A Congener Profile Analysis of Dioxin Emissions and Environmental Fate from the World Trade Center Fires of 2001. Part 1: Ambient Air 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. Dioxin emission sources often have a characteristic profile, which is then reflected in the media into which the emission occurs. The characteristic World Trade Center (WTC) profile has been studied in two other efforts. In one study, the researcher noted the predominance of the furan congeners in samples taken by the Environmental Protection Agency (EPA) near the site of the collapse and shortly after September 11 - this was the researcher's description of the "WTC profile", but then how the profile changed by December, 2001, when the more typical background profile dominated by dioxins and, in particular, OCDD emerged.[1] The second effort examined the congener profile by taking wipe samples from exterior building windows in October of 2001, and made the same observation about the furan congeners. They also examined homologue profiles and compared both sets of profiles to other emission source profiles.[2] This work continues on those efforts by examining the profile on air emissions directly at the WTC site, known as “Ground Zero” (GZ), and compares them to air and the window film congener profiles downwind. Part 2 of this study looks at dust congener profiles from WTC-impacted settled dust samples, and compares them to the emission profile and other dust congener 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.

Analysis Methods

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. An example of a congener profile is shown in Figure 1, which shows the archetype background air profile generated from data from Columbus, Ohio[3]. In this figure, the x-axis contains numbers 1-17, denoting first the seven dioxin congeners and then the ten furan congeners, and the y-axis is the percent of total. Several other congener profiles will now be examined using this approach. It is noted that the entire data bases used here contain tens to even thousands of samples. Individual samples that are representative of the trends are displayed in these papers, and qualitative observations are made about the trends. Future work on this effort will include statistical summaries of the data sets and more sophisticated statistical analyses, leading to more defensible conclusions. References will be provided for further details (analytical methods, e.g.) on these data. It is important to note that second column confirmation of 2378-TCDF was not conducted for EPA data. This is important because co-eluting tetra congeners can lead to a very elevated and incorrect reading of the 2378-TCDF concentration. A limited second column confirmation of the EPA data set suggested that 2378-TCDF measurements needed to be reduced by 84%, and this was done for all EPA samples in this report. The wipe sample data[2] was the only WTC data not generated by EPA, and second column confirmation was performed for this data set. Further details on this second column confirmation issue are provided in Paper 2. The WTC profiles were generated from laboratory reports supplied by EPA’s Region 2 Office in New York. TEQ quantities were generated using the 1998 WHO TEFs, and NDs were assumed equal to zero for profile and TEQ generation.

Congener Profiles Not Associated with the WTC

Figure 2 shows an air profile found indoors in the vicinity of a PCB transformer fire in an office building in Binghamton, New York[4], a stack emission profile from the Columbus Municipal Solid Waste Incinerator, and a profile directly downwind of this incinerator[3].

World Trade Center (WTC) Congener Profiles

Figure 3 shows the location of air samplers and the window film sample for WTC ambient air samples. The burning fires at GZ produced a profile shown by three different representative samples in Figure 4, including two air samples taken at GZ and a personal sample from a GZ worker. Figure 5 shows representative profiles downwind of GZ, including three air samples and a window film sample.

Observations

1) The archetype background air profile shown in Figure 1 is also found in soil and even food of terrestrial origin. This particular profile was from the Columbus Incinerator study, but is seen in virtually all background air samples taken in the United States. As seen, the predominant congener is OCDD (congener #7), comprising about 50% of the total concentration. Other congeners of note include the hepta dioxin congener, 1234678-HpCDD (#6), one of the hepta furan congeners, 1234678-HpCDF (#15), and OCDF (#17).

2) Figure 2 shows a profile taken near a transformer fire in a building in Binghamton, New York. The striking feature is the predominance of furans, with the excessive amounts of the 2378-TCDF (#9) congener. This Columbus incinerator, whose emission profile is shown in Figure 2, is of interest because of the exceedingly high dioxin emission rates – stack tests suggest annual emissions from this single source of 984 g TEQ/yr before the incinerator was shut down in 1995. Of note in the stack is the predominance of the same four background congeners, #6, #7, #15, and #17, but not in the same relative contribution as in the background profile: mainly that OCDD is not the predominant congener. Meaningful amounts of lower chlorinated furan congeners, the tetra-hexa congeners, are also being emitted out the stack, unlike background profiles. Downwind but still within the plume, the background profile begins to emerge (Figure 3b), with OCDD contributing over 30% of the profile, and the urban background profile from this site (Figure 1) shows the archtype background profile, as noted above.

3) The WTC emission profile shown in Figure 4 has some similarities to the Columbus incinerator profile, but the important difference is that the hepta and octa dioxin congeners (#6, #7) dominate the profile, more so than in the incinerator profile, while the OCDF congener in the WTC profile is much less prevalent as compared to the incinerator profile. Also of note is the fact that 2378-TCDF congener is virtually absent from the incinerator and downwind profiles, while it shows up in an amount of note at WTC. Other observations include: a) the personal sampler from a GZ Worker showed a high concentration, 79 pg TEQ/m^3, and a profile that were both similar to the high volume stationary sampler (shown in the southeast corner of GZ in Figure 4), and b) the profile from the very high concentration found on 9/23/01, 181 pg TEQ/m^3, is similar to the profile from the lower concentration of 3 pg TEQ/m^3 found on 10/26/01.

4) Key characteristics of the downwind impacted samples in Figure 5 (a, c, and d) are similar to the GZ emission profiles: OCDF (#17) is still very low, 2378-TCDF (#8) still is elevated downwind, and the hepta furan congener (#15) still is important in the profile. The downwind air samples suggest a shift to OCDD, similar to the background profile. By December 31, 2001, when the fires had been extinguished, the off-site air samples showed the archetype background profile, shown in Figure 6b. This was also observed by Webb[1]. The window film data may reflect a tendency of the vapor phase dioxins to accumulate in the organic layer of the films[2], explaining why the hepta and octa dioxin congeners (#6, #7) are lower here as compared to the air samples, but otherwise it is interesting that the window film data corroborates the high volume air sampler, particularly in reflecting the importance of 2378-TCDF (#8) and other furan congeners, #11, #13, and #15, in the profile.

References

1. Webb L, Kantz M., Winter M., Vallaro D., and Vette (2002) Organohalogen Compounds 59:235 - 238

2. Rayne S., Ikonomou M.G., Butt C.M., Diamond M.L., Troung G. (2005) Env. Sci. Tech; published on the internet in February, 2005.

3. Lorber M., Pinsky P., Gehring P., Braverman C., Winters D., Sovocool, W. (1998) Chemosphere 37: 2173-2197

4. New York State Department of Health (1989), Comparison of PCBs and PCDD/PCDFs in the Air and on Surfaces of the Binghamton State Office Building and Utica State Office Building.

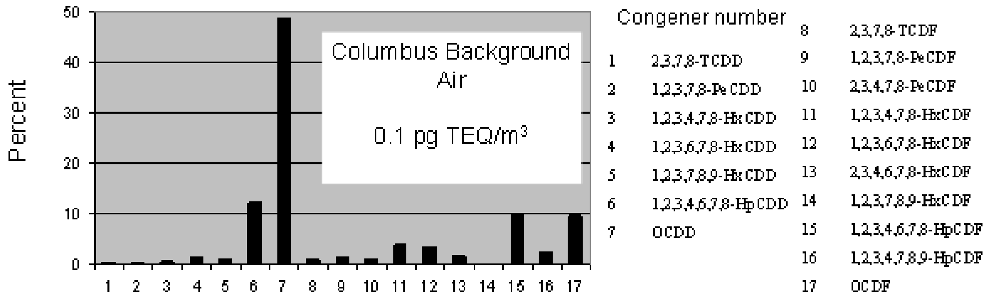
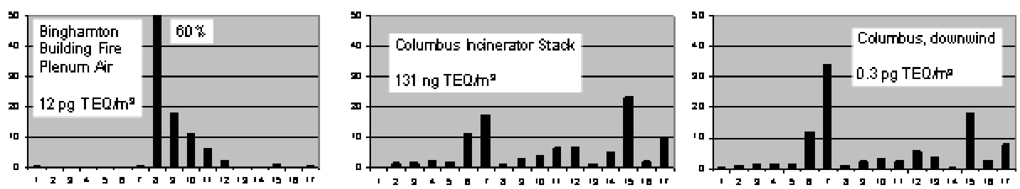


Figure 1. The archetype "background" congener profile in air as demonstrated by an air sample taken in the Columbus Incinerator study[3].



(a) (b) (c)

Figure 2. Unique congener profiles including (a) an indoor air profile from the Binghamton, NY, office fire[4], and (b), (c) profiles from the Columbus Incinerator site[3].

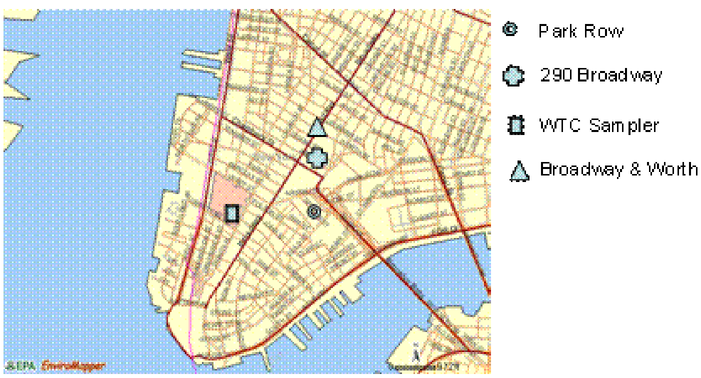
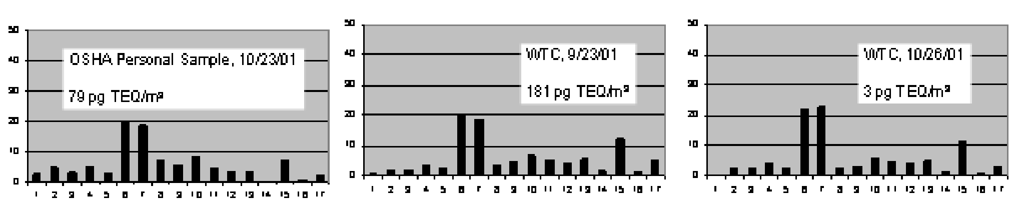


Figure 3. Locations of the Ground Zero sampler, the window film sample and the air samplers.



(a) (b) (c)

Figure 4. Profiles at Ground Zero, including (a) a personal sampler, and (b), (c) two samples from a stationary high-volume sampler at Ground Zero.

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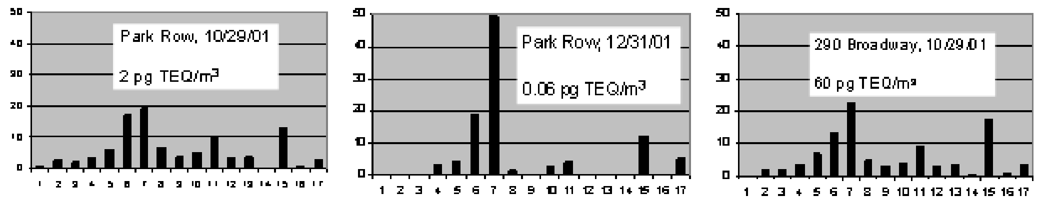
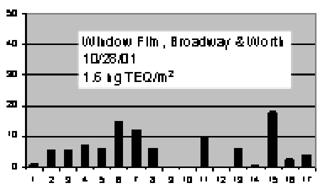


(a) (b) (c)



(d)

Figure 5. Profiles downwind of Ground Zero including air sampling profiles at Park Row on (a) Oct 29, 2001 and (b) Dec 31, 2001; at (c) 290 Broadway, and (d) a window film sample at Broadway and Worth.

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