PCDD/F TEQ INDICATORS AND THEIR MECHANISTIC IMPLICATIONS

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Introduction

Numerous research studies have been conducted to establish indicator compounds for fast and less costly prediction of polychlorinated dibenzo-p-dioxin/dibenzofurans (PCDD/F) toxic equivalent (TEQ) concentrations. Chlorobenzene has been suggested as one potential PCDD/F TEQ predictor[1], as have other compounds: Chlorophenols, polychlorinated biphenyls (PCBs), and polychlorinated aromatic hydrocarbons (PAHs)[2]. Good correlation results were reported between some mono- to tri-chlorinated PCDD/F isomers and TEQ values[1,3]. The interest in the use of mono- to tri-chlorinated isomers as possible indicator compounds for TEQ PCDD/F is due to the similarities of these compounds with TEQ-based congeners and the emergence of fast, in-situ, on-line measurements adapted to PCDD/F measurement, such as resonance enhanced multi-photon ionization (REMPI) with time of flight mass spectrometry (TOFMS)[4]. However, there is still uncertainty in using these compounds as indicators because their relationships with TEQ may be plant- and operating-condition-specific. The aim of this study is to assess and determine PCDD/F isomers which could be used as indicators for PCDD/F TEQ as well as to use the relationship between indicators and TEQ to understand formation mechanisms.

Methods

Two different data sets were used for the present study: one with 11 runs from a municipal solid waste incinerator (MSWI) near Norfolk, Virginia[3] and the other with 8 runs from a waste-firing North American Package Boiler (NAPB) facility in Research Triangle Park, North Carolina[5]. Samples were taken at different combustion conditions such as fuel type, combustion efficiency, input Cl concentration, etc. Detailed information on sampling and operating conditions has been described elsewhere[3,5]. All 210 PCDD/F isomers were analyzed in all of the samples by high resolution gas chromatography (HRGC)/low resolution mass spectrometry (LRMS) (Hewlett–Packard 5890/ 5971) with a DB-Dioxin® column.

Results and Discussion

The relationship between homologue concentrations and TEQ values for these two data sets (ranging from ~ 1 to ~ 70 ng-TEQ/m^3, 7% O_2) was investigated using PCA (principal component analysis). PCA is a multivariate statistical analysis that allows evaluation of the individual and relative importance of variables as well as graphical representation of the same[6]. The PCA "objects" were each sample run, and the "variables" were the homologue concentrations (ng/m^3) and TEQ values (ng-TEQ/m^3). The loading plot shows the relationship between homologue and

TEQ concentrations. As shown in Figure 1, the mono- and di-CDD/F and tri-CDD homologue concentrations are not proximal to the TEQ (located in the lower left corner), indicating that their concentrations did not relate well with the other PCDD/F homologues and TEQ values. It was reported that the mono- to tri-CDD/F homologues were more affected by operating conditions than the more highly chlorinated (≥ 4 Cl) DD/F homologues[7]. This result suggests that the formation mechanism of the low chlorinated DDs/Fs homologues is somewhat different from that of the higher chlorinated DDs/Fs, raising questions as to whether these low chlorinated DDs/Fs can be related to the TEQ value. Figure 1 also shows that the tetra- and penta-CDD homologues did not correlate well with other highly chlorinated homologues nor with TEQ.

The relationship between PCDD/F isomer concentrations and TEQ values in the separate and combined data sets was determined by a correlation analysis. The percentage of isomers within each homologue which showed a positive, moderate ($R^2 > 0.5$) correlation with TEQ for the separate and combined data sets are shown in Table 1. The last column of Table 1 shows the percentage of each homologue's isomers that satisfy the more rigorous criteria of a positive, strong ($R^2 > 0.7$) correlation with TEQ for both data sets. These common isomers, representing the intersection set of strongly correlating isomers from each combustion facility, therefore may be considered "strong" indicators and are presented in Table 1. A few percent of isomers in tri-CDD/F (8-30%) and tetra-CDF (18%) as well as most of the highly chlorinated furan/dioxin isomers show potential to be strong indicators. This result agrees well with the relationship between the homologues and TEQ values (Figure 1), with one exception (tri-CDD). 11 of the 17 isomers that are assigned toxic equivalency factors (TEFs) and, hence, comprise the TEQ measure, were found to be good TEQ predictors. The remaining 6 TEF isomers also showed a positive correlation with TEQ but none had a strong (>0.7) R^2 value. A considerable number of non-TEF isomers, including Tri-CDD/Fs, were also found to be strong TEQ predictors, supporting the case for online, correlative monitoring of PCDD/F emissions by measuring candidate TEQ indicator isomers such as 2,3,7- or 2,3,8 –TriCDF.

The many isomers found to be potential PCDD/F TEQ indicators raise mechanistic questions about isomer- and homologue-specific formation. For example, what mechanism is responsible for the different homologue, isomer, and TEQ relationships? Why are tetra- and penta-CDD not related with TEQ, and why are non-TEF-based isomers related with TEQ? Recently, similar isomer distribution patterns were reported in combustion samples from multiple sources[8], and mechanism-specific PCDD/F isomer distribution patterns were developed for different PCDD/F formation mechanisms: chlorination/dechlorination for PCDF and phenol condensation for PCDD[7~10]. The similarity in isomer distribution patterns and the transitive property explain why many other isomers besides TEF isomers have a correlative relationship with TEQ. In our study, good agreement was observed in the case of high chlorinated dioxin/furan isomers (almost 100% of the isomers were related with TEQ), but the lower chlorinated dioxin/furan isomers were not as correlative (~ 50% of the isomers were related with TEQ) (Table 1). Other researchers' reported similarities in isomer distribution patterns were limited to tetra- to octa-dioxin/furan[8]: no information about isomer similarity in the mono- to tri-chlorinated dioxin/furan was presented. Therefore, PCA was used in this study to examine isomer similarities in the mono- through octa-CDD/F homologues and to discern the existence of common, dominant formation pathways[8].

The loading plots (Figure 2) indicate that the samples' isomer distribution patterns were distinguished by facility type. Variations in lower chlorinated dioxin/furan isomer patterns were larger than that of high chlorinated dioxin/furan. This result suggests that different isomer distribution patterns and formation mechanisms, especially in low chlorinated dioxin/furan, may exist in a combustion facility during variation of combustion operating conditions such as feed type and rate. The sensitivity of the mechanisms that form the lowly chlorinated isomers to changes in operating conditions may have been the cause of the relatively low correlation of these compounds with PCDD/F TEQ values. Therefore, to find out the dominant formation mechanisms in this study, three different formation mechanism models which were reported previously [9~11] were tested with PCA on the Norfolk and boiler data. Mixed formation mechanisms were observed (PCA plots not shown) in the mono- to di-chlorinated DFs with facility type, whereas chlorination/dechlorination was dominant in the remaining chlorinated DFs (tri- to hepta-chlorinated) regardless of facility type. Chlorination/dechlorination mechanism might be a significant contributor to TEQ because of the ease of chlorination in the favored 2,3,7,8-positions[10]. The fact that most of the strong TEQ indicator isomers in the tri-CDDs/Fs in this study are the dominant ones in the DF chlorination mechanism confirms the close relationship between chlorination and TEQ.

For the PCDDs, mixed formation mechanisms were observed in the lower chlorinated DDs, but mainly, the phenol condensation mechanism was dominant. These results offer an explanation for why PCDFs have more strong TEQ isomers than PCDDs do and why TeCDDs and PeCDDs do not have any strong TEQ indicators. However, unlike the other PCDD isomers, most of the HxCDD and HpCDD isomers have the potential to be used as TEQ indicators because most of the isomers in these homologues are TEF and have a more consistent distribution pattern than those of low chlorinated dioxins. The PCDD isomer distribution patterns were more consistent than those of PCDFs.

These results suggest that the formation mechanism of PCDDs is more consistent than that of PCDFs and that the formation mechanism of high chlorinated furans is more consistent than that of low chlorinated furan despite variation of facility type and operating conditions.

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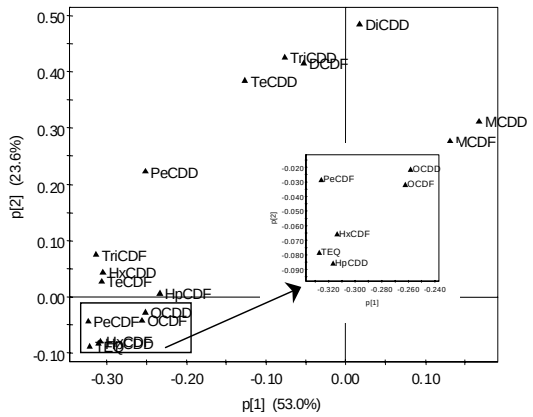

Figure 1. PCA results for the relationship between homologue concentrations and TEQ.

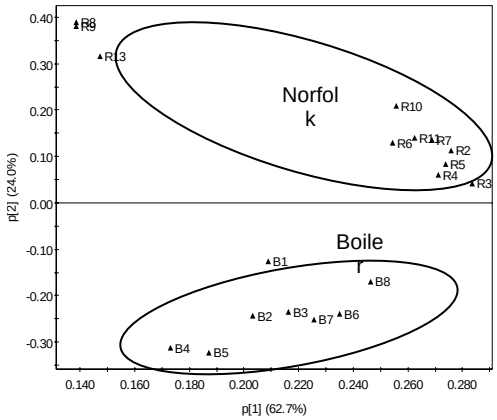

Figure 2. PCA results for isomer similarity with facility type (mono- and di-CDF).

Table 1. Percent of isomers which show positive correlation in each separate and combined data set.

	separate (R^2>0.5)		combined (R^2>0.5)	strong universal indicator isomers (R^2>0.7)
	Norfolk	Boiler	NF+ B	(isomer identification)
MCDF	0	0	0	0
DiCDF	0	42.9	0	0
TriCDF	94.1	82.4	58.8	29.4 (148/127, 123/247/178/146, 237, 238, 267)
TeCDF	70.4	63.0	59.3	18.6 (1278/2368, 1267/1469/2467, 2347, **2378**, 3467)
PeCDF	78.9	100.0	94.7	52.6 (13468, 12467, 12479/14678, 12478, 13469, **12378**, 12678/23468, 12369/12489/12679, 12349/**23478**)
HxCDF	100.0	100.0	100.0	66.7 (134678, 124678, 134679, 124679, **123478**, **123678**, 123467/123479, **234678**)
HpCDF	100.0	100.0	100.0	25.0 (**1234678**)
OCDF	100.0	100.0	100.0	0
MCDD	0	0	0	0
DiCDD	14.3	0	0	0
TriCDD	75.0	25.0	25.0	8.3 (237)
TeCDD	13.3	0	46.7	0
PeCDD	60.0	30.0	50.0	0
HxCDD	100.0	85.7	100.0	57.1 (123469/**123478**, **123678**, **123789**, 123467)
HpCDD	100.0	100.0	100.0	100.0 (1234679, **1234678**)
OCDD	0.0	100.0	100.0	0

/ - indicates co-eluting isomers, bold letter – TEF isomers