

# Relative Congener Scaling of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans to Estimate Building Fire Contributions in Air, Surface Wipes, and Dust Samples

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The United States Environmental Protection Agency collected ambient air samples in lower Manhattan for about 9 months following the September 11, 2001 World Trade Center (WTC) attacks. Measurements were made of a host of airborne contaminants including volatile organic compounds, polycyclic aromatic hydrocarbons, asbestos, lead, and other contaminants of concern. The present study focuses on the broad class of polychlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) with specific emphasis on the 17 CDD/CDF congeners that exhibit mammalian toxicity. This work is a statistical study comparing the internal patterns of CDD/CDFs using data from an unambiguous fire event (WTC) and other data sets to help identify their sources. A subset of 29 samples all taken between September 16 and October 31, 2001 were treated as a basis set known to be heavily impacted by the WTC building fire source. A second basis set was created using data from Los Angeles and Oakland, CA as published by the California Air Resources Board (CARB) and treated as the archetypical background pattern for CDD/CDFs. The CARB data had a congener profile appearing similar to background air samples from different locations in America and around the world and in different matrices, such as background soils. Such disparate data would normally be interpreted with a qualitative pattern recognition based on congener bar graphs or other forms of factor or cluster analysis that group similar samples together graphically. The procedure developed here employs aspects of those statistical methods to develop a single continuous output variable per sample. Specifically, a form of variance structure-based cluster analysis is used to group congeners within samples to reduce collinearity in the basis sets, new variables are created based on these groups, and multivariate regression is applied to the reduced variable set to determine a predictive equation.

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This equation predicts a value for an output variable, OPT: the predicted value of OPT is near zero (0.00) for a background congener profile and near one (1.00) for the profile characterized by the WTC air profile. Although this empirical method is calibrated with relatively small sets of airborne samples, it is shown to be generalizable to other WTC, fire source, and background air samples as well as other sample matrices including soils, window films and other dust wipes, and bulk dusts. However, given the limited data set examined, the method does not allow further discrimination between the WTC data and the other fire sources. This type of analysis is demonstrated to be useful for complex trace-level data sets with limited data and some below-detection entries.

## Introduction

The United States Environmental Protection Agency (EPA) and other national, state and local public agencies, institutes, and universities collected a wide variety of samples in response to the catastrophic destruction of the World Trade Center (WTC) on September 11, 2001 (9/11). The initial purpose was to provide rapid assessments of the environmental impacts and potential health effects from the building collapse and the subsequent fires that emitted smoke and soot into the air of New York City well into December. Outdoor pollutant levels in lower Manhattan were shown to mostly return to urban background after about 90–120 days as the fires were put out, and background conditions fully returned after about 200 days when the debris cleanup was completed (1–6). However, particulate matter from the disaster had also penetrated into commercial and residential buildings where it was thought to pose a continuing exposure risk. This concern prompted researchers to consider a variety of potential markers for the WTC contamination including polycyclic aromatic hydrocarbons (PAHs), man-made vitreous fibers, gypsum content, particle-bound metals, and polychlorinated dibenzo-*p*-dioxins (CDDs) and dibenzofurans (CDFs) to assess residual contamination levels (7–9; see also deliberations of WTC Expert Technical Review Panel, described at <http://www.epa.gov/wtc/panel>).

The fundamental approach has been to contrast concentrations and patterns of known WTC-impacted environmental samples with samples regarded as nonimpacted. Graphic analyses of CDD/CDF patterns in WTC-impacted samples have already been conducted by Rayne et al. (10) and Lorber et al. (8, 9). This effort builds on the initial qualitative examinations by Lorber (8) to produce a predictive framework that can have practical application beyond distinguishing WTC-impacted samples and background samples.

The WTC disaster was uniquely suited for assessing source contributions from an environmental disaster, especially for compounds of incomplete combustion. Under normal urban circumstances, background contaminant levels are a subtle mixture of numerous local sources (e.g., small fires, automobiles, diesel engines, and industrial facilities) and long-range transport (e.g., power plants, forest fires, incinerators, agricultural burning, and waste fires) making them difficult to attribute individually. In the case of the WTC disaster, however, the rubble fires dwarfed other combustion sources in lower Manhattan for about 30 days and continued to burn at some reduced/intermittent levels until mid-December, 2001. Air concentrations of CDD/CDFs reached a level of

170 pg TEQ/m<sup>3</sup>, (TEQ = toxic equivalent concentration) and were still regularly above 2 pg TEQ/m<sup>3</sup> through October, 2001 (TEQ data and sampling site map available from EPA at <http://www.epa.gov/wtc/dioxin/>). Although some of the early TEQ values measured directly on the WTC site greatly exceeded the normal urban background concentration of ~0.1 pg TEQ/m<sup>3</sup> (11), only the highest few values reached the EPA screening level of 160 pg TEQ/m<sup>3</sup>. This screening level was developed specifically for the WTC site and is defined as an average yearly exposure level set to protect against significantly increased risks of cancer and other adverse health effects (12; [http://www.epa.gov/wtc/dioxin/dioxin\\_fact\\_sheet.html](http://www.epa.gov/wtc/dioxin/dioxin_fact_sheet.html)). Given the initial excursions in CDD/CDF levels, the WTC source was considered dominant compared to the normal city mixture. Pleil et al. (1) showed the same to be true for PAHs, which were also significantly elevated over normal urban PAH levels in airborne particulates in the 30 day period after 9/11.

Although CDD/CDFs have very low background levels, e.g., on the order of 0.1 pg TEQ/m<sup>3</sup> in air in urban settings and lower in rural or background settings, they are highly lipophilic and bioaccumulate in animals, including fish and terrestrial animals raised for food (poultry, cattle, swine) (11). Food concentrations are typically in the range of 1 pg TEQ/g (ppt) lipid-based. Long-term exposures to these levels in food and to smaller, additional exposures via air and other exposure matrices, coupled with persistence in humans, lead to a relatively high accumulated body burden. The index compound, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), has a half-life in humans estimated in the range from 5.8 to 11.3 years (11) compared with <24 h for other contaminants of exposure concern such as benzene and vinyl chloride. EPA's draft Dioxin Reassessment (11) finds that CDD/CDFs are potent animal toxicants with potential to produce a broad spectrum of adverse effects in humans. Furthermore, it estimates that the current body burdens in the general population closely approach, within a factor of 10, the levels at which adverse effects might be expected to occur, based on studies of animals and highly exposed human populations. This makes the measurement and interpretation of CDD/CDF concentrations extremely important despite their low concentrations and related difficulty with ultra-trace-level analysis.

The number of airborne CDD/CDF samples near the WTC fires was limited due to logistics, sporadic electrical power for samplers, and more immediate concerns of rescue and safety. During the WTC emergency, EPA and others were constrained to using portable equipment including some personal samplers that operated at lower flow rates and for shorter collection times than standard ambient measurements that are traditionally made over 24 h with fixed site samplers filtering ~400 m<sup>3</sup> of air (13). Despite these difficulties, stationary samplers were established for CDD/CDF that collected 9 m<sup>3</sup> for 8 hour samples starting on September 16. This volume of air was sufficient to quantify CDD/CDF concentrations due to the high concentrations. A set of 29 samples were retrieved that characterize the CDD/CDF air concentrations from September 16 to the end of October, 2001 (14). These samples were classified as "known WTC impacted" based on spatial and temporal proximity and also based on having obviously high concentrations. We used a data set of city values from Los Angeles and Oakland, CA from the California Air Resources Board (CARB) from 2001 and 2002 for comparison (15). Based on these two existing "basis" sets (known as WTC vs non-WTC), we adapted standard statistical methods to accommodate the underlying data structure and developed a simple empirical calculation proposed to distinguish between the CDD/CDF pattern in the WTC sample set and the non-WTC sample set. When applied to other WTC data sets, non-WTC building fire data

sets, an incinerator combustion data set, and other available CDD/CDF data sets from background settings, the technique is shown to be surprisingly robust in distinguishing between these fire data sets and background data sets. However, this does not imply that all fire data sets are similar to the WTC fire data set. As will be discussed below, while data sets from other building fire and combustion sources share similarities with the WTC fire data, clearly there are differences among combustion sources. The general method developed and applied in this study has applicability to other situations, including distinguishing among other CDD/CDF sources and also discerning patterns for other classes of compounds found together in the environment, including PAHs, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and others.

## Experimental Section

**CDD/CDF Samples and Data Structure.** Like many classes of combustion products, "dioxin-like" compounds always occur as a complex mixture. They are characterized as chlorine-containing hydrocarbons; their basic structure comprises two benzene rings joined by either a single- or a double-oxygen bridge (furan or dioxin, respectively). There are 210 different possible arrangements based on the location of chlorine atoms on the available eight exterior carbon atoms. Of these, 7 dioxins (CDDs) and 10 furans (CDFs; 17 congeners in total) have demonstrated mammalian toxicity and are the primary suite of analytes for standard CDD/CDF analyses. For convenience and future reference, these have been labeled D1, D2, ... D7 and F1, F2, ... F10, respectively. The "D1" congener, 2,3,7,8 tetrachlorodibenzo-*p*-dioxin (2378-TCDD), is considered the most toxic and is assigned as the "index" compound against which all others are compared. To evaluate the overall toxicity of an environmental mixture of the 17 CDD/CDF congeners, a "toxic equivalency factor" (TEF) scheme is employed to derive a "toxic equivalent" (TEQ) concentration. In this scheme, 2378-TCDD is given a value of 1.00, and the other 16 compounds are given a value less than or equal to 1.00, and a TEQ concentration is simply calculated as,  $\sum \text{TEF}_i C_i$ , where  $\text{TEF}_i$  are the toxicity equivalency factors for the 17  $C_i$  congeners (16, 17). The WHO-1998 set of TEFs are used to calculate TEQ concentrations in this paper (16). These have been recently updated with a set of 2006 WHO TEFs (17). A cursory examination of a small number of samples suggests that the TEQ concentration would increase slightly, <5%, if applying the 2006 WHO values instead of the 1998 WHO values, mainly because the TEF value for OCDD increased from 0.0001 to 0.0003 in the 2006 WHO system. However, this is not relevant for the results of this study, as this analysis is based on actual and not TEF-corrected values.

Two primary "basis" sets include a set of air samples taken near WTC and a set of background air concentration from California. The air samples taken in the vicinity of WTC by EPA have been culled to a set of 29 that include only those with less than ~20% flagged values for all 17 congeners (14). Upon careful investigation of the original data reports, we found it necessary to insert 12 imputed values because the actual measurements were less than the limit of quantitation (LOQ); the imputed value was calculated as  $\text{LOQ}/\sqrt{2}$  according to accepted statistical practice for single-value imputation of log-normally distributed data with <50% missing values (18). A detailed discussion is given in the Supporting Information (Part 1). Other values ( $n = 56$ ) had been flagged by the laboratories as "not exceeding" certain levels due to potential analytical interference from matrix effect; here, we kept the best laboratory estimate as the accepted value. We have acquired CDD/CDF data from CARB archives from nine sites across the state collected in 3 week intervals (15). We accumulated values from 2001 and 2002

by sites and selected downtown Oakland (San Francisco area) and downtown Los Angeles (Boyle Heights site) as representative of urban background to randomly select the second basis data set of 29 samples. Although California reported an average of 6136 wild fires per year from 1999 to 2003, during our selected sampling period about 50% of the acreage burned occurred in San Diego County and the remaining major fires occurred in Santa Clara, Calaveras, Mariposa, and Butte Counties. No major fires occurred in Alameda and San Mateo counties (Oakland site) or in Los Angeles County (<http://www.fire.ca.gov/php/>). As such, none of the CARB samples we designated as urban are likely dominated by large forest fire sources.

In addition to the two basis sets, we have gained access to a variety of CDD/CDF data subsets from published and unpublished data associated with WTC, from other building fires and combustion sources, and representing general background. The congener results in these data are comprised of measurements from surface wipes, dusts, and air monitors (vapor + particulate phases). Specifically, WTC-related samples include window wipes collected near the WTC site and at a Brooklyn background location ( $n = 6$  and  $2$ , respectively) (10), indoor dust samples collected in the Deutsche Bank Building directly across from the WTC south tower collapse ( $n = 8$ ) (19), personal air samples from rescue personnel ( $n = 8$ ) (20), and outdoor dust samples collected in the vicinity of Ground Zero on 9/22/2001 by EPA ( $n = 5$ ) (14) and by university researchers on 9/16/2001 and 9/17/2001 ( $n = 3$ ) (3). As examples of non-WTC building fire impacted data, we have results of surface-wipes samples from an office fire in Binghamton, NY ( $n = 12$ ) (21) and soot and surface-wipe samples from a Philadelphia, PA building fire ( $n = 9$  and  $n = 8$ , respectively) (22). We also collected results representing an incinerator that was emitting a large amount of CDD/CDFs, nearly 1 kg TEQ/year, before it shut down in 1994. This municipal solid waste incinerator was located in Columbus, OH, and samples collected included stack emissions ( $n = 5$ ) (23), impacted air that had elevated CDD/CDF concentrations and was downwind while the incinerator was operating (one profile representing the average of two samples), unimpacted air in Columbus (one profile representing the average of five samples), background urban soil (one profile representing four samples), and air and soil sample profiles reported by Lorber et al. (24). In order to contrast this data representing fire-impacted situations and urban areas, we have a subset of rural background samples from EPA's National Dioxin Air Monitoring Network (NDAMN) program ( $n = 12$ ) (25, 26). These measurements are taken in more "pure" background settings in parkland and similarly remote areas that are far from combustion and other anthropogenic sources. CARB data from selected sampling sites are used to illustrate regional differences in airsheds. Some of the data sets contained samples for which one or more congeners were below the detection limit, so to avoid unduly biasing the pattern, we set an arbitrary limit to disregard samples where six or more congeners were missing measurements.

For consistency with the basis sets and to avoid mixing units (ng/m<sup>2</sup>, pg/g, pg/m<sup>3</sup>, for wipe data, soil and bulk dust data, and air data, respectively), all data are normalized to congener profiles. A congener profile for each sample was created by summing the concentration of each of the 17 individual congeners to determine a "total" concentration and then determining the fraction each made up of that total. The sum of the fractions of each congener within a sample naturally add to 1.00. A brief tabular description of the data sets and the means and range of the TEQ concentrations are provided in the Supporting Information (Part 2).

**Model Development—Basis Sets.** Data interpretation is restricted by the absolute number of impacted samples ( $n$

= 29) in contrast to the number of congeners ( $n = 17$ ) serving as random variables. Before any regression or other statistical modeling for patterns among sources is reasonable, one requires at least 10 or so samples per variable to avoid "overfitting"; this rule of thumb is generally accepted by statisticians (although other values may be set for specific reasons) and has been articulated in text books such as that by Harrell (27). To achieve this, we applied a variation of cluster analysis to reduce the degrees of freedom using the *proc varclus* procedure in SAS statistical software (SAS 9.13, Cary, NC). This method allows the combination of variables that have similar covariance structure into groups with the dual purpose of removing collinearity and reducing the impact of the occasional individual congener measurement below the analytical sensitivity (27). This is similar in approach to the contemporary applications of cluster analysis for mining gene and protein expression data (28, 29). Specifically, the congeners were reduced to nonoverlapping clusters, and the contributions were co-added within clusters for each sample.

An output variable (OPT) was assigned to each sample in the two basis sets: OPT = 0.00 for the background (CARB) set and OPT = 1.00 for the impacted (WTC) set. Multivariate regression analysis using the *proc reg* procedure in SAS was applied to the combined data set using the model

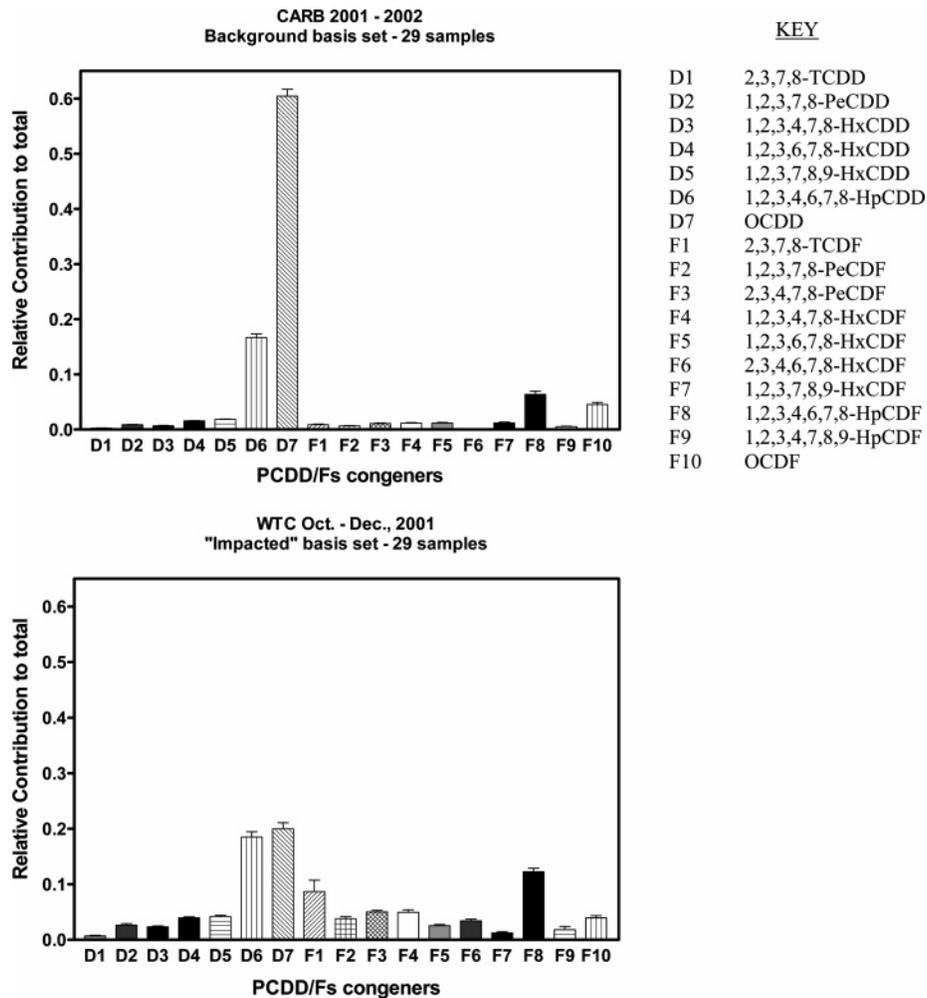
$$\text{OPT} = a_0 + a_1C1 + a_2C2 + \dots + a_nCn \quad (1)$$

where the C variables were subjected to forward elimination based on significance ( $p < 0.10$ ) resulting in a predictive equation of the form  $\text{OPT} = a_0 + a_x Cx + a_y Cy + \dots$ . At this point, the " $a_i$ " coefficients can be fixed, the number of terms are further reduced, and OPT is a continuous output variable on a scale where values near 0 are indicative of background patterns and values near 1 are indicative of impacted patterns. The resulting empirical regression equation can then be applied to other available CDD/CDF data sets to assess the predictive value. The results of the cluster analyses and the regressions can be further interpreted by removing one or more dominant individual congeners to establish subtleties of patterns and to provide alternative calculation schemes.

## Results and Discussion

**Graphical Interpretation.** The first step in any pattern recognition scheme is to observe the potential differences among groups of data. Figure 1 shows the bar graph results of the 17 congeners, including standard errors, for the two basis sets. cursory inspection suggests that there are some differences, such as in D7 (OCDD), which dominates the background profile, and the lower-chlorinated furans, particularly F1 (2,3,7,8-TCDF), which are more prominent in the WTC basis set. The problem with relying on such subjective observations is that CDD/CDFs are generally present in very low levels, and so small absolute quantitation differences, imputed values, different sample volumes, or analytical upsets could influence calculations of the contribution to the whole by any individual congener. Furthermore, other data sets could retain a dominance of key congeners, such as OCDD, yet have differences not immediately obvious among the remaining congeners. To investigate this possibility, we eliminated the D7 congener, OCDD, recalculated the contributions to the reduced totals, and present the results in Figure 2. We now see that in the absence of the overwhelming D7 influence, that F1 and F6 still remain as discriminators, F8 becomes equivocal, and that D6, F2, F3, F7, F9, and F10 appear as more important.

At this point, we caution that such qualitative observations must be treated within the context of statistical and analytical understanding. For example, some of the congeners are more difficult to analyze, and their bars in Figures 1 and 2 could



**FIGURE 1. Graphical comparison of the two basis sets; the major apparent differences are the D7, F1, F6, and F8 congeners.**

reflect more imputed or speculative values. Furthermore, relationships between samples may not be accurately reflected in the means of congeners across all samples. Therefore, we would like to mathematically interpret the patterns and also include as many relevant congeners as possible that show significant differences to make the discrimination scheme less reliant on one or two single values.

**Cluster Analysis.** As mentioned above, it is statistically difficult to model underlying patterns when the number of samples is less than 5 or 10 times greater than the number of variables. Furthermore, models are considered “ill-conditioned” when some of the input variables have strong covariance. The results of the SAS cluster analysis proc varclus indicates that collapsing the 17 congeners into 5 clusters within the WTC basis set still explains >71% of the total variance. Under the constraints of the total number of samples in the data set, we find this to be a favorable tradeoff. On the basis of these results, we construct the cluster-based variables for the WTC basis set as  $C1 = F_1 + F_3 + F_5 + F_7 + F_8$ ,  $C2 = D_7$ ,  $C3 = F_9$ ,  $C4 = D_3 + D_4 + D_6$ , and  $C5 = D_1 + D_2 + D_5 + F_2 + F_4 + F_{10}$ , where  $D_i$  and  $F_i$  are the fractions that each dioxin and furan congener contributes to the total concentration in the profile ( $\sum(D_i + F_i) = 1.00$ ). Upon applying cluster analysis to all available CARB data for 2001 and 2002 ( $n = 221$ ), we find that the 7 dioxin congeners and the 10 furan congeners form distinct clusters explaining more than 88% of the variance; this indicates that there is a difference in covariance structure between the two data sets and that the congener patterns are slightly more homogeneous among CARB samples. For the subsequent regression analyses, we

constructed a random stratified subset of the CARB data ( $n = 29$ ) to avoid bias. These samples were selected from data representing city background from the Los Angeles and San Francisco urban areas.

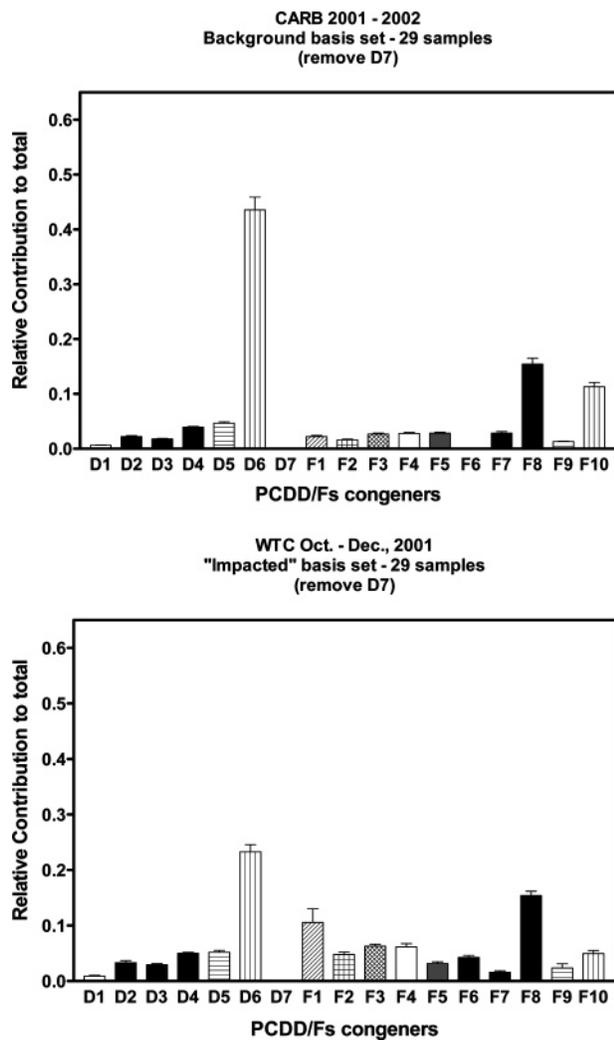
Cluster analysis was repeated for the WTC data set wherein the D7 congener had been removed. Under these conditions, the five cluster-based variables  $C'i$  were found:  $C'1 = D_5 + F_1 + F_3 + F_5 + F_7$ ,  $C'2 = F_8$ ,  $C'3 = F_9$ ,  $C'4 = D_3 + D_4 + D_6$ , and  $C'5 = D_1 + D_2 + F_2 + F_4 + F_{10}$  which, in the aggregate explain >75% of the variance.

We generated the reduced variable set based on these clusters and assigned output variable OPT for the two basis sets resulting in a more stable data structure for regression modeling in that there are 7 random variables for 58 samples. We found that the “within-cluster” values are normally distributed for the basis sets according to Shapiro–Wilk tests ( $p > 0.05$ ), and we require no further data transformation.

**Regression Analysis.** Using the condensed data from the two basis sets, the WTC-impacted and non-impacted CARB data, we constructed multivariate linear models of the general form indicated above (eq 1) for each of the identified clustered variable sets using forward elimination. The results from SAS proc reg show that the best-fit equations for the data sets with D7 (eq 2) and without D7 (eq 3) congener, respectively, are

$$OPT = 1.43336 - 2.5486(C2) \quad (2)$$

$$OPT' = 1.7545 - 2.3670(C'4) - 4.7268(C'2) + 3.4062(C'3) + 1.0788(C'1) \quad (3)$$



**FIGURE 2.** Graphical comparison of the two basis sets with the D7 congener removed and the contributions to the total recalculated; the apparent differences are now reflected in the D6, F1, F2, F3, F6, F7, F9, and F10 congeners.

As expected from the graphical inspection of data in Figure 1, we see that C2, which is composed only of D7, is the only statistically significant surviving cluster in eq 2. This final model has an  $r^2$  value of 0.9263. The remaining clusters do not add anything statistically significant after C2 is already in the model. This does not mean that the other congeners/clusters lack value; they are simply overwhelmed by the effect from the D7 congener, OCDD. Once D7 is removed and the contributions to the new total are recalculated, 11 congeners (all remaining except cluster C'5 composed of D1, D2, F2, F4, and F10) contribute to the discrimination between basis sets (eq 3); however, the  $r^2$  value of the multivariate regression model drops from 0.9263 to 0.5636. For eq 3, the most important cluster is C'1, with a partial  $r^2 = 0.2060$ , the second is C'3 with  $r^2 = 0.1411$ , and C'4 barely remains in the model with  $r^2 = 0.0078$ . It is interesting to note that C'1 contains the F6 congener, 2,3,4,6,7,8-HxCDF, and the F1 congener, 2,3,7,8-TCDF, which were identified earlier as important congeners based on visual examination of the profiles. These results demonstrate the trade-offs encountered; relying on a single major difference yields better discrimination power between the two specific basis sets but risks loss of generalizability.

**Internal Basis-Set Results.** Using eq 2 (including D7), we find that the WTC basis samples have mean output values  $\pm$  standard deviation:  $OPT = 0.9788 \pm 0.143$  and the CARB

basis samples exhibit  $OPT = 0.0174 \pm 0.138$ . Similarly, for eq 3 (not including D7), the values for WTC are  $OPT = 0.782 \pm 0.328$  and for CARB,  $OPT = 0.218 \pm 0.141$ . This indicates that the inclusion of the very important congener, D7, achieves a prediction model with better separation. However, even at the 95% confidence interval, we find that eq 3, which does not include D7, still separates the basis sets completely. This result can be interpreted as allowing a complementary assessment of a sample's position in the continuum from background to WTC-impacted status.

**Model Application to Other Data Sets.** Equations 2 and 3 (representing model 1 and model 2) were applied to the data sets listed above. Table 1 presents the summary data of OPT means and standard deviations for all available data sets annotated by the expected impact of sources and the results from both models (including or excluding D7). Both models are similarly robust for sample sets that are expected to be impacted by WTC and other fire sources, as evidenced by OPT values close to 1.00 for the base WTC set, for building fires in Philadelphia and Binghamton, and for a combustor emission source. Similarly, both models are near 0.0 for known background sets, including the base background set, and other sets from California, the NDAMN rural data, and background air and soil data from Columbus. However, there are anomalous findings to these trends, such as the Deutsche Bank dust wipe samples having a value of 0.14 for model 1. These anomalies will be discussed below.

The fact that most fire data sets produce an OPT value near 1.00 for both models does not imply that all fire sources produce a similar profile. Rather, this exercise suggests that among the fire-related profiles we have gathered, there exist similarities in key groupings of congeners that are distinct from the same groupings of congeners from a second group of known background samples. This is most easily demonstrated and discussed in the context of eq 2, model 1, showing OPT as a function of the single grouping, C2, which only includes D7 (OCDD). When OPT is close to 1.00, as in a fire-related source, D7 must be close to 0.17, and when OPT is close to 0.00, as in a background source, D7 must be close to 0.56 (these observations are easily derived from eq 2 by setting OPT to 1.00 and 0.00). An examination of all background sets shows that the D7 value is always greater than 0.50 (i.e., OCDD explains more than half of the entire profile in background samples). In contrast, the D7 value is near 0.20 or less in the fire-related sets.

However, there are some anomalies in this set, and one alluded to above was the Deutsche Bank dust wipe samples. This building is located adjacent to the WTC, and it was significantly impacted by the collapse of the towers. The side of the building facing WTC was torn open, and smoke poured in from fires burning through December, 2001. The building has never been rehabilitated and is slated for demolition. Wipe samples taken in the impacted areas of the building in 2003 were very high in CDD/CDF concentrations, averaging 28 ng TEQ/m<sup>2</sup>. This contrasts with wipe sample results of 0.693 ng TEQ/m<sup>2</sup> ( $n = 114$ ) from a background study of the indoor environment conducted by EPA in association with WTC (30). It also contrasts the concentration of outdoor window film wipe samples included in the background sets of this study, where the concentration was 0.024 ng TEQ/m<sup>2</sup>. Despite the high concentration, the profile suggested a background source, with an OPT value of 0.14. In viewing the data, the reason for this becomes clear as the fraction of D7, OCDD, in the profile, averages 0.52.

However, when removing OCDD, the OPT value increases to 0.54 for the Deutsche Bank samples, which is now at least closer to 1.0, the model value for the WTC fire source as described above, many more congeners come into play with eq 3, with the most important cluster being C'1, which is defined as the sum of D5, F1, F3, F5, and F7. As discussed

**TABLE 1. Summary Statistical Results for Different Data Sets Using the Two Models Based on WTC and CARB Basis Data<sup>a</sup>**

sample set	n	exp OPT	model 1 OPT (from eq 2) mean ± s.d.	model 2 OPT (from eq 3) mean ± s.d.
<b>I. fire impacted sample sets</b>				
WTC air (basis)	29	1	0.98 ± 0.14	0.78 ± 0.33
WTC window film, impacted	6	1	0.79 ± 0.33	0.47 ± 0.11
OSHA personal air <sup>b</sup>	8	1	1.12 ± 0.22	0.78 ± 0.75
Philadelphia soot	9	1	0.82 ± 0.13	0.81 ± 0.22
Philadelphia indoor wipes	8	1	0.65 ± 0.42	0.84 ± 0.18
Binghamton off wipes + air <sup>b</sup>	12	1	1.31 ± 0.13	1.60 ± 0.38
Columbus incinerator stack emission + impacted air	6	1	1.06 ± 0.24	0.65 ± 0.59
<b>II. ambiguous sample sets</b>				
Deutsche Bank dust	8	?	<i>0.14 ± 0.43</i>	0.54 ± 0.38
street dust a (WTC)	5	?	<i>0.011 ± 0.59</i>	<i>0.33 ± 0.34</i>
street dust b (WTC)	3	?	<i>-0.32 ± 0.18</i>	0.97 ± 0.17
<b>III. background sample sets</b>				
CARB urban air (basis)	29	0	0.017 ± 0.14	0.22 ± 0.14
WTC window film, background	2	0	-0.18 ± 0.27	0.09 ± 0.14
NDAMN air	12	0	-0.097 ± 0.26	-0.035 ± 0.08
Columbus urban background air + soil	2	0	-0.21 ± 0.62	<i>0.26 ± 0.59</i>
CARB (San Jose) air	20	0	-0.054 ± 0.14	0.0077 ± 0.12
CARB (Reseda) air	21	0	-0.13 ± 0.099	-0.12 ± 0.055
CARB (Sacramento) air	12	0	-0.069 ± 0.16	-0.12 ± 0.055
CARB (Livermore) air	25	0	-0.11 ± 0.20	-0.058 ± 0.12

<sup>a</sup> Results which appear not to fit the expected OPT are identified in italics. <sup>b</sup> Data with <6 bdl congeners only.

above in the graphical presentation section, visual inspection would suggest that lower-chlorinated congeners, particularly F1, are more prominent in WTC-impacted samples as compared with background samples, and this analysis appears to support that observation. So while OCDD still dominates the Deutsche Bank profile, clearly the relative prominence of the lower-chlorinated furans provides evidence of the WTC fire source. This evidence only became clear upon removing OCDD from the profile and redoing the statistical model.

If, in fact, the dust was heavily impacted by smoke from the smoldering WTC fires, it is not clear why OCDD would be so prominent in the profile. One possible explanation is that, given 2 years of weathering from the time the fires went out in late 2001 until the samples were collected in 2003, the lower-chlorinated congeners may have degraded in or volatilized from the dust while the more tightly sorbed and persistent OCDD retained high initial values. This is the explanation most often provided as to why OCDD dominates CDD/CDF profiles in background settings (24). It might also indicate that, while concentrations significantly higher than background that are indicative of an impact may remain for many years, the profile might weather and shift toward a background-looking profile.

Not all dust samples collected near the WTC have the WTC-fire signature, however. Bulk dust samples collected outside in September and October of 2001 near the WTC site appear not to be as influenced by fire as compared with the Deutsche Bank dust wipe samples. The OPT values for both sets of bulk dust samples, and for both models, ranged from -0.31 to 0.97, but only one of the four OPT values was higher than 0.33. Not surprisingly, the fractions of OCDD in the bulk dust profiles are near 0.70. Without OCDD, the OPT value increases in both data sets, from 0.011 to 0.33 in one data set and from -0.32 to 0.97 in the other data set. An examination of the individual data shows that while OCDD dominates the profiles (hence, OPT in model 1 is near 0, suggesting a background profile), 2378-TCDF has the highest or second-highest concentration of all furan congeners. This is clearly not the trend for background samples, but more like the trend for WTC-impacted samples, as seen in Figures 1 and 2.

These anomalous results do not imply a fault in the model, however, but instead indicate a potential benefit for differentiating among various source-impacted and background sample sets. Second, some of the anomalous data sets have large internal variance with relatively few members such as model 2 for Columbus OH ( $n = 2$ ) and the WTC dusts ( $n = 3, n = 5$ ), respectively. As was noted above, this application was not designed to distinguish between different sets of data associated with fires. It was developed to distinguish between the specifically chosen background air CDD/CDF profile and the air profile that emerged from the collapse of the WTC. Perhaps not by coincidence, it also appears to work well with other WTC data and other fire sets (21, 23, 31-34). A more detailed discussion of other data sets and other studies is given in the Supporting Information (Part 3).

**Recommendations for Further Study.** We recommend that the models be further investigated in two areas. First, it may be useful to bring in more combustion-related data to see if the regressions built on distinguishing WTC fire data versus background data are robust enough to distinguish among many different fire sources. A brief examination of the profile from the Binghamton office fire above suggests that there may be meaningful differences among different combustion profiles (see Supporting Information Part 3). Second, it may be useful to generally develop larger basis sets representing distinct geographic regions and distinct dominant sources as well as a full set of the NDAMN rural background data. This data set includes 27 sites from around the country and several years of data; only 3 sites and 1 year's data was available for this effort. Finally, the effect of weathering on the patterns should be studied; there may be finer adjustments required to correct for the age of particle-bound CDD/CDF congeners that could explain some of the variance in the WTC dust results.

This approach is not limited to CDD/CDF congener data. We suggest that this methodology could be used for other aggregate exposures to suites of compounds such as the PAHs, the PCBs, the PBDEs, and the perfluorinated compounds. Of particular interest would be the development of diagnostic analyses for unknown samples of complex dilute mixtures in air, water, and soil of these compound classes based on

previously established upwind/downwind, upstream/downstream, before/after, etc. basis sets.

## Acknowledgments

Disclaimer: The United States Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to Agency administrative review and approved for publication. The authors are indebted to the contributions of a number of individuals who provided data to this effort and comment to this manuscript, including EPA colleagues Joseph Ferrario, Dennis Santella, Marcus Kantz, Peter Egeghy, Larry Cupitt, and David Cleverly, and John Kominsky from Environmental Quality Management, Cincinnati, OH. We are also thankful for the expert advice regarding statistical analyses by Stephen Rappaport, Amy Herring, and Sungkyoon Kim from the University of North Carolina.

## Supporting Information Available

Supporting information rationale for imputed values, toxic equivalents table for various studies, and dioxin patterns reported in the literature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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*Received for review March 22, 2007. Revised manuscript received August 1, 2007. Accepted August 7, 2007.*

ES070714A