granite wall panels) containing PCBs. It is estimated that the fire released approximately 83 kg of PCBs into the building during the fire. Dioxin-like compounds were also produced during the combustion of the PCB-containing materials and other chlorine-containing materials. These compounds were deposited on surfaces throughout the building in tenant areas, in mechanical and electrical shafts, inside the central heating systems, on the exterior wall of the building, and on other building surfaces. Figure 4 shows four representative congener profiles from this fire including: a soot sample, an exterior granite wall surface wipe, and two surface wipe samples from file cabinets.

Observations from the Representative Profiles

1) The background soil profile (Figure 1a) is similar to the background air profile, but now the OCDD overwhelmingly dominates the profile, comprising 80% of the total. Meaningful contributions are seen from the hepta dioxin (#7), the hepta furan (#15), and OCDF (#17), but the lower chlorinated dioxins and furans are virtually absent from the profile. The Binghamton office building transformer fire dust profile (Figure 1b) looks similar to the air profile from this building in that the lower chlorinated furan congeners (tetra thru hexa; #8 - #14) dominate the profile, except that the 2378-TCDF (#8) no longer so overwhelmingly dominates as it did in the air profile. This profile showing a dominance of furan congeners is the signature for dioxin-like compounds produced from PCB combustion.

2) All "impacted" WTC samples, including the 130 Liberty "gash" and "below gash" samples, the apartment ledge sample, the sample taken at GZ on 9/22, and the sample taken on 9/16 at Market St, share some common themes: a) in contrast to the background profile, furan congeners including the lower chlorinated congeners and in particular, 2378-TCDF, *are* showing up in the profile. Similar to the background profile, the lower chlorinated dioxin congeners (tetra through hexa, #1 - #5) *are not* showing up in the profile; b) in the Market St. sample, the GZ sample, and the impacted "gash" sample from 130 Liberty, the 2378-TCDF congener was prominent among the lower chlorinated furan congeners. This was not true for the window ledge impacted sample; c) The main difference between the impacted air and the impacted dust is that, OCDD now becomes very important in the overall impacted dust profile, almost similar to background soil.

3) Unlike the impacted "gash" (Figure 3a) and "below gash" (3c) samples, the WTC profile could not be found in samples from less impacted portions of 130 Liberty Street, as seen in the "above gash" (3b) and "opposite gash" (3d) profiles in Figure 3. Lower chlorinated dioxins and furans were not detected and, in fact, with OCDD at 80%, the "opposite gash" sample looks like a background sample.

4) The Philadelphia building fire showed distinct similarities to the WTC and other profiles discussed above. The exterior granite panel sample showed a predominance of the 2378-TCDF congener, with other lower chlorinated congeners also important in the profile, very similar to the Binghamton office building transformer fire, where the profile was driven by the combustion of PCBs. The interior soot and the file cabinet samples were similar to the gash and below gash impacted samples from the 130 Liberty St building – importance of lower chlorinated furan congeners contrasting the absence of lower chlorinated dioxin congeners, while OCDD now also the dominant congener in the profile.

5) The importance of the lower chlorinated furan congeners and, in particular, the 2378-TCDF in the WTC and building fire profiles is interesting. This could be indicative of PCB combustion. Lower chlorinated furans dominated the Binghamton, New York transformer building fire (Figure 1b), and this was speculated to be due to PCB combustion. The unusually high presence of 2378-TCDF in some of the profiles could be an analytical anomaly. It is known that several tetra furan congeners co-elute with 2378-TCDF in the first GC column, and second column confirmation is required to distinguish 2378-TCDF from other co-eluting tetra congeners. Rayne⁵ identified these five co-eluting congeners in their WTC window film wipe sampling study: 2348-TCDF, 2347-, 2346-, 1246-, and 1249-. They conducted second column confirmations to arrive at their reported results on dioxins in window films near GZ. In a limited second column confirmation indicated that the first column 2378-TCDF apparent concentration measured in EPA air samples was reduced 84% with a second column confirmation. Since there were no second column confirmations regularly done on EPA air samples, all EPA air samples reported in this two-part abstract included that correction factor for 2378-TCDF. Without it, the 2378-TCDF congener would appear to be the most dominant congener in EPA GZ and

downwind air samples. It may be possible that second column confirmations were not done for the analysis of the Binghamtom or the Philadelphia office fire samples, where some samples were dominated by 2378-TCDF.

References

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(a) (b)

Figure 1. A dust profile from the Binghamton office building ransformr fire (a) and (b)a typical background soil profile.



(a) (b) (c)





(d)

50

40

з

20

10

Π.

(d)

51%

1 2 3 4 5 6 7 8 9 10 11 12 13 14

Outside ledge

280 pg TEQ/g

Figure 3. Congener profiles from interior surfaces from 130 Liberty St including: (a) impacted "gash", (b) unimpacted "above gash", (c) impacted "below gash", and (d) unimpacted "opposite gash."



(a) (b) (c)



Figure 4. Congener profiles from the Philadelphia building fire including: (a) wipe sample from a file cabinet on floor 25, (b) interior soot, (c) wipe sample from an exterior granite surface, and (d) wipe sample from file cabinet on floor 29.