



# Effects of combustion parameters on polychlorinated dibenzodioxin and dibenzofuran homologue profiles from municipal waste and coal co-combustion

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## Abstract

Variation in polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) homologue profiles from a pilot scale (0.6 MW<sub>t</sub>, 2 × 10<sup>6</sup> Btu/h), co-fired-fuel [densified refuse derived fuel (dRDF) and high-sulfur Illinois coal] combustion system was used to provide insights into effects of combustion parameters on PCDD and PCDF pollutant formation. A 24-run, statistically designed test matrix varied dRDF and/or coal firing rates (at a constant targeted energy release rate) along with a range of process variables including calcium hydroxide injection, hydrogen chloride (HCl) concentration, flue gas temperature, quench, and residence time such that the results would be relatable to a wide variety of combustion conditions. Statistical analysis of the molar homologue profiles enabled interpretation based on non-confounding variables. A multivariate, generalized additive model, based on transformations of the design variables, described 83% of the variation of the profiles characterized by log ratios of the homologue molar concentrations. This method identifies the operating parameters that are most significant in determining the PCDD/F homologue profiles. The model can be exercised to predict homologue profiles through input of these system-specific operating parameters. For example, both higher HCl and sulfur dioxide concentrations favor higher relative formation of the lower chlorinated PCDF homologues. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The discovery of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from waste combustion sources and the increased understanding of the toxic effects of these chemicals have prompted extensive study over the last 10 or so years on

how these trace compounds are formed in combustion systems. Despite significant impediments to understanding the PCDD/F formation mechanisms, considerable progress has been made toward understanding conditions of formation and, hence, methods for preventing or controlling formation. One way of understanding how PCDD/F forms is through examination of the homologue<sup>3</sup>

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<sup>3</sup> Some mention of definitions and nomenclature is appropriate. PCDD and PCDF *homologues* are defined by the number of chlorine (Cl) atoms on the dibenzodioxin (DD) and dibenzofuran (DF) molecule, respectively. The eight PCDD and eight PCDF homologues are respectively called mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octa-chlorinated forms of PCDD and PCDF. In this paper their concentration values are expressed as a ratio, and they are simply referred to as MC\*, DiC\*, TrC\*, TC\*, PeC\*, HxC\*, HpC\*, and OC\* where "\*" refers to either DD or DF. *Isomers* are defined as chemical compounds that differ only in the position, but not the number, of the Cl atoms on the aromatic rings (e.g. 2,3,7,8-TCDD and 1,2,3,4-TCDD are two of the 22 isomers in the tetrachlorinated dibenzodioxin homologue). *Congeners* are the individual and structurally distinctive chemical compounds, differing in both number and position of Cl atoms, that comprise the PCDD and PCDF families. There are 135 congeners of DF and 75 congeners of DD. In this work, the conventions of Rappe [1], are adopted such that the term *profile* refers to the relative concentration distribution across the homologues. The term *pattern* is used to refer to the relative concentration distribution of the isomers within a single homologue [although it has become common to refer to the mass distribution of the 17 compounds assigned toxic equivalency factors (TEFs) as the 2,3,7,8-Cl-substituted pattern]. Since this work does not focus on individual isomers or on PCDD/F toxicity values, patterns are not presented in this work.

concentration profiles and how these profiles change with operating conditions, fuels, and combustor types.

Until recently more attention was paid to distribution patterns of the 17 congeners that are fully chlorinated in the 2,3,7,8 positions (hereafter termed 2,3,7,8-Cl-substituted) and that comprise the PCDD/F toxicity measure, the toxic equivalency (TEQ). However, Rappe [1], has noted that the homologue profiles (tetra- to octa-Cl congeners only) show a larger variation than the isomer patterns. For PCDF, the highest concentrations are found for the tetra-, penta-, and hexa-Cl congeners, while the typical profile for PCDD was the inverse of the chlorination degree. Ishikawa et al. [2], used homologue (tetra- to octa-Cl congeners only) and congener profile analyses to provide mechanistic insights and ideas for process control. Sampling at four locations through a fluid bed system, they found little change in the overall homologue profile, confirmed by principal components analysis (PCA). Little variability in congener profile is evident, suggesting that thermodynamic considerations control this distribution. However, Rigo et al. [3,4], found that profile differences (tetra- to octa-Cl only) within municipal waste combustor (MWC) facilities which exceeded method imprecision and sampling/analytical limitations were caused by different sampling locations within each facility and not related to the normal range of operating conditions, variations in feed material composition, or purposely altered levels of Cl.

A translated Poisson process model used structural equations to show the effect of operating parameters and Poisson model properties on sampled homologue distribution (tetra- to octa-Cl) and total yield [5]. Other efforts [6] modelled homologue profiles via two binomial functions describing the amount of each homologue group formed and the coordination of halogens [number and type, bromine (Br) and Cl] among each homologue group. The former is effected by the hypothetical parameter "reactivity" which is a characteristic of the halogen substituents. The authors calculated distributions for each Cl/Br input ratio and for a range of reactivities [0,1, by 0.01]. Then, using pattern recognition software (PCA), they selected the reactivity based on a best fit analysis.

The work reported in this paper examined the existence of variation in PCDD and PCDF homologue profiles from a pilot scale, co-fuel combustion project. This project was designed to provide insights into post-combustion PCDD and PCDF pollutant formation mechanisms through development of a model to explain sampled homologue profiles. The statistically designed test matrix employed variation in firing rate of densified refuse derived fuel (dRDF) and/or high-sulfur Illinois coal along with a range of process variables such as calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] injection, hydrogen chloride (HCl) concentration, flue gas temperature,

quench, and residence time. Previous papers [7-10] have reported on the effect of these operating parameters on the PCDD and PCDF yields. Significant suppression of PCDD/F yields was noted by runs with co-fired coal (>5 wt%) and high temperature (700°C) sorbent injection. In this current paper, the effect of significant process variables on the molar ratios of the mono- to octa-chlorinated dioxin and furan homologues was determined through development of a profile-predictive model. Extension of the common analyses to include mono- to tri-chlorinated homologues provided additional mechanistic information regarding chlorination and dechlorination reactions.

## 2. Experimental

Tests were run in the EPA's Multifuel Combustor (MFC) facility, rated at 0.6 MW<sub>t</sub> ( $2 \times 10^6$  Btu/h) and capable of burning a wide variety of solid fuels including municipal solid waste, dRDF, biomass, and coal (see Fig. 1). Extensive details on the design of the facility are included elsewhere [7]. The primary fuel for the MFC consisted of a commercial dRDF derived from processed municipal waste. The coal was an Illinois No. 6 coal (donated by Monterey Coal Company, Carlinville, IL). The coal was fed using a screw feeder and entered the stoker at the same location as the dRDF. Waste and coal composition details are shown elsewhere [7].

The experimental parameters (and their settings) varied in the tests included dRDF feed rate (high or low), coal feed (on or off), quench rate in the convective section (low or high), sorbent injection (on or off), and HCl gas addition (on or off). The near collinearity of predictor values was compensated by careful experimental design, varying the predictors to exercise as wide a range of values as possible. The experiments were structured to provide information on all main effects and two-factor interactions among these parameters for statistical modelling. A total of 24 tests, plus quality control runs with natural gas, were run with various parameter settings. The full test matrix is shown in Table 1, and the simple statistics for the test runs are shown in Table 2.

During each test, the fuel feed rate was adjusted, whenever necessary, to maintain a constant flue gas temperature throughout the radiant section of the furnace. For low dRDF feed rate runs, natural gas was co-fired to compensate for the decrease in heat release and to maintain similar temperature ranges between runs. The residence time and quench rate across this convective section were varied in our tests by changing the temperature set point of water in the interior cooling coils. For runs with gaseous HCl addition, there was about a 150 ppm increase in flue gas HCl concentration. For runs with sorbent injection, a commercial hydrated

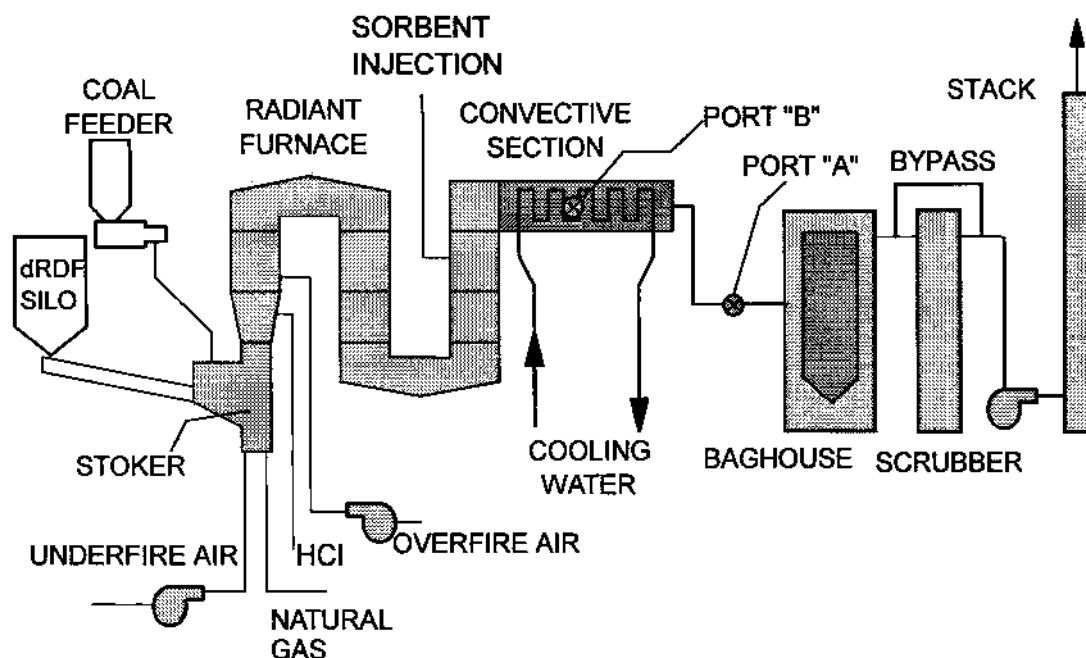


Fig. 1. Multifuel combustor facility. Port "A" was the sampling location.

Table 1  
Test matrix design conditions

Run no. <sup>a</sup>	dRDF rate	SO <sub>2</sub> (coal rate)	Sorbent rate	Added HCl	Quench rate
7	H <sup>b</sup>	N	N	N	H
9	H	N	N	N	L
11	M	Y	N	N	H
12	L	N	N	N	L
13	H	N	N	N	L
14	H	N	N	Y	L
15	H	N	N	Y	H
18	L	N	N	N	L
19	L	N	N	Y	L
20	L	N	N	N	H
21	L	N	N	Y	H
23	L	N	N	Y	H
24	H	Y	N	N	L
25	H	Y	N	Y	L
26	L	Y	N	N	L
27	H	Y	N	N	H
28	H	N	Y	N	H
29	L	N	Y	N	H
30	L	N	Y	N	L
31	H	N	Y	N	L
32	H	N	Y	Y	L
34	H	N	Y	Y	H
35	L	N	Y	Y	L
36	L	N	Y	Y	H
37	H	Y	Y	N	L

<sup>a</sup> Missing run numbers are incomplete tests.

<sup>b</sup> H = high, L = low, M = medium, Y = yes, N = no.

lime [Ca(OH)<sub>2</sub>] was injected as a slurry at a nominal calcium (Ca)/Cl stoichiometric ratio of 1.5/1. The sorbent slurry feed rate was about 0.65 kg solids/h and the injection temperature was approximately 700°C.

The flue gas was sampled for approximately 2 h from port A, prior to the air pollution control devices, and analyzed for PCDD/F according to a slightly modified EPA Method 23 [11]. Measurements were also made at upstream port B, but were not used in this effort. Before and after running Method 23 trains, a velocity traverse of the duct was carried out to measure the flue gas flow rate. The samples were analyzed in EPA's in-house Organics Support Laboratory (OSL), via procedures described elsewhere [12]. A modified Method 23 analysis was expanded to quantify mono-, di-, and tri-Cl dibenzodioxin (DD) and dibenzofuran (DF) congener totals as well as select isomers using the isotope dilution technique. Labelled 2,8-DiCDF and 2,3,7-TrCDD surrogates were added to the XAD-2 prior to sampling to assess overall measurement performance and 2,7-DiCDD was used as an internal standard. Consideration of these lowly chlorinated homologues is not typical since the compounds that comprise the international toxic equivalency (I-TEQ) measure reside completely within the tetra- to octa- homologues. However, it is clear that considerations of mechanisms require analysis of the full range of homologues. Clearly, the commonly ignored mono- to tri-Cl DD/F may undergo further chlorination and end up as one of the 17 toxic 2,3,7,8-Cl-substituted DD or DF.

### 3. Data analysis

For each test, run averages of temperature and flue gas composition were calculated for the duration of

Table 2  
Test condition statistics and nomenclature

Parameter <sup>a</sup>	Minimum	Maximum	Average	Median
dRDF feed rate, RDF (kg/min)	0.257	1.931	0.974	1.115
Coal feed rate, COAL (kg/min)	0.083	0.295	0.119	0.090
SO <sub>2</sub> concentration, SO <sub>2</sub> (g/min)	0	6.709	1.607	0.011
HCl concentration, HCL (g/min)	0.254	5.000	2.367	1.958
SO <sub>2</sub> /HCl concentration SO <sub>2</sub> /HCL (no units)	0	13.729	0.119	0.025
Sorbent rate, CA (g/min)	0	10.8	NA <sup>b</sup>	NA
Quench rate, QU (°C/s)	304	531	419	426
Sampling temperature, port A, TSA (°C)	146	196	170	173
Sampling temperature, port B, TSB (°C)	296	380	340	335
Residence time to port A, RESA (s)	1.655	3.692	2.189	2.137
Residence time to port B, RESB (s)	0.375	1.937	0.921	0.719
Port A PCDD/F Yield <sup>c</sup> [ng/dscm (ng/min)]	0(0)	3153 (8887)	356(1033)	(326)
Port B PCDD/F Yield <sup>c</sup> [ng/dscm (ng/min)]	3(26)	4073 (10,477)	442(1536)	(446)

<sup>a</sup> Selected Model-7MM predictors are in **boldface**.

<sup>b</sup> NA = Not applicable. Sorbent was either on or off.

<sup>c</sup> Mono- to octa-Cl.

PCDD/F sampling so that these values correspond to the measured PCDD/F. With the total flue gas flow rate known from the velocity traverse data, the average flue gas temperature profile data were used to determine the flue gas residence times at the sampling ports. In the temperature profiles, the residence time variable,  $t_R$ , is set to zero at 650°C. The choice of 650°C stems from the fact that most PCDD/F formation is known to take place below this temperature. The quench rate values were determined by fitting an exponential equation to the temperature/time values and solving for the slope at a temperature, 350°C, associated with high rates of PCDD/F formation. Tests with low dRDF feed rate were accompanied by co-fired natural gas (and its stoichiometric combustion air) to maintain the system firing rate. Since this effectively dilutes the dRDF-derived flue gas without the equivalent increase in oxygen (O<sub>2</sub>), normalizing the PCDD/F data with 7% O<sub>2</sub> would underestimate the PCDD/F yields. For this reason, mass flow parameters are expressed in temporal rate form (units of mass/min). For comparison purposes, this work reports homologue concentrations expressed in molar quantity ratios, since the OCDD/F congeners are about twice as heavy as an equimolar amount of MCDD/F congener. Throughout this paper, the *homologue profiles* are expressed in units of molar ratios, defined by the molar concentration of the homologue in ratio with the total sum of the homologues (e.g. mol TCDD/mol total PCDD + PCDF).

The homologue profile from one dRDF-only run (Run CRDF-07) is shown in Fig. 2. This figure is displayed in picomoles (pmol)/dscm and ng/dscm to illustrate the more commonly used conventions. Use of molar concentrations has the obvious effect of reducing the relative concentration of the more highly chlorinated homologues.

#### 4. Modelling

The objective of modelling was to determine which of the exogenous variables and their derivatives had a direct role in affecting the homologue profile at sampling port Port A, and to be able to use those variables to predict profiles. Relative homologue yields were modeled to ensure that the high yield run conditions did not have a disproportionate effect on the model. The relative homologue composition is represented by the ratio of the specific homologue concentration,  $p_i$ , with the concentration of a prevalent homologue, the OCDF ( $p_{OCDF}$ ). This common normalization factor for both PCDD and PCDF is used because it is not clear whether yields of the two families are related or not. To compensate for lack of yield normality, natural logarithm ratio transformations were used to characterize the compositions of the homologue profiles.

The generalized additive model, Model-7MM, predicts  $y_i$  where  $y_i = \ln[(p_i + \epsilon)/(p_{OCDF} + \epsilon)]$ . Note that our choice of OCDF to normalize the ratios is not critical: the statistical analyses give the same result regardless of which category of response is chosen as the baseline category (also see Ref. [13]). A negligible starter value of  $\epsilon = 0.001$  was used to compensate for zero yields. Inversion of the log ratio transforms is necessary to obtain the predicted composition,  $p_i'$ .

We considered 2- and 3-factor solutions. The 2-factor model accounted for 57% of the total variance, and the 3-factor solution improved to 70%. However, the solutions were unenlightening. Log ratios of homologue measurements were highly correlated with the first factor and run condition measurements correlated with the second and third factors, confirming the obvious fact that the homologue measurements and run conditions

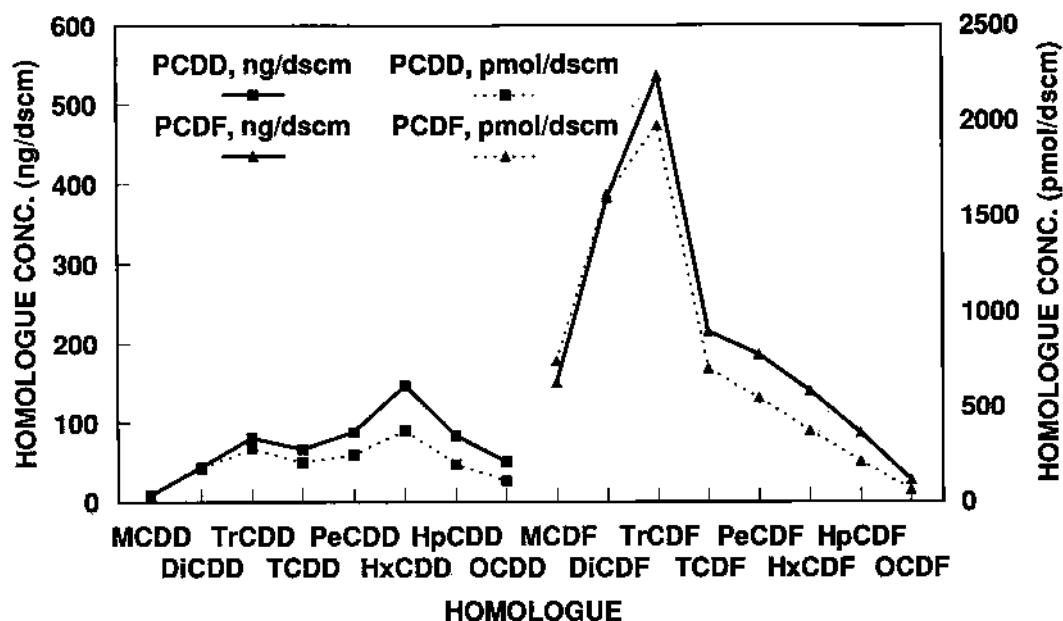


Fig. 2. Homologue profile from Run CRDF-07 (high dRDF feed rate) in units of pmol/dscm and ng/dscm.

are two separate phenomena. Hence, factor analysis was rejected for its inability to shed much light on causal forces which affect homologue composition.

The best 3- to 6-monotone-predictor, generalized additive models (GAMs) were constructed to develop a multivariate model for prediction of log ratios of the homologue yields. SAS procedure TRANSREG [14] was used to obtain optimal, empirical, monotone transforms of all possible subsets of the 11 available predictors (COAL, RDF, CA, HCL, SO<sub>2</sub>, SO<sub>2</sub>VHCL, QU, TSA, TSB, RESA, and RESB — see nomenclature in Table 2). The principal criterion for predictor selection was based on redundancy ( $R^2$ ), defined here as the average squared multiple correlation of models for predicting all variables of the multivariate response. Use of optimal transforms for the selected predictors increased average  $R^2$  from 0.451 to 0.731 for even a 3- predictor model. A 6-predictor model (Model-7MM) was selected based on its high average  $R^2$  (0.88722) and the ability of this model to increase precision for the individual homologue log ratios with introduction of a minimal number of additional predictors. This selection was based on an examination of fits by 11 1-predictor, 55 2-predictor, 165 3-predictor, 330 4-predictor, 462 5-predictor, and 462 6-predictor models for a total of 1485 generalized additive models.

The selected model predictors and estimated regression coefficients for Model-7MM, using as predictors the transformed values, are included in Table 3. Table 4 contains the corresponding squared, semi-partial correlations for Model-7MM.

## 5. Model discussion

The selected predictors (Table 2, **boldface**) for modelling homologue profiles (mol/mol) have terms common to those chosen for modelling tetra- to octa- homologue PCDD + PCDF yields (ng/min) as discussed in a previous paper [7]. Similar parameters selected included **HCL**, **SO<sub>2</sub>**, and **QU**. The yield model [7] resulted in selection of the additional terms **RDF** and **CA**. In this current work, the terms **RDF** and **CA** did not show sufficient significance (relative to selection of other parameters) in explaining homologue profiles that would warrant their inclusion. This difference could be due to the different range of homologues modelled in the earlier work (only the sum of the tetra- to octa-homologues was modelled) and/or real differences in the influence that predictors have on yields versus profiles. Another difference in this work's predictor selection and that of the previous paper [7] is the allowance of multiple interactive predictor terms in the latter.

The ability of Model-7MM to predict the sampled data through use of the transformed predictors is shown by the homologue-specific  $R^2$  values (Table 3). The most favorable prediction is for the HpCDF ratio ( $R^2=0.941$ ), and the least favorable prediction is for HpCDD ( $R^2=0.493$ ). Curiously, the  $R^2$  values for HpCDD prediction were always low, never exceeding 0.5 for all combinations of 3- to 6-predictor models. The  $R^2$  for HpCDD is unique, since the next lowest  $R^2$  (0.737) for PeCDD is much higher. The overall model  $R^2$  was 0.833, indicating that over 83% of the variation

Table 3

Model-7MM transformed predictors of log ratios with OCDF as baseline,  $R^2$  values, and estimated regression coefficients

Homologue ratio		MCDD	DiCDD	TrCDD	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Homologue ratio $R^2$		0.887	0.850	0.764	0.741	0.737	0.886	0.493	0.866
Transfer predictor	Coef.								
Intercept	NA	136.7603	126.4635	-5.7504	16.1741	27.3371	-39.9329	12.7949	17.1258
THCL	B1	5.0657	5.7804	3.9372	4.4434	2.8385	2.6284	1.2247	0.5540
TSO2	B2	-10.3826	-11.8507	-8.7633	-9.6443	-6.3311	-6.2722	-2.6027	-1.2559
TQU	B3	-0.2399	-0.2341	-0.0283	-0.0630	-0.0632	0.0329	-0.0273	0.0198
TRESA	B4	-52.7148	-51.8030	-13.7564	-20.8764	-17.5267	-0.5543	-7.4126	2.000
TRESB	B5	51.6587	51.9637	17.3855	24.8810	18.8737	4.7000	7.8218	-0.7901
TSO2VHCL	B6	17.6343	19.9561	14.6694	16.1576	10.5864	10.2623	4.2971	2.1099

Homologue ratio		MCDF	DiCDF	TrCDF	TCDF	PeCDF	HxCDF	HpCDF	OCDF
Homologue ratio $R^2$		0.877	0.925	0.801	0.906	0.888	0.927	0.941	(BL) <sup>a</sup>
Transfer predictor	Coef.								
Intercept	NA	77.7152	-9.3058	-11.1279	-40.0097	-44.1052	-26.2519	-21.7768	(BL)
THCL	B1	6.0223	7.3645	7.6854	4.4862	3.1254	2.7934	1.3292	(BL)
TSO2	B2	-11.3664	14.3889	-16.7835	-9.8060	-6.9785	-6.1031	-3.0043	(BL)
TQU	B3	-0.1571	-0.0494	-0.0560	0.0157	0.0338	0.0118	0.0188	(BL)
TRESA	B4	-39.2581	-22.1783	-25.3343	-6.3576	-0.7183	-3.5977	0.4881	(BL)
TRESB	B5	40.4144	28.3596	33.4426	12.4566	6.2430	8.0292	2.1575	(BL)
TSO2VHCL	B6	19.4039	23.8798	27.6192	16.0664	11.4448	9.9196	4.8944	(BL)

<sup>a</sup> BL = baseline.

Table 4

Type II squared semi-partial correlations for Model-7MM

Homologue ratio	MCDD	DiCDD	TrCDD	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Transfer predictor								
THCL	0.464	0.662	0.457	0.556	0.418	0.299	0.241	0.176
TSO2	0.454	0.648	0.527	0.610	0.484	0.396	0.254	0.219
TQU	0.576	0.600	0.013	0.062	0.114	0.026	0.066	0.130
TRESA	0.679	0.718	0.075	0.166	0.215	0.000	0.119	0.032
TRESB	0.679	0.752	0.125	0.245	0.260	0.013	0.138	0.005
TSO2VHCL	0.470	0.659	0.530	0.615	0.486	0.380	0.248	0.222

Homologue ratio	MCDF	DiCDF	TrCDF	TCDF	PeCDF	HxCDF	HpCDF	OCDF
Transfer predictor								
THCL	0.518	0.540	0.556	0.474	0.334	0.379	0.268	(BL) <sup>a</sup>
TSO2	0.429	0.480	0.617	0.527	0.388	0.421	0.318	(BL)
TQU	0.195	0.013	0.016	0.003	0.022	0.004	0.030	(BL)
TRESA	0.297	0.066	0.082	0.013	0.000	0.008	0.000	(BL)
TRESB	0.328	0.112	0.148	0.051	0.019	0.044	0.010	(BL)
TSO2VHCL	0.449	0.474	0.600	0.508	0.374	0.400	0.303	(BL)

<sup>a</sup> BL = baseline.

of the sampled homologue profiles could be accounted for by varying the predictors over their experimental ranges. No explanation can be offered for the diminished ability to model HpCDD. The ability of Model-7MM to reflect the actual sampled data is shown in Fig. 3 for run CRDF-07.

The predictors RESA and/or RESB were common to all of the 3- to 6-predictor models, lending confidence to their role in predicting homologue profiles, and

their eventual inclusion in the chosen Model-7MM. The predictors HCL, SO<sub>2</sub>, and SO<sub>2</sub>VHCL were candidate predictors based on their demonstrated role in promoting (HCL) and preventing (SO<sub>2</sub>) PCDD/F formation. The term SO<sub>2</sub>VHCL, defined as the ratio of the SO<sub>2</sub>/HCL concentrations, was also a likely predictor based on earlier work [7–10,15] which shows that, when this ratio reaches or exceeds a value around unity, formation of PCDD/F is often greatly reduced. However, the inclusion

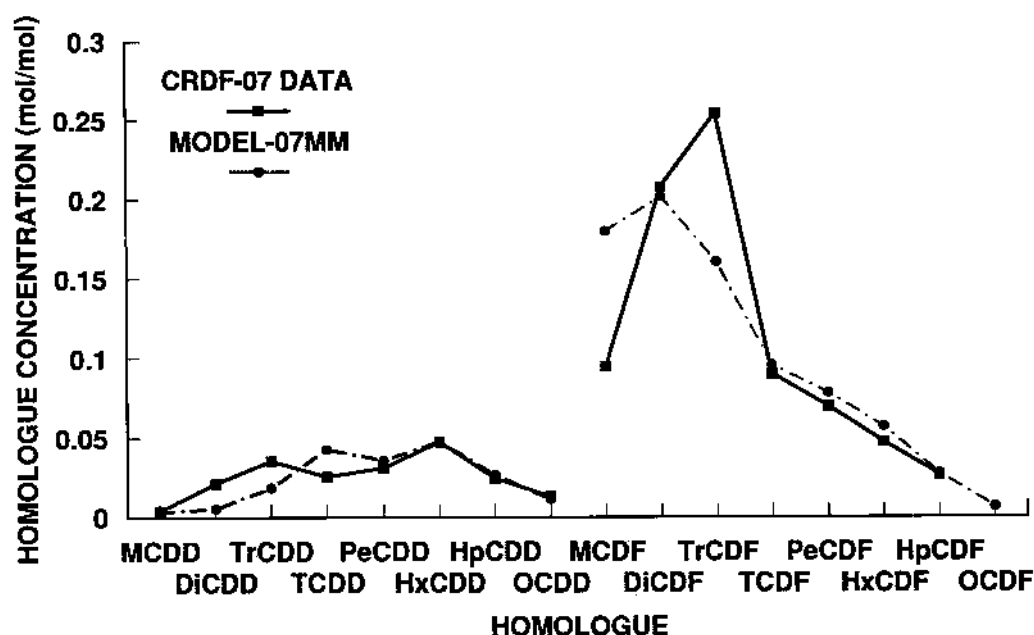


Fig. 3. Comparison of sampled homologue profile from Run CRDF-07 with Model-7MM prediction.

of HCL (and SO<sub>2</sub>) as a significant Model-7MM predictor, along with the interactive SO<sub>2</sub>VHCL term, suggests a second-order effect in which HCL (and SO<sub>2</sub>) concentration has a mechanistic role in addition to that played by the ratio term. Selection of the QU term as significant is not surprising. Quench rate has been shown to have a role in affecting PCDD/F formation in pilot- and full-scale facilities. Rapid reduction of flue gas temperature prior to the particle cleaning device is often cited as an effective prevention/control strategy.

The shapes of the predictor transforms determine the influence of varying each particular predictor upon Model-7MM. One qualitative feature, which is apparent by comparing transforms of the same predictor across all of the 3- to 6-predictor models in which it appears, is the constancy of the shape of the transform (not shown). This lends support to the ability of the models to consistently reflect a common effect of each predictor.

Transform THCL of HCL indicates an approximate first order response across the major range of its values (Fig. 4). Transforms TSO<sub>2</sub> and TSO<sub>2</sub>VHCL (not shown) both resemble adsorption isotherms or the response of a catalyst-mediated reaction (such as Michaelis–Menton kinetics for enzyme/substrate complexes). These three transforms are interrelated, so their effect on profiles cannot be discerned by simple examination of a single transform value and coefficient. This effect will be explored later in this paper. Transform TQU of QU, shown in Fig. 5, indicates a rapid increase in the TQU value with increasing quench rate from 300 to 350°C/s. Further changes in QU have little apparent effect on TQU. This suggests that, after our system had reached a quench rate of 350°C/s, further increases in

quench rate had a constant effect only on the homologue profile. The transforms (not shown) of flue gas residence time to Port “B” (TRESB) and to Port “A” (TRESA) display rapid increases in the transform values with initial changes in residence time, after which the remainder of the data show only slight increases. This suggests that reactions which affect the homologue profile become relatively insignificant at longer residence times.

Since the form of the transforms represents the effective response of changes in the relative homologue profile to variation of operating parameters, the statistically based selection of the particular parameter as a predictor and the shape of its transform should both have mechanistic significance. Ideally, the transform shapes should mimic known physical or chemical phenomena, such as the concentration response of a first order reaction or the time response of an adsorption-limited reaction. Practically, however, the limited number of data, the complexity of multiple reactions, the possibility that significant parameters were not considered as predictors, and the likelihood that the controlling mechanistic phenomena change throughout the course of PCDD/F formation temper the likelihood of finding such standard responses.

Table 3 shows an orderly, progressive change of the coefficients through the homologues, for both PCDD and PCDF. The magnitudes and signs of the coefficients are consistent, lending support to the predictor selection, the interrelationship among neighboring homologues, the similarity between same-Cl-number PCDD and PCDF mechanisms, and model robustness.

The squared, semi-partial correlations (Table 4) show that the transformed predictors THCL, TSO<sub>2</sub>, and

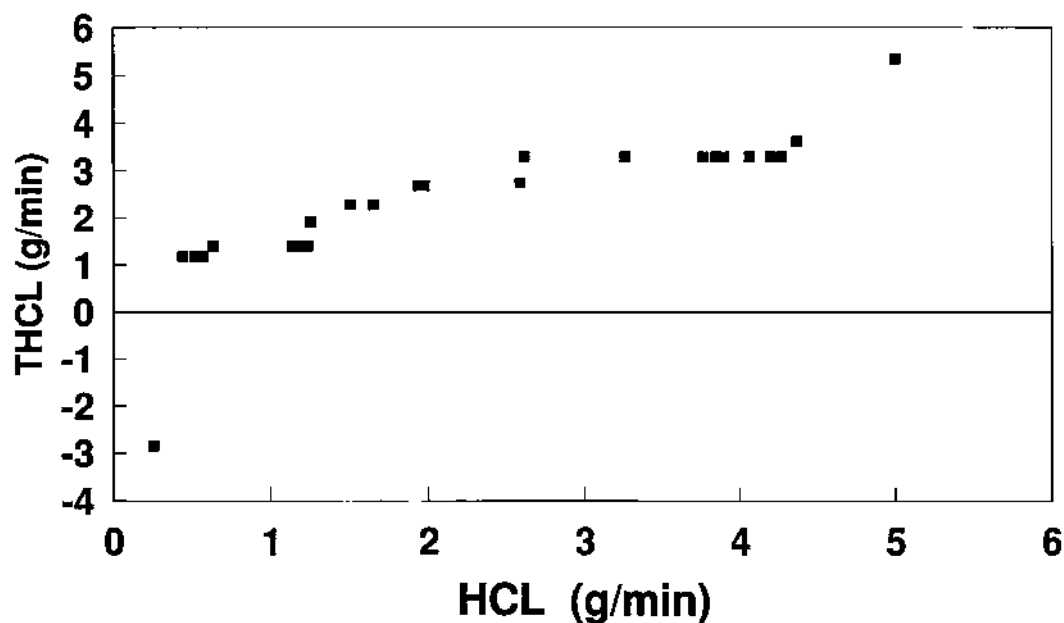


Fig. 4. Transform THCL of HCL.

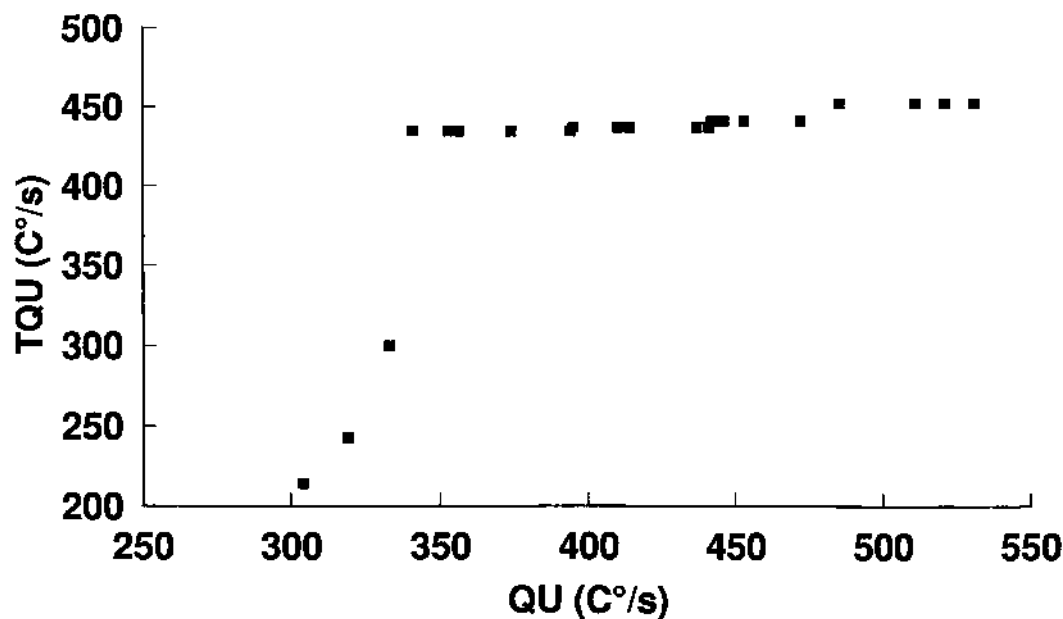


Fig. 5. Transform TQU of QU.

TSO2VHCL are most influential on the composition of the lower order Cl homologues, mono- to tetra-, for both PCDD and PCDF. The transformed predictors TRESA, TRESB, and TQU primarily influence the mono- and di-Cl homologues for PCDD and, to a lesser extent, the log ratios of MCDF. The more highly chlorinated homologues, from which the 17 toxic 2,3,7,8-Cl-substituted PCDD/F are found, are dominated by the influence of the transformed predictors THCL, TSO2, and TSO2VHCL.

The regression coefficients from Table 3, combined with the values of the transforms, predict the homologue distribution. In this work, the transform for SO2VHCL is represented by a fitted Michaelis-Menton model. All other transformed predictor values are determined by look-up tables based on actual modelled values. The Model-7MM prediction of the homologue profile for the run displayed in Fig. 2 (Run CRDF-07) is shown in Fig. 6. This figure also shows results of exercising the model at two different HCl concentrations,



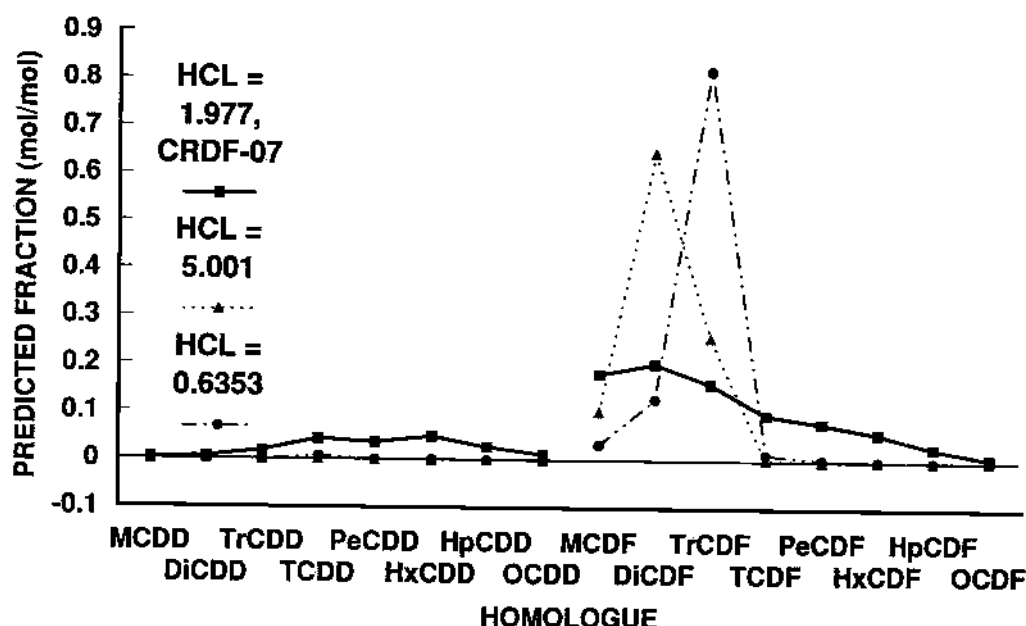


Fig. 6. Model-7MM prediction of the effect of varying HCL-only (g/min) from Run CRDF-07 conditions.

one above and one below the “baseline” Fig. 2 run conditions. The model is able to predict the influence of changing one variable while partialling out (holding constant) the effects from all of the other predictor variables. Both higher and lower HCL concentration conditions resulted in reduction of the tetra- to octa-chlorinated PCDD and PCDF but increases in the relative concentrations of DiCDF and TriCDF. Since HCL is an interactive parameter with SO<sub>2</sub> and plays two roles in the model (THCL and TSO<sub>2</sub>VHCL), simple examination of Fig. 4 will not necessarily reveal the model behavior at higher HCL concentrations. Note that these changes reflect profile shifts and not yields; earlier work [7] demonstrated conditions in which the tetra- to octa-PCDD/F yields significantly increased with increasing HCL concentration.

Increases in SO<sub>2</sub> concentration reflect substitution of high sulfur coal (5 to 10 wt%) for some of the dRDF feed. Increases in SO<sub>2</sub> concentration from the baseline conditions of dRDF-only Run CRDF-07 show significant changes in the homologue profile (Fig. 7). Higher SO<sub>2</sub> resulted in strong leftward shifts of the PCDF homologue profile; MCDF becomes the dominant species. Little effect is noted on the PCDD with increased SO<sub>2</sub>. Again, like HCL, SO<sub>2</sub> is an interactive predictor, making predictions of its effect unlikely based on simple examination of TSO<sub>2</sub>. Since earlier work [7] showed that increases in SO<sub>2</sub> concentration significantly reduced the tetra- to octa-PCDD/F yield, the minor effects on the homologue profile suggest that the effect of SO<sub>2</sub> is fairly universal across all of the homologues, with the exception of MCDF. The role of SO<sub>2</sub> may then be that of preventing molecular chlorination or encouraging dechlorination.

Changes in the homologue profile at different values of quench rate, QU, are shown in Fig. 8, again using the run conditions of CRDF-07 as a baseline. While it is conventionally believed that increases in quench rate reduce PCDD/F formation, earlier analyses of this data set [7] found this to be true (for tetra- to octa-chlorinated homologues) only at high HCL concentrations. This current work shows that decreasing QU results in large reductions in the fraction of the more highly chlorinated homologues for both PCDD and PCDF. At intermediate values of QU (414°C/s), MCDF becomes the dominant species. At even lower values of QU (319°C/s), MCDF becomes the dominant species. Coupled with the earlier (tetra- to octa-) yield results [7], this shows that the effect of increasing quench rate is to reduce yields while concurrently increasing the relative fraction of the tetra- to octa-chlorinated species.

Selection of RESB as a significant predictor of Port “A” homologue profiles is not obvious: it seems likely that our method of computing the residence time for Port “B” incorporates some intrinsic thermal property of the system that is reflected by RESB. Rearrangement of the TRESA and TRESB terms of Model-7MM shows that the B4 coefficient reflects the effect of variation in the residence times between Ports “B” and “A” [B4 (TRESA–TRESB)]. Since the B4 coefficient (Table 3) is always negative (except for OCDD and HpCDF), a longer residence time between these two sampling ports always decreases the relative fraction of the homologues at Port “A”. Since the magnitude of the B4 coefficients are highest for the more highly chlorinated homologues, longer residence times in the flue gas duct will lead to larger decreases in the lower, rather than the higher, chlorinated homologue fractions; i.e.

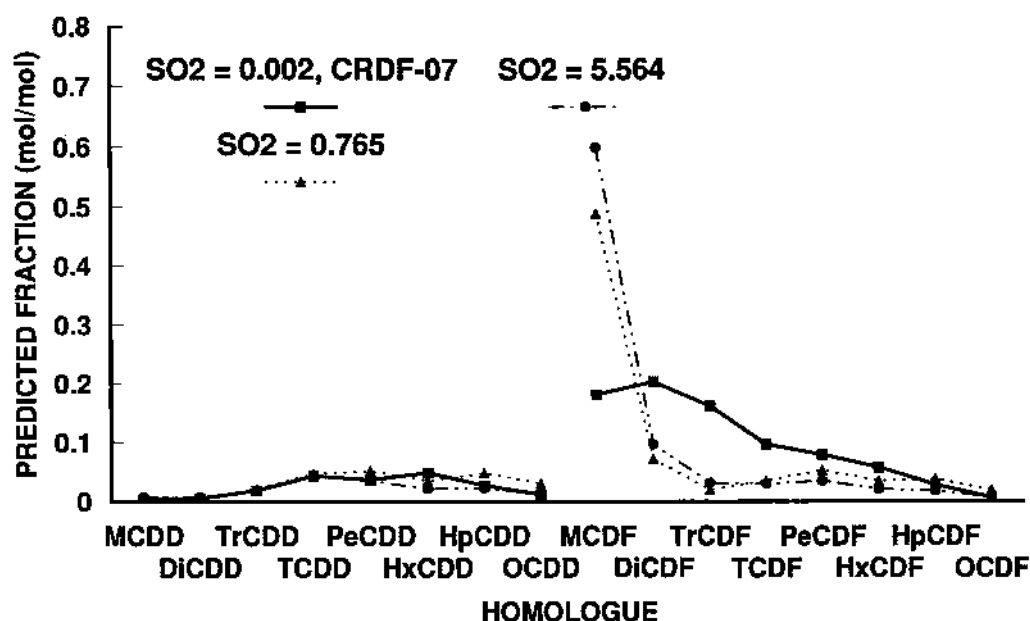


Fig. 7. Model-7MM prediction of the effect of varying  $\text{SO}_2$ -only (g/min) from Run CRDF-07 conditions.

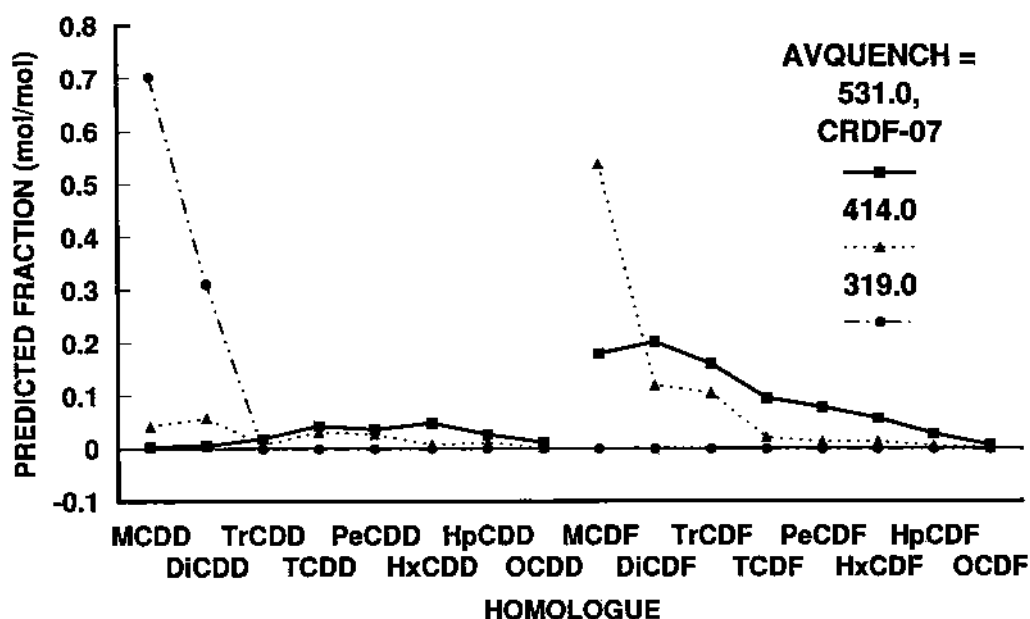


Fig. 8. Model-7MM prediction of the effect of varying QU-only ( $^{\circ}\text{C/s}$ ) from Run CRDF-07 conditions.

the homologue pattern will shift to the right. Similarly, concurrent increases in both RESA and RESB will likely reduce PCDD formation. Since TRESA is generally always greater than TRESB, the sum of the product of the Table 3 coefficients with the transform values will be negative for all PCDD homologues. In contrast, higher residence times will likely favor the more highly chlorinated PCDF homologues. Separately, increases in TRESA tend to shift the homologue profile to the right (more highly chlorinated PCDDs and PCDFs). Since earlier work by Gullett et al. [7], found

little, if any, increase in yields from Port "B" to Port "A", these combined findings suggest that continued chlorination reactions occur after formation, favoring the higher chlorinated PCDFs.

## 6. Conclusions

Analyses of tests run under varying conditions of RDF feed rate, supplemental coal combustion, HCl addition, and sorbent injection showed that the resultant

homologue profiles could be modelled ( $R^2=0.887$ ) using transformed predictors comprised of significant parameters including  $\text{SO}_2$ , HCl, quench rate, residence time, and  $\text{SO}_2/\text{HCl}$ . Operating parameters related to fuel feed rates, sampling temperature, and sorbent injection were not found to be significant predictors of homologue profiles. Variation of the model predictors shifts the mono- to octa-homologue profiles. Common predictors were associated with same-Cl-number dioxins and furans, implying mechanistic similarities between formation of these compounds. The flue gas residence time and quench parameters were significant predictors of the lowly chlorinated PCDD and PCDF (especially MCDD, DiCDD, and MCDF) but had virtually no effect on the more highly chlorinated homologues. The minimal effect of temperature, time, and quench parameters on the homologue profiles suggests that chlorination/dechlorination reactions are not greatly influenced by these variables. The full range of relative PCDD and PCDF homologue concentrations were associated with the parameters relating to HCl and  $\text{SO}_2$  concentration, although greater influence was observed on the lower chlorinated homologues. Increased  $\text{SO}_2$  (due to coal co-firing) resulted in significantly larger fractions of MCDF due to a leftward shift in the homologue profile; little proportional effect seems evident on the PCDD profile. HCl at the high and low extremes of this testing exhibits a leftward shift in the PCDF profile accompanied by significant increases in the proportion of DiCDF and TrCDF. Shifts in homologue profiles due to changes in HCl concentration indicate the complexity in assigning a causal effect to waste Cl composition, especially if only tetra- to octa-chlorinated compounds or I-TEQ values are measured.

## 7. Disclaimer statement

Any opinions, findings, conclusions, or recommendations expressed herein do not necessarily reflect the view of the ICCI, who sponsored this work in part. A detailed disclaimer from ICCI is available upon request.

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## References

- [1] Rappe C. Dioxin, patterns and source identification. *Fresenius Journal of Anal Chem* 1994;348:63–75.
- [2] Ishikawa R, Buekens A, Huang H, Watanabe K. Homologue profile and congener pattern of PCDD/Fs at different positions of a municipal waste incineration plant. *Organohalogen Compounds* 1997;31:512–5.
- [3] Rigo HG, Chandler AJ, Lanier WS. The relationship between chlorine in waste streams and dioxin emissions from waste combustors. vol. 1. Report ASME-CTRD-36. New York: ASME, 1995.
- [4] Rigo HG, Chandler AJ. Is there a strong dioxin:chlorine link in commercial scale systems? *Organohalogen Compounds* 1996;27:56–61.
- [5] Gullett BK, Dunn JE. Modelling of polychlorinated-dioxin and -furan congener profiles from municipal waste combustion. *Proceedings: International Specialty Conference on Solid Waste Management: Thermal Treatment & Waste-to-Energy Technologies*, EPA/AEERL, 18–21 April 1995, Washington, DC.
- [6] Funcke W, Hemminghaus H-J. Evaluation of PCDF/D, PBDF/D and PBCDF/D profiles in flue gas of combustion facilities using a statistical distribution function. *Organohalogen Compounds* 1993;11:345–50.
- [7] Gullett BK, Raghunathan K, Dunn JE. The effect of co-firing high sulfur coal with municipal waste on formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran. *Environmental Engineering Science* 1998;15(1):59–70.
- [8] Raghunathan K, Gullett BK, Lee CW, Kilgroe JD. Reducing dioxin formation through coal co-firing. *Proceedings: 1997 Incineration Conference*, 12–16 May 1997, Oakland, CA.
- [9] Raghunathan K, Gullett BK, Lee CW, Kilgroe JD, Dunn JE. Prevention of PCDD/PCDF formation by coal co-firing. Presented at the North American Waste to Energy Conference, 22–25 April 1997, Research Triangle Park, NC.
- [10] Raghunathan K, Gullett BK. Role of Sulfur in Reducing PCDD and PCDF Formation. *Environmental Science & Technology* 1996;30(6):1827–34.
- [11] Method 23, Title 40 code of federal regulations, Washington, DC: US Government Printing Office, 1991 [Part 60, appendix A].
- [12] Gullett BK, Lemieux PM, Dunn JE. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzodioxin and polychlorinated dibenzofuran formation during waste combustion. *Environmental Science & Technology* 1994;28(1):107–18.
- [13] Aitchison J. The statistical analysis of compositional data. New York: Chapman and Hall, 1986.
- [14] SAS/STAT user's guide; vol. 2, version 6. 4th ed. Cary, NC: SAS Institute, 1990.
- [15] Gullett BK, Raghunathan K. Observations on the effect of process parameters on dioxin/furan yield in municipal waste and coal systems. *Chemosphere* 1997;34(5–7):1027–32.

