Chlorobenzenes, chlorophenols, PAHs and low chlorinated dioxin/furan as post-boiler toxicity indicators in municipal solid waste incinerators

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Introduction

Numerous research studies have been conducted to establish indicator compounds for fast and less costly predictive monitoring of polycholorinated dibenzo-p-dioxin and furan (PCDD/F) toxic equivalent concentrations (TEQs). Many studies have shown that chlorobenzenes and chlorophenols had a good correlation with TEQ, suggesting that these compounds could be used as PCDD/F TEQ indicators[1-3]. Good correlation results were reported between some low mono- to tri-chlorinated PCDD/F isomers and TEQ[4]. Resonance enhanced multi-photon ionization (REMPI) with time of flight mass spectrometry (TOFMS) has shown the ability to monitor certain low chlorinated PCDD/F isomers[9] and is, therefore, considered a promising on-line TEQ monitoring technique. However, there is still uncertainty in using these compounds as universal indicators because their relationships with TEQ may be plant- and operating-condition specific[3]. Indeed, one study has shown that different correlations between low chlorinated dioxin/furan and TEQ existed in two incinerators[5]. Given that indicator/TEQ relationships may be plant- and location (temperature) specific, past efforts to determine indicators using combined data from multiple facilities[3] and multiple locations within a single facility[1,2] that are limited in number of samples and species may be insufficient to determine robust indicators.

The objective of this study is to determine indicator compounds based on intra-facility measurements under different operating conditions and to examine the effect of sampling position on potential indicator/TEQ relationships. An expanded indicator set, including chlorobenzenes (ClBzs), chlorophenols (ClPhs), polyaromatic hydrocarbons (PAHs) and low chlorinated dioxin/furan were analyzed to identify the relationship between these compounds and TEQ.

Method

Twelve samples were collected from the flue gas just before the spray drier absorber (SDA) in a municipal solid waste incinerator system near Virginia. This incinerator has four independently fired boilers with each having its own air pollution control system (SDA and bag house). The feed rate was varied for each run on the unit one boiler. U.S. EPA method 23 was used for PCDD/F

sampling, and the sample was comprised of two parts analyzed separately; the filter for particle phase targets and the resin for gas phase targets. The collected water in the sampling trains was analyzed for ClBzs and ClPhs. For this analysis, a liquid/liquid extraction was performed with methylene chloride after adding ^{13}C-labelled ClPh, ^{13}C-labelled ClBz internal standards, and HCl (to acidify the water). The collected filter and resin samples were extracted separately in a Soxhlet apparatus with methylene chloride and toluene for 16 hours each. ^{13}C-labelled ClPh, ^{13}C-labelled ClBz, deuterated PAHs, and ^{13}C-labelled PCDD/F internal standards were added to the samples before extraction. For ClBzs and ClPhs analysis, a ¼ fraction of the methylene chloride extract was used without clean-up. Acetylation was performed for ClPhs analysis. Another ¼ fraction of the methylene chloride and toluene extracts were used for PAHs analysis. A ½ fraction of the methylene chloride and toluene extracts were combined for PCDD/F analysis.

All 210 PCDD/F isomers were analyzed by high resolution gas chromatography (HRGC)/low resolution mass spectrometry (LRMS) (Hewlett packward 5890/5971) with a DB-Dioxin column and ClBzs, ClPhs, and PAHs were analyzed with a DB-5MS column. All data were obtained in the single ion monitoring (SIM) mode.

Result and Discussion

The PCDD/F, ClBz, ClPh, and PAH concentrations are presented in Table 1.

Homologue and isomer distribution patterns according to sample type.

The PCDD/F homologue distributions as a function of sample type, such as operating condition and sampling position, were examined with PCA (principal component analysis)[8] in Figure 1.. Principal component 1 (P[1]) explained 91.4% of the total variance in the PCDD/F homologue distribution, indicating that all samples had a similar homologue distribution pattern[10]. Principal component 2 (P[2]) divided the samples into two groups according to their sampling position, with the exception sample 2-1 [Figure 1(a)]. Low chlorinated dioxin/furan (mono- to tetra-) in group 2 was slightly more prevalent than in group 1. It is known that the low chlorinated dioxin/furan are more sensitive to operating conditions than are high chlorinated dioxin/furan.[6] Two shut downs of boiler 2 occurred during sampling, perhaps lead to a relatively higher fraction of low chlorinated dioxin/furan in the SDA-2 samples.

Concentration of 11 ClBz and 19 ClPh isomers were used to examine the isomer similarity between sample types. The R^2 value of PC1 was 70.7% for ClBz [Figure 1(b)] and 85.6% for ClPhs [Figure 1(c)], indicating similar isomer distribution pattern regardless of sample type. Except for two samples (2-4 and 2-6), the ClPhs showed less scatter than the ClBzs. For the ClPhs, samples 2-4 and 2-6, which both had a shut down of the boiler during the sampling, were located far away from the other samples. In the 2-4 and 2-6 samples, 246-triClPh was predominant compared to the other samples. However, in general, ClBzs and ClPhs didn't show distinctive distribution patterns according to sampling position.

The 16 PAHs examined in this study had a R^2 value for PC1 of 99%. There was no distinction according to sampling position and naphthalene and phenanthrene were dominant.

The isomer pattern within each PCDD/F homologue group was examined for all collected samples according to sampling location (SDA-1 and SDA-2). Overall, a similar isomer distribution pattern was observed regardless of sampling point. The R^2 value of PC1 for each homologue group was > 75%, with the exception of TeCDD (54.9%). However, samples 2-4 and 2-6 showed a different isomer distribution pattern compared to the other SDA-2 samples (not shown).

The relationship between ClBzs, ClPhs, PAHs, low chlorinated dioxin/furan isomers, and TEQ

The correlation coefficients (R^2) among ClBzs, ClPhs, PAHs, low chlorinated dioxin/furan isomer concentrations, and TEQ were obtained from SDA-1 and SDA-2 samples separately and also from a combined data set of all SDA-1 and SDA-2 samples. All ClBz and ClPh isomers in the SDA-1 samples had a positive correlation ($R^2 > 0.5$) with TEQ and half of them showed a very good relationship ($R^2 > 0.8$) (Table 2 and 3). However, the SDA-2 did not show a positive correlation with TEQ for all ClBz and ClPh isomers. Use of log [concentration] SDA-2 improved the relationship with TEQ (Table 2 and 3). The operating conditions in SDA-2 varied greatly, especially in the "shut down" cases, compared to SDA-1. These unstable situations might have caused the large variation observed for the concentrations of certain isomers, especially for ClPhs and PAHs (Table 1). These large variations were damped using a log-log scale which resulted in a higher R^2 value compared to the linear scale. For example, the major isomer in ClPhs, 246-triClPh, did not have a strong correlation with TEQ because of the high concentrations measured in the "shut down" cases, but this relationship was improved using a log-log scale (Figure 2). The fraction of 246-triClPh in the tri-ClPhs increased from 50% to 90% in the shut down cases. This increase suggests that certain isomers, such as 26-, 24/25-, 246-triClPh, are very sensitive to operating conditions; their concentrations increased exponentially in shut down cases. This also suggests that an exponential curve for a TEQ prediction model should be considered for an incinerator which has dynamic operating conditions (e.g., shut down).

For PAHs, no positive correlation with TEQ was observed, although the concentrations increased extremely in shut down cases, 2-4 and 2-6 (Table 1). Blumenstock et al. also reported a drastic change in PAH concentrations measured at the post-combustion chamber during malfunctions.[7] Most of the low chlorinated dioxin/furan isomers (from mono- to tri-) had a positive correlation with TEQ in both data sets (SDA-1 and SDA-2). The R^2 for SDA-2 increased when the log [concentration] unit was used, also indicating the sensitivity of low chlorinated dioxin/furan formation with operating conditions.

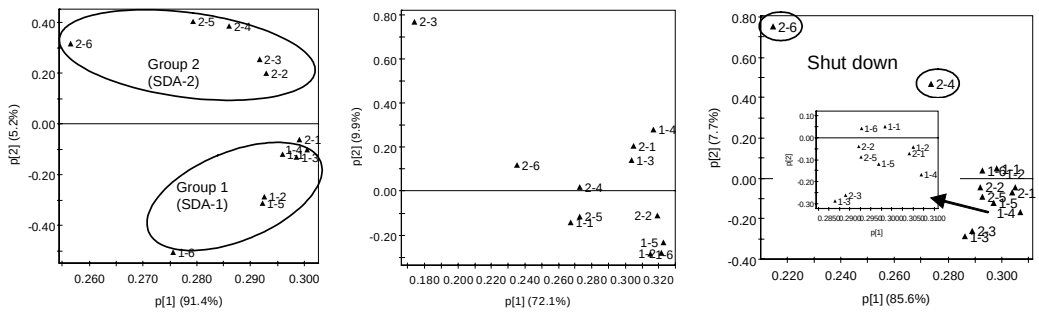
A sensitivity analysis showed that the R^2 values for SDA-2 were more sensitive than those of SDA-1. Leave-one-out cross-validated correlation coefficients obtained from ClBz, ClPh, and low chlorinated dioxin/furan isomers in SDA-1 were not changed as much as those for SDA-2. However, leave-one-out cross-validated correlation coefficients did not change as much when the combined SDA-1 and SDA-2 data set was used.

The correlation analysis results indicate a potential close relationship between ClBz, ClPh and PCDD/F formation and further suggest the possibility of on-line monitoring with the REMPI technique using low chlorinated compounds (such as mono- and di-ClBz/ClPh/CDD/CDF) as indicator compounds for TEQ. However, this work also shows that severe operating conditions, like shut downs, can cause concentrations of certain kinds of compounds (such as PAHs, 246-

triClPh, etc.) to significantly increase downstream of the boiler. There are still some questions remaining before applying these results directly to the REMPI technique because (1) REMPI can measure only gas-phase compounds and (2) the correlations developed in this paper are based on multi-hour integrated concentrations. Therefore, studies regarding particle/gas partitioning of PCDD/F and other potential indicator compounds, as well as time-resolved correlations, are currently on-going.

Table 1. Pre-SDA PCDD/F (ng-TEQ/m^3), ClBz, ClPh and PAH concentrations (µg/m^3). (7% O_2, WHO-TEF based)

sampling position	run	PCDD/F	ClBz	ClPhs	PAHs
	1-1	69.3	33.8	83.0	22.3
	1-2	32.7	12.8	20.3	6.6
SDA-1	1-3	27.1	15.8	24.0	37.4
(boiler 1)	1-4	70.5	33.3	51.0	50.8
	1-5	28.1	6.8	7.8	5.8
	1-6	36.3	14.3	18.5	6.0
	2-1	50.5	24.7	26.1	7.6
	2-2	108.2	37.9	46.6	7.4
SDA-2	2-3	68.2	44.1	42.7	36.7
(boiler 2)	2-4	64.5	46.1	118.5	91.5
	2-5	5.7	6.1	5.9	2.7
	2-6	124.4	90.1	210.9	506.8



(a) PCDD/F homologues (b) ClBz isomers (c) ClPh isomers

Figure 1. PCA results for PCDD/F, ClBz, and ClPh, by run.

Table 2. R^2 values between ClBzs and TEQ

(a) concentration units

ClBz Isomers	SDA-1	SDA-2	SDA(1+2)
13	0.74	0.28	0.44
14	0.84	0.74	0.77
12	0.92	0.69	0.73
135	0.53	0.48	0.53
124	0.84	1.00	0.95
123	0.96	0.63	0.69
1245/1235	0.63	0.80	0.67
1234	0.96	0.69	0.76
PCB	0.86	0.55	0.64
HxCB	0.73	0.38	0.48

(b) log [concentration] units

ClBz Isomers	SDA-1	SDA-2	SDA(1+2)
13	0.60	0.71	0.58
14	0.85	0.83	0.57
12	0.85	0.84	0.74
135	0.45	0.83	0.56
124	0.78	0.98	0.80
123	0.86	0.84	0.76
1245/1235	0.57	0.95	0.77
1234	0.86	0.88	0.84
PCB	0.82	0.83	0.82
HxCB	0.75	0.73	0.73

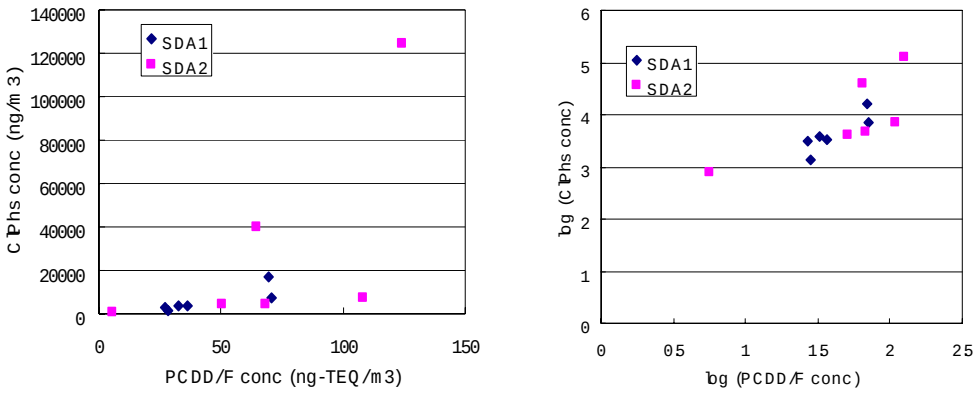
Table 3. R^2 values between ClPhs and TEQ

(a) concentration units

ClPh Isomers	SDA-1	SDA-2	SDA(1+2)
2	0.81	0.41	0.53
3/4	0.91	0.48	0.59
26	0.74	0.17	0.32
24/25	0.71	0.31	0.38
23	0.78	0.80	0.79
35	0.81	0.75	0.77
34	0.82	0.77	0.76
246	0.69	0.42	0.46
235	0.79	0.78	0.79
236	0.81	0.73	0.78
245	0.91	0.80	0.80
234	0.91	0.81	0.80
345	0.85	0.81	0.78
2356	0.86	0.62	0.67
2346/2345	0.83	0.85	0.40
PCP	0.60	0.50	0.34

(b) log [concentration] units

ClPh Isomers	SDA-1	SDA-2	SDA(1+2)
2	0.74	0.64	0.65
3/4	0.78	0.70	0.75
26	0.79	0.51	0.58
24/25	0.74	0.54	0.55
23	0.62	0.77	0.69
35	0.72	0.75	0.70
34	0.61	0.72	0.68
246	0.78	0.61	0.67
235	0.66	0.76	0.73
236	0.63	0.71	0.69
245	0.71	0.75	0.69
234	0.71	0.72	0.68
345	0.58	0.71	0.59
2356	0.61	0.66	0.60
2346/2345	0.69	0.75	0.52
PCP	0.47	0.71	0.42



(a) standard scale (b) log-log scale

Figure 2. The relationship between 246-ClPhs and PCDD/F TEQ.

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