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Polychlorinated Dibenzofurans and Dibenzo-p-Dioxin in Tree Bark from an Industrialized Area: What the 2,3,7,8-Cl Substituted Congeners Tell Us, and What Is Missing

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Abstract

We analyzed polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD) in 27 tree bark samples from the industrialized area near Sauget, Illinois, USA. The trees were located within 4 km of the W. G. Krummrich (WGK) plant, the oldest and largest chemical plant in Sauget, with 24 of 27 samples collected from residential areas. The percent of total PCDF or PCDD profiles of ten 2,3,7,8-Cl substituted PCDF and seven PCDD congeners is homogeneous: 90% of the variance among the samples is explained by 3 eigenvalues in a principal components analysis. The homogeneity of the data suggests that samples were affected by similar types of sources which may have been influenced by electric power generation, chemical waste incineration, and large-scale thermal production of chlorinated chemicals. Quantitatively, the 2,3,7,8-Cl substituted congener analysis does not account for 90% of the concentration of tetra- and penta-Cl homologues and 80% of hexa-Cl and 50% of hepta-Cl homologues. The World Health Organization stated during establishment of toxic equivalence factors (TEF, 2005 version) that calculation of toxic equivalents (TEQs) is not suitable for abiotic matrices, such as tree bark, which are not involved in human exposures. Our results show that the non-2,3,7,8-Cl substituted congeners have high concentrations and should be included in analysis.

Keywords

Tree Bark, Polychlorinated Dibenzofurans, Polychlorinated Dibenzo-p-Dioxins,

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Principal Components Analysis

1. Introduction

The analysis of polychlorinated dibenzofurans (PCDF) and dibenzo-p-dioxins (PCDD) in environmental samples typically focuses on the 2,3,7,8-Cl substituted congeners which have been determined to be the most toxic substances to humans in these classes of compounds. As a result, samples submitted to laboratories are usually analyzed for only the 7 PCDD and 10 PCDF congeners with 2,3,7,8-Cl substitution. The remaining 193 congeners in both classes may be reported as total homologue concentrations, with the mono-Cl, di-Cl and tri-Cl homologues not reported at all. In human exposure studies, the emphasis on the toxic 2,3,7,8-Cl congeners must be emphasized, but in abiotic research, where toxicity is not important but identifying potential sources is vital, the congener list should be expanded.

Tree bark has been used as a passive air sampler for a variety of organic contaminants, including PCDD/PCDF, polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs), and chlorinated pesticides [1]-[7]. We analyzed PCDF/PCDD in tree bark in this investigation in order to identify areas of high and low concentrations in an effort to elucidate sources. Another way of looking for sources is investigation of congener or homologue profiles. For example, a congener profile showing high concentrations of lower molecular mass PCDFs or PCDDs suggests recent thermal production and release because some thermal processes inhibit full chlorination of PCDF or PCDD molecules, especially in the presence of SO_x [8]. On the other hand, the lower molecular masses 2,3,7,8-Cl PCDF and PCDD are not highly persistent, and their decomposition is more favored than octa-CDF (OCDF) and octa-CDD (OCDD) so that dominance of the congener profile by OCDF and OCDD indicates that lower molecular masses PCDF and PCDD have partially decomposed. Here we investigate the 2,3,7,8-Cl PCDF and PCDD profiles in a forensic effort to identify a source of these contaminants in trees growing in a residential area adjacent to a highly industrialized area that is predominantly upwind. The analytical results have been reported [1]. In this paper, we expand on that work by reporting and discussing results of a chemometric anlaysis of these data. We also show that analysis of non-2,3,7,8-Cl substituted congeners would be valuable for identifying sources.

2. Methods

We analyzed 10 2,3,7,8-Cl substituted PCDF congeners, and 7 PCDD congeners, and total homologue amounts for tetra-Cl through octa-Cl homologues in 27 tree bark samples from Sauget, IL, USA and surrounding communities using EPA method 1613B at a commercial laboratory. All tree bark samples were collected within ~4 km of the W. G. Krummrich (WGK) plant, the largest and oldest chemical plant in Sauget. Using this method, 193 specific congeners are not analyzed, including no report at all for mono-Cl, di-Cl and tri-Cl PCDF (48 congeners) and PCDD (26 congeners) [9]. The results, with QC methods and data, were reported earlier [1]. Among the results was calculation of percent of total PCDF or PCDD for each reported congener. We also calculated percent of total homologue for each of the 2,3,7,8-Cl congeners in order to identify how much of each homologue concentration was comprised of the 2,3,7,8-Cl congeners.

Analysis of these percent of ΣPCDD or ΣPCDF profiles was accomplished using a principal components analysis (PCA). PCA is widely used in environmental forensics to reduce the dimensionality of large multivariate data sets, and allow visualization of the interrelationships among samples and variables [10]. PCA was performed using Matlab script programmed by the second author (GWJ). Data transformations and goodness of fit diagnostics were performed following methods outlined by Johnson, *et al.* [10]. The data matrix was transformed using a percent transform, followed by an autoscale. Eigenvalue decomposition was accomplished using the Matlab singular value decomposition (svd) function, followed by calculation of scores and loadings [10].

3. Results

Results of PCDF & PCDD analysis show ΣPCDF homologue (tetra- through octa-Cl) to range from 1110 $pg \cdot g^{-1}$ lipid to 26,744 $pg \cdot g^{-1}$ lipid. ΣPCDD homologue (tetra- through octa-Cl) results range from 3302 $pg \cdot g^{-1}$ lipid to 88,603 $pg \cdot g^{-1}$ lipid. $\Sigma PCDF_{10}$ (Σ of ten 2,3,7,8-Cl congeners) range from 355 to 13707 $pg \cdot g^{-1}$ lipid, while

$\Sigma PCDD_7$ (Σ of seven 2,3,7,8-Cl congeners) 2214 to 71821 $pg \cdot g^{-1}$ lipid [1].

Figure 1 shows the average profile of % of ten 2,3,7,8-Cl substituted PCDF congeners of ΣPCDF and % of seven PCDD congeners of ΣPCDD. In both cases, the octa congener dominates, suggesting that all 17 of these PCDF and PCDD congeners have been in the environment long enough that some decomposition of the lower-chlorinated congeners has occurred [1]. The only congeners making up >9% of the total (other than OCDF and OCDD) in either class are 1,2,3,4,6,7,8-HPCDF and 1,2,3,4,6,7,8-HPCDD. The most toxic congeners, according to TEF values [11], are 2,3,7,8-TCDD and 1,2,3,7,8-PECDD which together comprise only 0.34% of ΣPCDD. The most toxic PCDF congener, 2,3,7,8-TCDF (only 10% as toxic as 2,3,7,8-TCDD and 1,2,3,7,8-PECDD congeners), is 7.8 % of ΣPCDF.

Figure 2 shows the 3-component scores plot from PCA of the congeners shown in **Figure 1**. The cloud is very tight, suggesting a very homogeneous set of congener profiles. The only standout, ECS-1, was a sample showing evidence of exposure to a comparatively recent and unknown burning event [1], because the relative contribution of TCDF, PECDF and HXCDF is higher than other samples, shown in **Figure 1** (and other "outliers" in **Figure 3**). The other standouts from the cloud in **Figure 2** are ECS-24, the most concentrated sample, ECS-15 a sample collected upwind from 23 of the other 26 samples, and the second-least concentrated [1]. The "outlier" congener profiles are shown in **Figure 3**. **Figure 4** shows goodness of fit diagnostics (coefficient of determination (CD) scatter-plots). As discussed by Johnson, *et al.* [10] these graphics allow the user to evaluate the number of principal components for each individual congener. The CD values in the upper left of each plot is the r^2 of the regression line of 1-to-1 back calculation against measured values [10]. Of 17 PCDF and PCDD congeners, only 5 of them have CD values < 0.9, and 4 of them are PCDFs (2,3,7,8-TCDF, 1,2,3,7,8,9-HXCDF (some values < detection), 1,2,3,4,7,8,9-HPCDF and OCDF), and one is 2,3,7,8-TCDD. The overall high CD values again show that the relationship remains strong across measured values and values calculated from a PCA model [10]. None of the relatively high values of ECS-1 in the TCDF, PECDF and HXCDF congeners causes lower CD values in **Figure 4**. In general, these CD results verify the homogeneous nature of the data. Note on **Figure 4** that the majority of results for 1,2,3,7,8,9 HXCDF were reported as below detection (red symbols). We could have opted to remove this congener from the analysis, but we left it in because 1) the PCA results with and without this congener were not appreciably different; and 2) it may be instructive to reader to see how these plots are used to evaluate goodness of fit for a PCA in the presence of censored data.

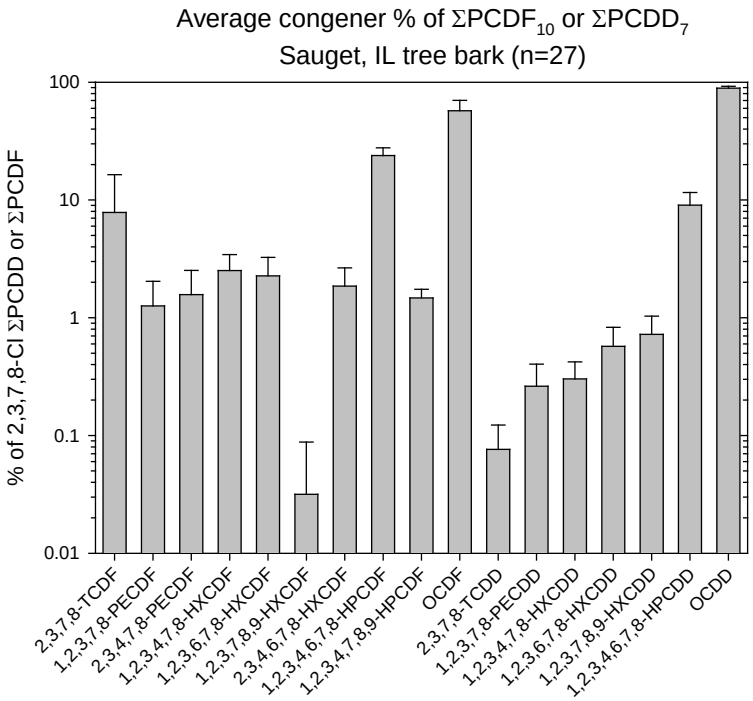

Figure 1. Average congener % of total PCDF or PCDD. Error bars = 1 std dev. Reprinted from Hermanson and Johnson [1] with permission. Copyright 2015 American Chemical Society.

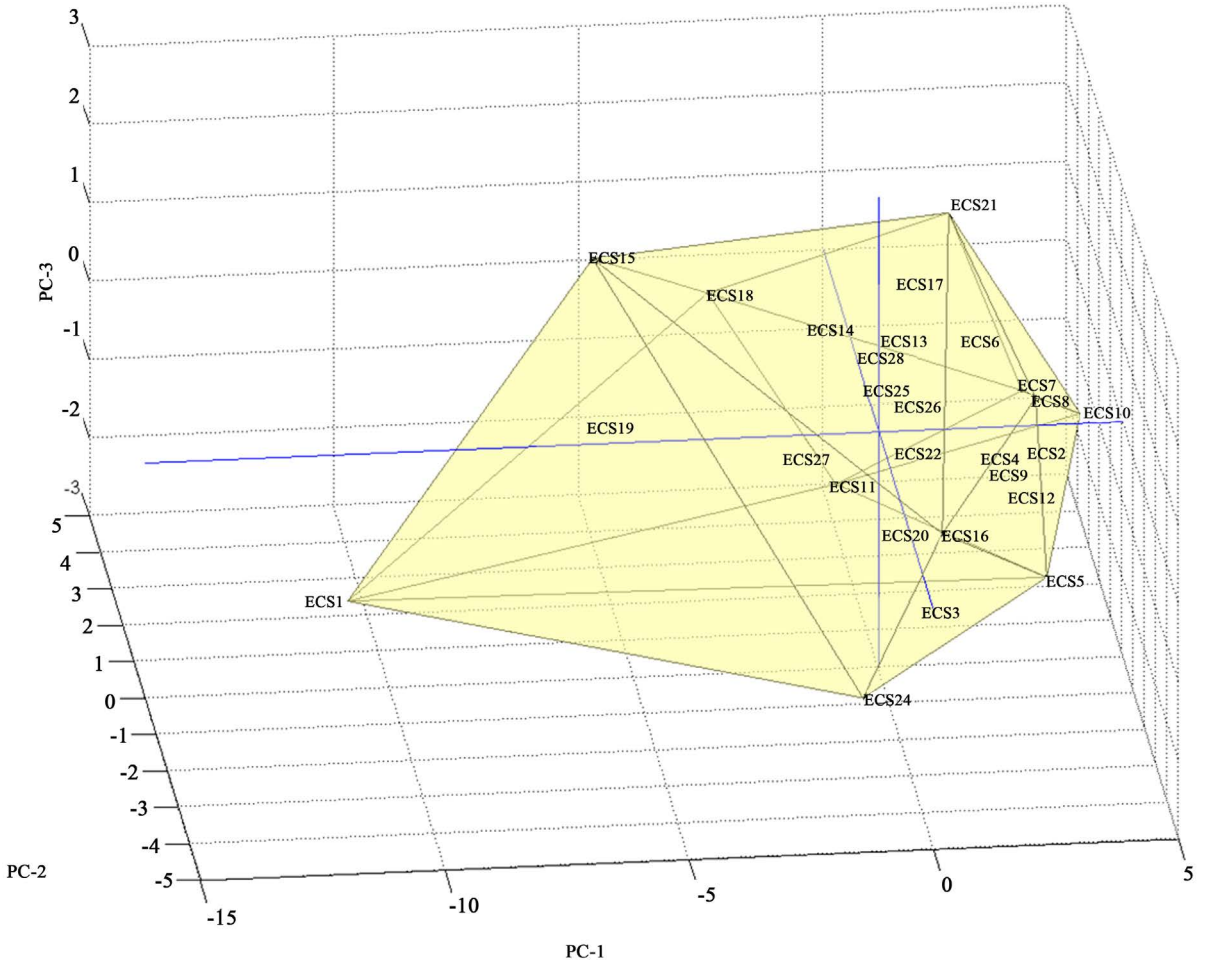

Figure 2. Three component scores plot from PCA of 2,3,7,8-Cl substituted PCDD and PCDF in Sauget area tree bark samples. Three principal components explain 90% of the variance (additional goodness of fit diagnostics shown in **Figure 4**). ECS-1 is the only standout from the cloud of other samples, suggesting influence of a source different from other samples. ECS-21 was collected in St. Louis, upwind from the Sauget Area #2 chemical waste landfills. ECS-24 was the most concentrated with PCDD and PCDF. For sampling site information, see Hermanson and Johnson [1].

Figure 5 shows the average congener % of homologue for the 17 2,3,7,8-Cl PCDF and PCDD congeners. This plot reveals that TCDF, PECDF, TCDD and PECDD homologues have nearly or >90% of data missing in the form of 1,4,6,9-Cl substituted congeners. Missing data for HXCDF = 81.7% and HXCDD = 78.2%. Specifically, the TCDF congener represents 10.8% of its homologue, PECDF 7.9%, HXCDF 18.3% and HPCDF 50.5%. For the PCDD, TCDD represents 2.8% of its homologue, PECDD 7.9%, HXCDD 21.8% and HPCDD 41.5%. Clearly the 1,4,6,9-Cl substituted congeners form a large component of data which were not analyzed. Considering that all 27 samples have a very similar 2,3,7,8-Cl profile, having data for other congeners within these homologues may help identify what the sources might have been. In addition, it would be useful to analyze the mono-Cl, di-Cl and tri-Cl congeners which would add 48 PCDF congeners and 26 PCDD congeners.

Sundqvist *et al.* [12] analyzed all congeners in the tetra through octa homologues of PCDD and PCDF in Baltic sea surface sediments in an effort to identify possible sources without relying only on 2,3,7,8-Cl congeners. Later, the same group used the analysis of all tetra through octa CDD and CDF in Baltic Sea sediments to identify trends over time and space [13] [14] showing that an expanded analysis of these PCDD and PCDF congeners adds to the ability to identify likely sources, even though several of the added congeners coeluted on the chromatographic column used (DB-5).

Considering the unfavorable view by the WHO TEF group [11] of using the TEF system for calculating TEQs in abiotic samples like tree bark, an alternative approach for abiotic samples would be to analyze at least all tetra

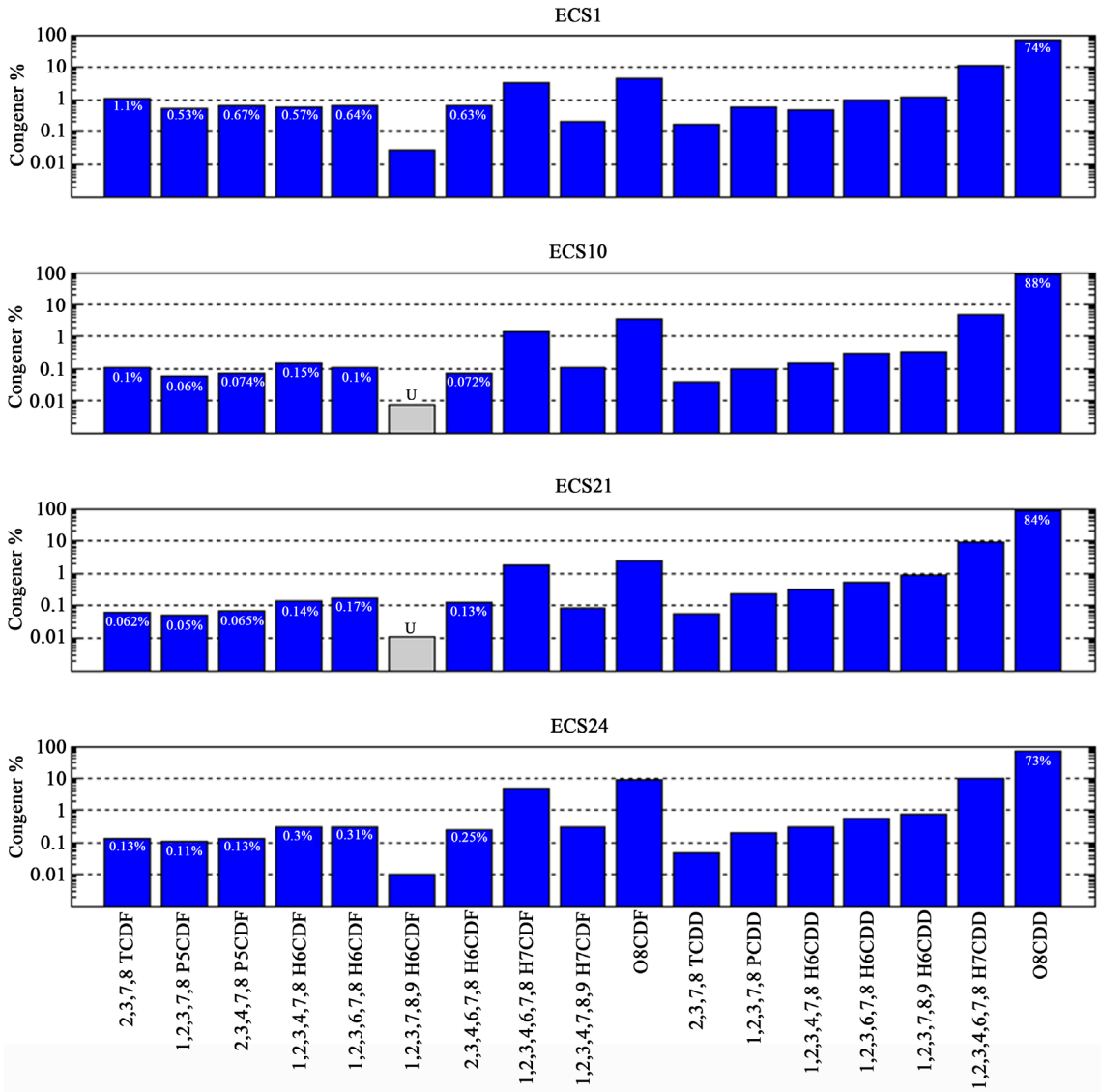

Figure 3. 2,3,7,8-Cl substituted PCDD and PCDF congener profiles for 4 of the extreme samples from PCA results in **Figure 2**. Differences are subtle, and the primary difference in ECS1 pattern is higher proportions of tetra, penta and hexa CDF.

through octa PCDD and PCDF congeners, shown to be successful by Umeå University [12]-[14]. The WHO TEF committee [11] recognized that some regulatory agencies require use of TEQ calculation for dioxins and furans in abiotic samples, but an expanded congener list would not prevent compliance with the requirement.

4. Conclusions

The results of tree bark analysis from 27 samples in Sauget show Σ tetra-octa-Cl homologue concentrations to range over a factor of 24 for PCDF (1110 to 26,744 pg·g^{-1} lipid) and a factor of 27 for PCDD (3302 to 88,603 pg·g^{-1} lipid). The results of ten 2,3,7,8-Cl congener analysis for PCDF range over a factor of 39 from 355 to 13,707 pg·g^{-1} lipid, and seven PCDD congeners over a factor of 32 from 2214 to 71,821 pg·g^{-1} lipid. Our results show that while these samples had quantitative variability, the qualitative results, in the form of congener PCDF and PCDD profiles, are very consistent. The average congener profile suggests that PCDF and PCDD have been in the environment long enough for decomposition of some lower molecular mass compounds. The results of PCA analysis show that only three eigenvalues are required for explanation of 90% of variance among samples, showing a homogeneous profile. The slight outliers from the average profile include one sample showing some

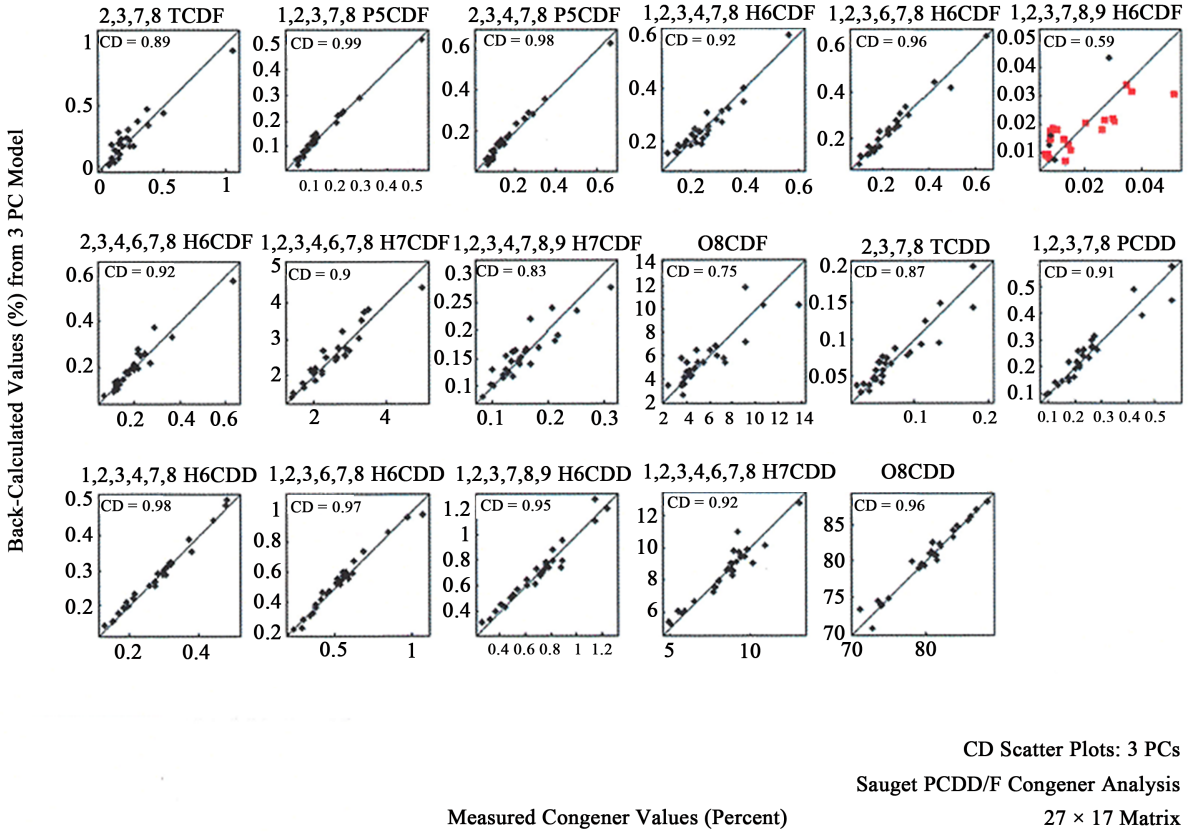

Figure 4. Congener-specific goodness of fit diagnostics (Coefficient of Determination scatter plots based on Johnson, *et al*., 2014, [10]) for three principal component model. Red symbols indicate analytes below detection.

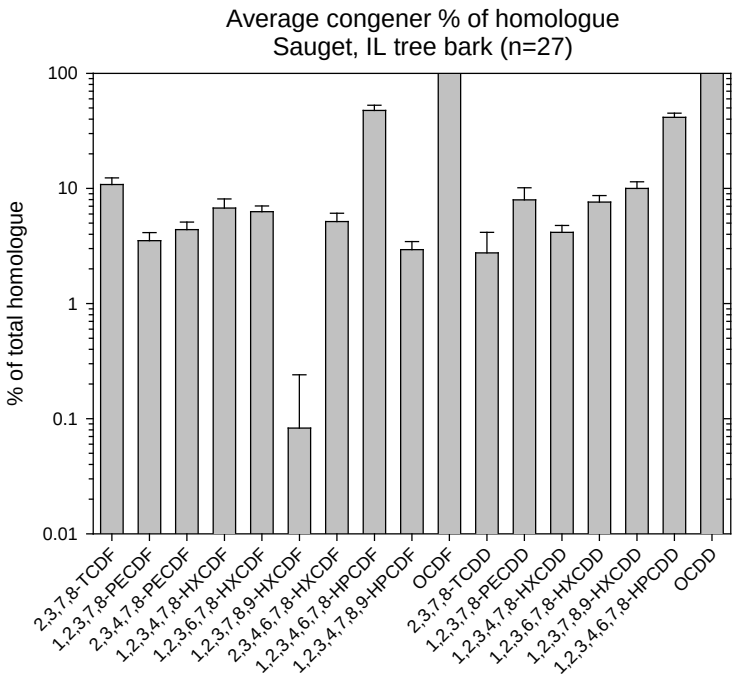

Figure 5. Average PCDD or PCDF congener % of homologue for 27 tree bark samples from Sauget, IL, USA. Error bars = 1 std dev. Reprinted from Hermanson and Johnson [1] with permission. Copyright 2015 American Chemical Society.

apparent effect of local combustion overlaying a background profile similar to other samples. Another slight outlier was the most concentrated sample of the group.

The homogeneous nature of the 2,3,7,8-Cl congener profiles does not lend the results to easy identification of likely sources of these compounds to the trees that were sampled, a goal of a forensics study like this. An evaluation of the amount of each 2,3,7,8-Cl congener contributing to the total homologue showed that the tetra-Cl and penta-Cl congeners explain not >10% of the total homologue, while hexa-Cl congeners identify ~20% and hepta-Cl ~40% - 50%. This result shows that analysis of the 1,4,6,9-Cl substituted PCDF and PCDD congeners would give a stronger data set of the more persistent congeners, especially in the TCDF, TCDD, PECDF and PECDD homologues. In addition, analysis of all 210 PCDF and PCDD congeners would include 48 PCDF and 26 PCDD congeners in the mono-Cl, di-Cl and tri-Cl homologues which apparently are not reported in the PCDD or PCDF environmental literature.

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