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Mono- to tri-chlorinated dibenzodioxin (CDD) and dibenzofuran (CDF) congeners/homologues as indicators of CDD and CDF emissions from municipal waste and waste/coal combustion

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Abstract

Total homologue concentrations and select congener concentrations from amongst the mono- to tri-chlorinated dibenzodioxins (CDDs) and dibenzofurans (CDFs) are used to model both Total (mono- to octa-) CDD + CDF emissions and the toxicity equivalent (TEQ) of the 2,3,7,8-chlorine-substituted emissions. Analysis of emission data from two facilities indicates that use of total homologue concentrations shows limited, facility-specific correlations with Total CDDs/CDFs and TEQ. Concentrations of select mono- to tri-CDD/CDF congeners show promising correlation with CDD/CDF TEQ across facilities, suggesting that these compounds can act as TEQ indicators.

1. Introduction

Knowledge of the congener patterns and homologue profiles of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) is important because toxicity is linked to the concentration distribution of the 17 congeners that are fully chlorinated in the 2,3,7,8 positions. A mechanistic understanding of how chlorine (Cl) partitions among and within the homologues will enable approaches toward reducing overall formation of PCDD/Fs and/or reducing the concentration of the 17 congeners that comprise the toxic equivalency (TEQ) value. Efforts have been made to model equilibrium distributions of congeners using computational molecular modelling (Unsworth and Dorans, 1993). Modelling of homologue distributions has used binomial reactivity functions (Funcke and Hemminghaus, 1993). The homologue profiles appear much more dynamic than the congener patterns and have been linked through Principal Component Analyses (PCAs) to ash characteristics and operating parameters (Pitea et al., 1990; Manninen et al., 1996) and through a combination of Poisson process/structural equations modelling (Gullett and Dunn, 1995) to gas concentrations and operating parameters. Recent efforts (Gullett et al., 1998) have modelled homologue profiles and concentrations using generalized additive models to develop a multivariate model with input of six operating and flue gas parameters.

The effort reported here uses homologue concentrations and a subset of the mono- to tri-chlorinated PCDD/F congeners to predict both PCDD/F TOTAL (sum of mono- to octa- CDD/F concentrations) and TEQ values. The ability to establish correlations between PCDD/F measures (particularly TEQ values) and concentrations of a limited subset of the 74 mono- to tri-CDD and CDF congeners is particularly valuable since

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current instrumentation development shows promise for measuring these lower chlorinated congeners in an on-line, real-time mode (Oser et al., 1998). Sampling results from two facilities and a wide range of operating conditions are used to establish the robustness of the predictions for application to other facilities and fuels. Strong relationships between lower chlorinated congeners and PCDD/F measures (such as TEQ) coupled with further development of methods to monitor the concentrations of these congeners in flue gas should provide a valuable tool for understanding the mechanism of PCDD/F formation and finding process control methods to reduce or prevent their formation.

2. Experimental

A municipal waste combustor near Norfolk, Virginia, burning processed fluff refuse derived fuel (RDF), was the site for 13 pre-spray-dryer sampling tests (''Norfolk''). This facility fired RDF-only or co-fired RDF with two types of coal during this testing. One coal was low sulfur (S, 0.7 wt%) and one coal from Illinois was high S (3.5 wt%). Co-firing up to 5 wt% high S coal with RDF reduced the pre-spray-dryer PCDD/F concentration by up to 70% from the initial baseline. Sampling and analytical methods were expanded to quantify mono-, di-, and tri-CDD/CDF congener totals as well as select isomers using the isotope dilution method. Labelled di- and tri-CDF and di- and tri-CDD surrogates were also added to XAD-2 prior to sampling to assess overall measurement performance.

The pilot scale Umeå reactor is a solid fuel combustor that burns artificial pellets on an underfire/overfire air supplied grate. The nominal burn rate is 18 MJ/h (1 kg/h). A triple looped convection section, 5 m per section, allows for simulating quench rates in field units. Further details can be found in Wikström et al. (1998), Wikström and Marklund (1998).

Two test groups were run in this reactor. ''Umeå-1'' run parameters varied total air flow from 90 to 150 L/min, flow in the secondary air varied from 20 to 70%, and the temperature of the secondary air varied from 50 to 350°C (the test matrix is shown in Wikström and Marklund, 1997). The ''Umeå-2'' tests were run under non-varied combustion conditions. The purpose of these tests was to simulate full scale combustion with an artificial municipal solid waste to study formation of PCDD/Fs.

3. Results, analyses, and discussion

Thirteen tests at the Norfolk site and 16 tests at the Umeå pilot plant resulted in a fairly wide range of PCDD/F TOTAL and TEQ values, with the common dominance of PCDFs over PCDDs. As is commonly found, the intra-group PCDD/F TOTAL and TEQ values appear linearly correlated (Fig. 1). Variation in the slopes is consistent with differences found in inter-source comparisons (Cleverly et al., 1997). Each group's homologue profiles (Norfolk – Fig. 2, Umeå-1 – Fig. 3, and Umeå-2, Fig. 4) exhibit consistent, intra-group profiles, although the magnitude and peak homologue group vary considerably between the three test groups. The stability of the homologue pattern is not surprising, although Umeå-1, with planned operation beyond the limits of desirable combustion conditions, might have been expected to exhibit a larger profile variation based on work by Gullett et al. (1999). Their work showed shifts or magnitude changes in the homologue profile that were associated with changes in operational parameters of sulfur dioxide (SO_2) and hydrogen chloride (HCl) concentrations, residence time, and quench rate.

SAS® procedure REG (SAS/STAT User's Guide, 1990) was used to obtain the best group-specific one-, two-, and three-predictor models (Table 1) of run-

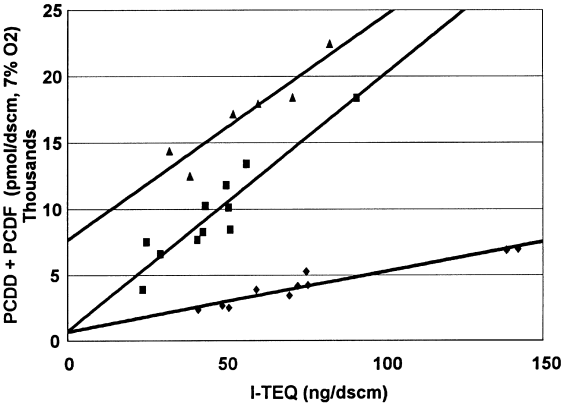

Fig. 1. Comparison of Total PCDD + PCDF [mono- to octa-PCDD/F (pmol/dscm)] and TEQ (ng/dscm) for Norfolk (■), Umeå-1 (◆), and Umeå-2 (▲) tests.

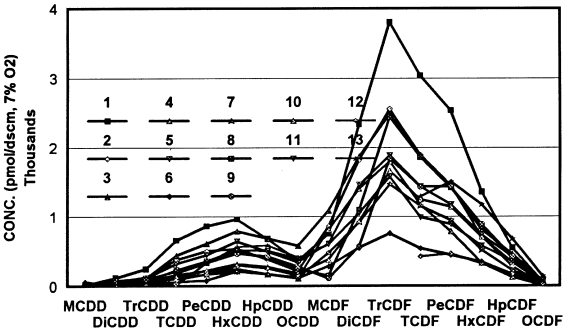

Fig. 2. Run-specific homologue profiles from Norfolk tests.

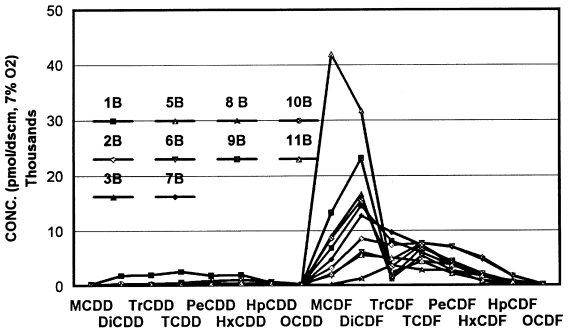

Fig. 3. Run-specific homologue profiles from Umeå-1 tests.

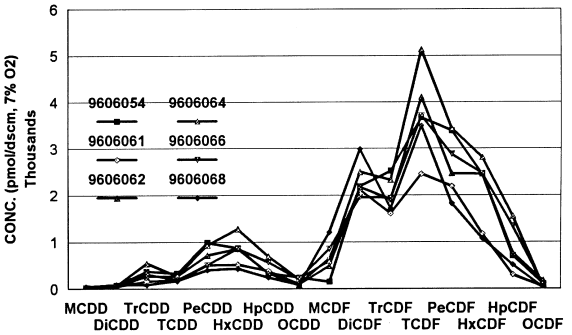

Fig. 4. Run-specific homologue profiles from Umeå-2 tests.

specific ln (TEQ, ng/dscm). For each test group, predictors were selected from among the six total concentrations [pmol/m^3, 7% oxygen (O_2)] of the mono- to tri-CDD/F homologues for each run. Logarithms of the dependent variable were evaluated to ensure a normal distribution of the data. Model selection criterion is based on maximization of R^2 and minimization of the predictor p values. The p values for each predictor indicate the probability of rejecting the null hypothesis (no linear relationship between the predictor and the dependent variable) in error. Use of the mono- to tri-CDD/F homologues as potential predictors of TEQ shows that the Norfolk and Umeå-2 data result in single-predictor models which show good prediction of TEQ ($R^2 = 0.767$ and 0.948, respectively). The low (<0.05) P values show that each selected predictor is not likely selected by chance. However, the Umeå-1 data were not successfully modelled and none of the three data sets resulted in selection of a common, single-homologue predictor.

Extension of the analyses to include up to three predictors improves the models' R^2. This is particularly true for both Norfolk and Umeå-2 where $R^2 = 0.868$ and 0.996, respectively, are obtained. These models also result in selection of the same predictor homologues. However, the same predictors for each model have different coefficient signs (+/−) and the Norfolk predictors have high (>0.05) P values, lending doubt to the models' universal mechanistic significance. The three-predictor model for the Umeå-2 group data has a high R^2 value with low P values (<0.03) for all three terms, suggesting that homologue correlations with TEQ may be appropriate under some circumstances for facility-specific application.

Prediction of TEQ with the Umeå-1 homologues is poor, even when extended to a three-predictor model. This is particularly noteworthy in that the Umeå-1 profile is a result of combustor operation at extreme conditions of air flow and temperature, unrepresentative of the normal operating mode. The homologues are dominated by mono-CDF (MCDF) and di-CDF (DiCDF) homologues, yet the concentrations of these lower chlorinated compounds do not readily reflect the higher chlorinated compounds that comprise the TEQ measure. These results suggest that homologue totals may be useful in predicting TEQ only on a facility-specific basis.

Switching now from a regulatory focus (TEQ) to a mechanistic focus (TOTAL), Table 2 shows the best one-, two-, and three-predictor models for PCDD/F TOTAL from among the mono- to tri-CDD/Fs. Single homologue totals do well at predicting TOTAL, although (as in Table 1) the selected predictors are not consistent between the data sets. Only modest improvements in R^2 are noted with selection of additional

Table 1
Regression models for TEQ using mono- to tri-CDD/F homologue totals

Norfolk (13 runs)			Umeå-1 (10 runs)			Umeå-2 (6 runs)		
Predictor(s)	P value	R^2	Predictor(s)	P value	R^2	Predictor(s)	P value	R^2
TrCDF	0.000	0.767	MCDF	0.141	0.250	TrCDD	0.001	0.948
DiCDF, TrCDF	0.199, 0.003	0.813	MCDF, TrCDF	0.262, 0.619	0.278	TrCDD, DiCDF	0.003, 0.243	0.969
DiCDD, DiCDF, TrCDF	0.129, 0.053, 0.008	0.868	DiCDD, TrCDD, MCDF	0.296, 0.286, 0.412	0.390	DiCDD, DiCDF, TrCDF	0.013, 0.021, 0.003	0.996

Table 2
Regression models for TOTAL using mono- to tri-CDD/F homologue totals

Norfolk			Umeå-1			Umeå-2		
Predictor(s)	*P* value	R^2	Predictor(s)	*P* value	R^2	Predictor(s)	*P* value	R^2
DiCDD	0.001	0.761	DiCDF	0.002	0.731	TrCDD	0.010	0.838
MCDD, DiCDD	0.410, 0.001	0.782	DiCDF, TrCDF	0.000, 0.048	0.852	MCDD, TrCDD	0.281, 0.014	0.897
MCDD, DiCDD, TrCDD	0.505, 0.199, 0.676	0.787	MCDF, DiCDF, TrCDF	0.744, 0.020, 0.074	0.855	TrCDD, MCDF, TrCDF	0.176, 0.331, 0.394	0.917

Table 3
Regression models for TEQ selecting from 12 mono- to tri-CDD/F congeners[a]

Norfolk			Umeå-1			Umeå-2		
Predictor(s)	*P* Value	R^2	Predictor(s)	*P* Value	R^2	Predictor(s)	*P* Value	R^2
1,2,3-TrCDF	0.001	0.679	2,4,6-TrCDF	0.037	0.438	2,4,6-TrCDF	0.442	0.442
1,2,3-TrCDF, 1,6-DiCDD	0.009, 0.000	0.843	1,2,3-TrCDF, 2,4,6-TrCDF	0.005, 0.006	0.832	1,2,3-TrCDF, 2,4,6-TrCDF	0.060, 0.025	0.856

[a] 1-MCDD; 2-MCDD; 1,6-DiCDD; 2,3-, 2,7-, 2,8-,DiCDD; 1,2,3-, 1,7,8-TrCDD; 2-MCDF; 4-MCDF; 2,4-DiCDF; 2,8-DiCDF; 1,2,3-TrCDF; 2,4,6-TrCDF, 2,4,8-TrCDF.

predictors. Unlike Table 1, the Umeå-1 R^2 value is high for even the single-predictor model, likely reflecting the ability of the homologue to predict itself (the profile is dominated by MCDFs and DiCDFs). This difference in the ability of the Umeå-1 homologue data to predict TOTAL versus TEQ may be indicative solely of the high concentration of the lower chlorinated compounds in this sample. For all of the data sets there is surprising frequency of PCDD homologue (rather than PCDF homologue) selection to reflect TOTAL, since TOTAL is dominated by PCDF compounds. When models are extended beyond a single predictor, the *P* values increase significantly, lending doubt to the significance of their inclusion within the models.

Finally, we evaluated the ability of select mono- to tri-CDD/F congener concentrations (pmol/m^3, 7% O_2) to predict the logarithm of TEQ either singly or in combination with another congener (Table 3). Twelve potential predictors were evaluated from among the concentrations of 15 congeners (some predictors consisted of the sum of co-eluting peaks) for which we (EPA) had chromatography standards. These same 12 predictors were used as candidates to model the Norfolk, Umeå-1, and Umeå-2 datasets for TEQ. The joint model selection criteria are maximization of R^2 and preference for non-co-eluting congeners. Table 3 shows that the concentrations of select TrCDF compounds, particularly 1,2,3-TrCDF and 2,4,6-TrCDF, show reasonable correlations with TEQ. For example, knowledge of the concentration of a single congener, 1,2,3-TrCDF, allows prediction of over 67% of the variation in the TEQ values for the Norfolk data. Significant improvement in R^2 (>80% for all three data sets) is obtained with addition of a second predictor. It should be noted that selection of the specific congeners cited in Table 3 is not necessarily unique; other statistically selected congeners (not shown) may be substituted without large loss of R^2. The actual prediction of ln (TEQ) in units of ng/dscm can be written as a weighted linear combination of the selected predictors using the regression coefficients (not shown) as weights. These results suggest that the gas-phase concentrations of a limited number of mono- to tri-chlorinated congeners can serve as indicators of flue gas CDD/CDF concentrations. Recent instrumental developments (Oser et al., 1998) in the ability to monitor these congeners in real time and at observed flue gas concentrations suggest a possible method for predicting TEQ emissions and providing feedback to control combustor performance.

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