

## USE OF INDICATORS FOR MEASURING REAL-TIME PCDD/F TOXIC EQUIVALENCY IN COMBUSTION EMISSIONS

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### Introduction

The ability to measure combustion source emissions of polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) in a timely manner would enable operating methods to prevent formation as well as provide assurance that facilities were complying with emission regulations. These needs require speed of analysis in order to respond to changes in operating conditions, as well as selectivity and sensitivity, to measure the 17 toxic PCDD/F congeners at concentrations < 1 ng/dscm.

While these measurement needs are not technically possible at this time, a number of rapid and sensitive analytical techniques and methods are under development to attempt such measurements. These developing analytical techniques include resonance-enhanced multiphoton ionization coupled with time-of-flight mass spectrometry (REMPI-TOFMS) and its more sensitive and selective variant, Jet REMPI-TOFMS; chemical ionization mass spectrometry (CIMS); and cavity ring-down spectroscopy (CRDS). Many of these methods employ measurement of precursors or indicator (P/I) compounds from which preestablished relationships are used to derive estimates of PCDD/F toxicity equivalence (TEQ) levels. The advantages of using P/I compound measurements are that these compounds would be less numerous and of higher concentration than the 17 toxic PCDD/F congeners, making them more readily detectable. The disadvantage is that they provide an indirect measure for which prior knowledge of the P/I relationship with the PCDD/F toxicity must be ensured with some certainty in order to successfully and confidently predict PCDD/F levels. This prior knowledge of relationships must be established from an understanding of reaction mechanisms based on a combination of statistical, theoretical, and experimental efforts. Failing this understanding, relationships between P/I compounds and the TEQ level must be determined on a facility-specific basis through correlations determined by a comprehensive field sampling and analysis effort.

Researchers have found PCDD/F TEQ correlations with measurements of monochlorobenzene<sup>1,2</sup>, mono- to trichlorobenzene<sup>3</sup>, mono- to hexachlorobenzene<sup>4</sup>, chlorophenols<sup>5</sup>, tetra- to hexachlorobenzenes<sup>6</sup>, vinyl chloride and 1,2 dichloroethene<sup>7</sup>, pentachlorobenzene<sup>8</sup>, penta- and hexachlorobenzene<sup>9,10</sup>, trichlorophenol<sup>11,12</sup>, and mono- to triCDD/F congeners<sup>13</sup>. This paper expands previous efforts<sup>13</sup> to establish P/I relationships with TEQ from two facilities by examining an expanded list of mono- to tetraCDD/Fs, chlorophenols (CPs), and chlorobenzenes (CBzs).

### Experimental

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Data for this research were derived from two sources, a municipal waste combustor (MWC) located near Norfolk, Virginia (USA), and a pilot-scale reactor at the University of Umeå (Sweden).

During the course of the sampling, Norfolk MWC operation consisted of 13 runs with interspersed waste-only firing and waste/coal-cofired tests (see details in Ref. 14). Analysis of chromatograms (DB-Dioxin™ column) of the mono- to triCDD/F homologues led to detection of 60 out of 74 peaks, 18 of which were unambiguously identified, 2 of which were coeluters, and 40 of which were of uncertain isomer specificity. Unidentified peaks (for which retention times on the DB-Dioxin column are not known) were Avariable-labelled@, such as a-DiCDF, where Aa@ indicates the first unidentified DiCDF isomer. The Umeå reactor burned pellets (nominal burn rate 18 MJ/h or 1 kg/h) in 11 runs simulating household waste under varied combustion conditions (see details in Refs. 15,16). Simultaneous high (650 °C)- and low-temperature (250 °C) sampling was followed by data analysis via high resolution (HR) gas chromatography (GC)/HR mass spectrometry (MS) using a Supelco 2330™ column for published<sup>17</sup> retention times of all isomers.

## Results

A meta analysis was done of the mono- to tetraCDDs/Fs (nmol/dscm, 7% O<sub>2</sub>) of the combined Norfolk and Umeå data sets (35 runs) that were positively identified from published retention time indices and/or available standards. The analysis allowed for predictor selection based on preference criteria of high model R<sup>2</sup>, minimal number of predictors, and predictor significance criteria of p < 0.05. To account for isomers that co-elute with the 2,3,7,8-Cl-substituted compounds and thereby inflate the TEQ (ng/dscm, 7% O<sub>2</sub>), the mass of the non-2,3,7,8-Cl-substituted isomer is added to that of the toxic isomer in the companion dataset in order to arrive at an inflated, yet comparable, TEQ index, termed "NUTEQ." The upward adjustment of the Umeå TEQ value was as much as 42%. Zero-intercept regression analyses (such that TEQ = 0 when P/I concentrations = 0) resulted in models which maximized the adjusted squared multiple correlation, R<sub>a</sub><sup>2</sup>, between observed and predicted values.

The best single predictor of NUTEQ from the combined Norfolk and Umeå datasets was 2,3,4,8-TeCDF at R<sub>a</sub><sup>2</sup> = 0.9437. The best nine 2-predictor models all contain 2,3,4,8-TeCDF in combination with another predictor. Three of the best, zero-intercept, 2-predictor models are shown in Table 1. In the first model, standardized regression

Table 1. Optimal, 2-predictor, zero-intercept models of NUTEQ for combined Norfolk and Umeå datasets, restricted to identified, common mono- to tetra-chlorinated isomers.

Predictors	R <sub>a</sub> <sup>2</sup> /R <sup>2</sup>
2,3,4,8-TeCDF and 1,3,7,8-TeCDD	0.9727/0.9456
2,3,4,8-TeCDF and 1,3,6,8-TeCDD	0.9653/0.9317
2,3,4,8-TeCDF and 2,4,8-TrCDF	0.9637/0.9316

coefficients (not shown) indicate that the partial effect of varying 2,3,4,8-TeCDF is nearly twice that for 1,3,7,8-TeCDD. The relative importance of 2,3,4,8-TeCDF in these models is reinforced by examining the semi-partial correlations: this predictor alone accounts for over 94 % of the modelled variation in NUTEQ.

Further analyses limited the potential predictors to only the 14 identified, common, mono- to tri-chlorinated isomers from the Norfolk and Umeå datasets, in recognition of the greater spectroscopic challenges with the tetra-chlorinated homologues. Predictable erosion of the R<sup>2</sup> value

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results (Table 2). However, the  $R^2$ -indicated predictive capability shows sufficient promise to suggest that a larger database of identified congeners (there are 74 total mono- to tri-chlorinated isomers) would likely improve the TEQ-predictive capability of these P/Is between these two facilities. To explore this possibility, the full complement of non-coeluted isomers from each separate facility were used in regressions analyses of the facility's respective TEQ values. The results of a zero-intercept regression analysis for mono- to tri-chlorinated DD/F isomers, chlorophenols, and chlorobenzenes are shown in Table 3, indicating promise for their use as TEQ predictors.

This illustrates that predictors chosen from among a single facility data set are not necessarily universally indicative of TEQ.

Table 4 shows a comparison of non-PCDD/F P/I compounds and homologues from this work with those of others, using non-zero intercept models. Clearly, this limited comparison shows little success in finding a P/I compound that satisfactorily predicts TEQ across facilities, and may be indicative of mechanistic or limiting reagent differences in these facilities. More comprehensive, isomer-specific information of facility emissions, including chlorophenols, chlorobenzenes, and mono- to tri-chlorinated PCDDs/Fs will be necessary in order to determine the efficacy of applying common P/I as universal TEQ indicators. In the absence of such information, however, it is clear from our current understanding that an on-line measurement of a limited subset of isomers, predetermined by facility-specific measurements, can be used to provide an indication of TEQ concentrations.

Table 2. Optimal, 1-, 2-, and 3-predictor, zero-intercept models of NUTEQ for combined Norfolk and Umeå datasets, restricted to identified, common mono- to tri-chlorinated DD/F isomers.

Predictors	$R_a^2/R^2$
2,4,6-TrCDF	0.7585/0.5567
2,4,8-TrCDF	0.6475/0.3829
1,6-DiCDD and 2,4,6-TrCDF	0.8735/0.7617
2,6-DiCDF and 2,4,6-TrCDF	0.8229/0.6661
1,6-DiCDD and 2,4,6-TrCDF and 1,3,6-TrCDF	0.8934/0.7979
1,6-DiCDD and 1,2,3-TrCDF and	0.8864/0.7920

Table 3. Optimal, 1- and 2-predictor models of TEQ for each separate facility, restricted to mono- to tri-chlorinated DD/F isomers, chlorophenols, and chlorobenzenes.

Norfolk		Umeå	
Predictor	$R_a^2/R^2$	Predictor	$R_a^2/R^2$
k-DiCDF	0.9419/0.7179	1,6,7-TrCDF	0.9103/0.8585
2,8-DiCDF	0.9333/0.6413	3,4,6-TrCDF	0.9101/0.8505
1,2,3-TrCDF and 2,3,8-TrCDF	0.9721/0.8464	1,6,7-TrCDF and 1,2,9-TrCDD	0.9593/0.9302
		1,2,3-TrCBz	0.8410/0.7456
		PcCIP and 1,2,3-TrCBz	0.9739/0.9535

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Table 4. Comparison of Umeå Non-PCDD/F TEQ Predictors with Others= Work (non-zero intercepts).

P/I	Umeå R <sup>2</sup>	Others= R <sup>2</sup>	Ref.
2,3,5-TrCPH	0.1008 <sup>a</sup>	0.81 <sup>bc</sup>	5
2,3,4,5,6-PeClPh	0.8817	0.34 <sup>bc</sup>	5
PeCBz	0.4209	0.37 <sup>b</sup>	3
HxCBz <sup>1,1</sup>	0.1285 <sup>a</sup>	0.81 <sup>b</sup>	6
1,2-DiCBz	0.0981 <sup>a</sup>	0.50 <sup>b</sup>	3
1,3-DiCBz	0.3792	0.38 <sup>b</sup>	3
PeCBz <sup>1,1</sup>	0.4040	0.85 <sup>b</sup>	6
Total CBz	0.5209 <sup>d</sup>	0.81 <sup>b</sup>	4

a: Does not meet criteria of  $p < 0.05$ : model predictor not significant. b: From correlation, R, values. c: Gas phase only,