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Mono- to Octa-Chlorinated PCDD/Fs in Stack Gas from Typical Waste Incinerators and Their Implications on Emission

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S *Supporting Information*

ABSTRACT: Mono- to octa-chlorinated dibenzo-*p*-dioxins and dibenzofurans (mono- to octa-CDD/Fs) were determined in 14 stack gas samples from two municipal solid waste incinerators and two medical waste incinerators. The total PCDD/F concentrations were 5.1−390 ng/Nm^3, and the mono- to trichlorinated homologues contributed 53.2−94.5% of the total concentrations. The homologue profiles were dominated by the MoCDF, ranged from 1.51 to 113.1 ng/Nm^3, and the proportion that each PCDF homologue group contributed to the total concentration decreased with increasing chlorination level. The toxic equivalent concentrations (I-TEQs) were 0.01−2.81 ng I-TEQ/Nm^3, with 2,3,4,7,8-PeCDF being the biggest contributor, at 30.6−60.0%. Correlations were found among the PCDD/PCDF ratios (D/F ratios), the degree of chlorination, and the TEQ. Stack gases with low I-TEQs had higher proportions of the less chlorinated homologues and lower D/F ratios, which could be attributed to the removal of the more chlorinated isomers by the air pollution control systems used by the incinerators. 2,8-DiCDF, 2,4,8-TrCDF, DiCDF, and TrCDF can be used as TEQ indicators for monitoring PCDD/Fs. 2,8-DiCDF and 2,4,8-TrCDF correlated well with the TEQ because they strongly correlated with 2,3,4,7,8-PeCDF, implying possible correlations in their formation mechanisms.

■ INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are hazardous pollutants that are formed during various thermal and chemical processes. They are classed as persistent organic pollutants because of their toxicities, persistence, ubiquity in the environment, and potential to accumulate in the tissues of organisms. Since these compounds were first detected in emissions from combustion sources,[1] other anthropogenic sources have been extensively investigated, including municipal solid waste incineration,[2] the manufacture of chlorinated pesticides,[3] metallurgical facilities,[4] and chlorine bleaching in paper mills.[5]

Although studies of tetra- to octa-CDD/F (abbreviations used later are tetra = Te; penta = Pe; hexa = Hx; hepta = Hp; and octa = O) homologues have provided valuable information on the sources and sinks of PCDD/Fs,[6] complete profiles of the mono- to octa-chlorinated homologues and congeners would better illuminate their formation mechanisms.[7] Mono- to tri-CDD/Fs (abbreviations used later are mono = Mo; di = Di; and tri = Tr) have been found to be produced in a wide range of combustion processes.[8] In early studies, conducted in the 1990s, Mo- to Tr-CDD/Fs were measured to test their potential for use as toxic equivalent concentration (TEQ) indicators in real-time monitoring techniques, such as resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS).[9] Wikström et al.[10] assessed the influence of various parameters, such as the carbon and chlorine sources and the moisture content, on PCDD/F formation in pilot-scale incinerators by measuring complete PCDD/F homologue profiles. Gullett et al.[11] discovered that sulfur in cofiring coal had an impact on the Mo- to OCDD/F homologue profiles. Lundin et al.[12] found high abundances of less chlorinated PCDFs in some fly ash samples from full-scale municipal solid waste incinerators (MSWIs). Different theoretical models have been tested by comparing homologue and congener profiles.[13]

However, as most previous studies have been focused on formation mechanisms, actual incinerator emission data for the Mo- to Tr-CDD/Fs are limited. In other words, the environmental impact and behavior of the less chlorinated PCDD/F congeners have not been comprehensively studied. It has been proposed, from some early *in vivo* animal studies, that some MoCDF congeners are mutagenic and embryotoxic.[14] A very recent study in Korea produced an impressive data set containing Mo- to OCDD/F concentrations in human serum

Table 1. Detailed Incinerator Information

incinerator	type	treatment capacity	furnace	air pollution control system	no. of samples	sampling time
MA	MSWI	800 t/day	grate stoker	semidry scrubber, activated carbon, fabric filter	4	Aug 2012
MB	MSWI	200 t/day	grate stoker	water screen duster, fabric filter	4	Nov 2012
MC	MWI	30 t/day	rotary kiln	quench system, semidry scrubber, activated carbon, fabric filter	3	Sept 2012
MD	MWI	15 t/day	rotary kiln	semidry scrubber, fabric filter	3	Nov 2012

samples,[15] unexpectedly showing that the Mo- to Tr-CDFs accounted for more than 95% of the total PCDF concentrations in sera from MSWI operators and nearby (within 300 m) residents and that the MoCDFs contributed 83%. This research emphasized the possible significant impact that less chlorinated PCDD/Fs may have on humans and the environment, which has been almost ignored. It is well-known that Te- to Pe-CDD/Fs are prone to partitioning into the gas phase[16] and may spread widely in the environment because they have higher vapor pressures than the Hx- to OCDD/Fs.[17] The Mo- to Tr-CDD/Fs are more volatile than the TeCDD/Fs, so it is natural to be interested in obtaining a full picture of the Mo- to OCDD/Fs in stack gases and in exploring the main factors that influence PCDD/F emissions, because they have direct impacts on the atmospheric environment.

To achieve this goal, four typical incinerators were selected, and a series of stack gas samples were collected from them. The complete PCDD/F homologue profiles were measured, and correlations between the PCDD/PCDF ratios (D/F ratios), the degree of chlorination, and the TEQs were investigated. The relationships between the congener concentrations and the TEQs were also assessed and potential TEQ indicator congeners are proposed. This study improves our understanding of PCDD/F emissions to the ambient environment and will help address public concerns about waste incinerators.

■ MATERIALS AND METHODS

Stack Gas Sampling. Four continuously operating full-scale incinerators in northern China were studied. Two were MSWIs and two were medical waste incinerators (MWIs), and detailed information on the incinerators is given in Table 1. We defined MA and MC as typical incinerators with good incineration conditions and well-equipped air pollution control systems (APCSs), while we defined MB and MD as having relatively poor facilities.

The stack gas samples were collected using an automatic isokinetic sampling system, Isostack Basic (Tecora Corp., Milan, Italy), following the EU standard method EN-1948. Details of the sampling methods can be found elsewhere.[18] The sampling system consisted of a heated probe, a filter box with a quartz fiber filter, and a water-cooled XAD-2 sorbent trap. A ^{13}C-labeled standard (EN-1948 SS; Cambridge Isotope Laboratories, Andover, MA, USA) was added as a sampling standard.

Mono- to Octa-CDD/F Analysis. The pretreatment and analysis of the samples for Te- to OCDD/Fs followed the standard method EN-1948, which has been described previously.[19] Briefly, each sample was spiked with 1 ng of a ^{13}C-labeled PCDD/F internal standard mixture (EN-1948 ES; Cambridge Isotope Laboratories) and then solvent extracted in a Soxhlet apparatus. The extract was split into two aliquots, one being analyzed for the Te- to OCDD/Fs and the other being analyzed for the Mo- to Tr-CDD/Fs. The Te- to OCDD/Fs aliquot was purified using an acidic silica gel column, a multilayer silica gel column, then a basic alumina column, and

the final extract was concentrated to 20 μL and spiked with 1 ng of a ^{13}C-labeled injection standard (EN-1948 IS; Cambridge Isotope Laboratories) before instrumental analysis.

The Mo- to Tr-CDD/Fs aliquot was processed differently because no standard methods are available for these congeners. A ^{13}C-labeled internal standard (EDF-4955; Cambridge Isotope Laboratories) containing six congeners (2-MoCDD, 2,3-DiCDD, 2,3,7-TrCDD, 2-MoCDF, 2,8-DiCDF, and 2,4,8-TrCDF) was added before Soxhlet extraction,[20] and the extract aliquot was concentrated and purified using a multilayer silica gel column eluted with 100 mL of hexane. The extract was then evaporated and separated on an 8 g basic alumina column eluted with 80 mL of 2% dichloromethane in hexane and then 150 mL of 12% dichloromethane in hexane. The latter fraction contained the Mo- to Tr-CDD/Fs and was concentrated to 40 μL of nonane under a nitrogen flow before instrumental analysis. Recoveries were quantified in the blank experiments.

The Mo- to OCDD/Fs were analyzed using an Agilent 6890 high resolution gas chromatograph (Agilent Technologies, Santa Clara, CA, USA), equipped with a DB-5 MS column, coupled to a Waters Autospec Ultima high resolution mass spectrometer (Waters Corporation, Milford, MA, USA). The mass spectrometer had a resolution of at least 10000 and was operated in selected ion monitoring mode. For the Mo- to Tr-CDD/Fs, six congeners that have ^{13}C-labeled standards available were quantified and qualified using the ^{13}C-labeled standards. 1-MoCDF, 3-MoCDF, and 4-MoCDF were analyzed using ^{13}C-labeled 2-MoCDF, and 1-MoCDD was analyzed using ^{13}C-labeled 2-MoCDD. Field and laboratory blanks were incorporated into the analytical procedure for quality control. The recovery range for the 17 2,3,7,8-chlorinated PCDD/Fs was 67−149%, and the recoveries of the six Mo- to Tr-CDD/F congeners were between 41% and 93%. Detailed recoveries of the Mo- to Tr-CDD/Fs are given in the Supporting Information (Table S1).

■ RESULTS AND DISCUSSION

Congener Description. Detailed data for the 10 less chlorinated and 17 2,3,7,8-chlorinated PCDD/Fs are given in the Supporting Information (Table S2). 2-MoCDF was the dominant congener, with concentrations of 0.58−35.9 ng/Nm³, followed by 3-MoCDF, at 0.48−20.6 ng/Nm³. The 1-MoCDD and 2-MoCDD concentrations were ND−0.48 and 0.019−2.94 ng/Nm³, respectively. The less chlorinated PCDF congeners 2,8-DiCDF and 2,4,8-TrCDF were found at significantly higher concentrations than the less chlorinated PCDD congeners 2,3-DiCDD and 2,3,7-TrCDD. 1,2,3,4,6,7,8-HpCDF was the predominant 2,3,7,8-chlorinated PCDF congener, at 0.022−6.20 ng/Nm³, while OCDD was the most abundant PCDD congener that has a toxic equivalence factor, at 0.021−2.16 ng/Nm³. The concentration of the most toxic PCDD/F, 2,3,7,8-TeCDD, ranged from ND to 0.13 ng/Nm³, which was relatively low compared with the concentration of the other PCDD/Fs. The TEQs were estimated using the accepted international toxic equivalence factors. Similar to the findings of
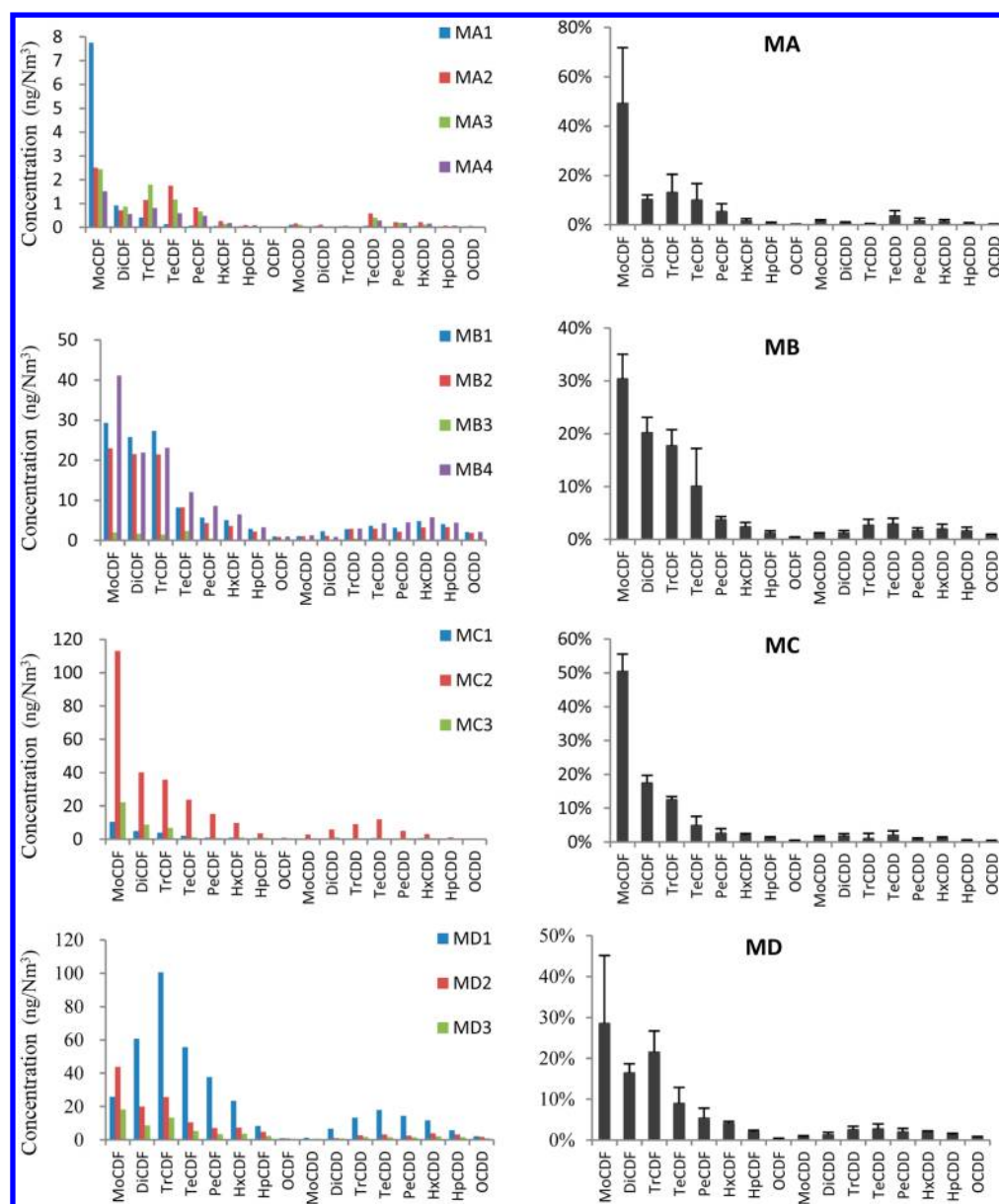
Figure 1. PCDD/F homologue profiles in the samples, expressed as mass concentrations (ng/Nm^3) on the left, and as average molar proportions (with bars representing the standard deviation) on the right.

previous studies,[6,21] 2,3,4,7,8-PeCDF was the major contributor, at 30.6−60.0%, to the total TEQs in the samples.

The TEQs for the samples from MA were lower than the national emission standard set by the Ministry of Environmental Protection of China, and some of the samples from MB, MC, and MD exceeded the emission standard (0.1 ng I-TEQ/Nm^3 for MSWIs and 0.5 ng I-TEQ/Nm^3 for MWIs). The average I-TEQs for the MA, MB, MC, and MD incinerator samples were 0.026, 0.50, 0.45, and 1.33 ng I-TEQ/Nm^3, respectively. On average, MA and MC met the emission standard, while MB and MD did not, which is why we defined MB and MD as incinerators with poor APCSs. Comparing the average I-TEQs and the description of the APCSs installed in the incinerators, we speculate that the better APCSs in incinerators MA and MC led to their lower PCDD/F emissions. The larger variances found in the MC and MD homologue concentrations (see Figure 1) could be attributed to the fact that they are MWIs.[22] MWIs are less likely than

MSWIs to achieve stable and complete combustion, so the organic matter and chlorine contents can be higher in MWI wastes than in MSWI wastes.

Homologue Profiles. The total PCDD/F concentrations in the MSWI and MWI stack gas samples are given in the Supporting Information (Table S3). The homologue profiles found in the samples were analyzed using the mass concentrations and average molar proportions and are shown in Figure 1.

It can be seen from Table S3 and Figure 1 (left) that the total PCDD concentrations ranged from 0.42 to 72.8 ng/Nm^3, while the total PCDF concentrations ranged from 4.26 to 313.1 ng/Nm^3. The Mo- to Tr-CDD/Fs were present at higher concentrations than the Te- to OCDD/Fs in all of the stack gas samples and contributed 53.2−94.5% of the total PCDD/F concentrations. Looking at the individual incinerators, the samples from MA contained PCDD/Fs at 5.07−9.83 ng/Nm^3, MB and MC emitted higher concentrations, 9.81−143.5 ng/

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Table 2. D/F Ratios and the Degree of Chlorination (#Cl) in Samples from the Four Incinerators

	D/F ratios			#Cl		
incinerator	$Cl_{1-3}DD/Fs$	$Cl_{4-8}DD/Fs$	$Cl_{1-8}DD/Fs$	PCDD	PCDF	PCDD/F
MA	0.04 ± 0.02	0.49 ± 0.13	0.14 ± 0.07	3.88 ± 0.58	2.04 ± 0.55	2.30 ± 0.67
MB	0.09 ± 0.03	0.61 ± 0.21	0.22 ± 0.01	4.39 ± 0.46	2.43 ± 0.11	2.70 ± 0.03
MC	0.06 ± 0.03	0.45 ± 0.04	0.13 ± 0.04	3.59 ± 0.46	1.95 ± 0.18	2.09 ± 0.22
MD	0.08 ± 0.03	0.47 ± 0.05	0.20 ± 0.04	4.46 ± 0.29	2.64 ± 0.45	2.86 ± 0.40

Nm^3 and 27.3−281.8 ng/Nm^3, respectively, and the concentrations emitted from MD were still higher, at 66.1−385.9 ng/Nm^3. Lower PCDD/F concentrations are emitted from MA and MC than from MB and MD because MA and MC are relatively well-equipped incinerators.

The PCDF homologue concentrations generally decreased with increasing chlorination level. The most abundant PCDF homologue was MoCDF, which contributed 6.7−78.9% of the total PCDD/Fs in the samples. DiCDF and TrCDF were also abundant homologues, contributing 4.2−22.2% of the total PCDD/Fs. In contrast, the proportions that the PCDD homologues contributed to the total PCDD/F concentrations were within a relatively narrow range. There was no dominant PCDD homologue, but TeCDD generally contributed a slightly higher proportion (0.6−6.6% of the total PCDD/Fs) than the other PCDD homologues contributed. These trends are clear in Figure 1 (right), which shows the average molar proportions each homologue contributes to the total PCDD/Fs. There were some similarities between the homologue profiles found in this study and in previous studies.[23]

PCDD/PCDF Ratio and the Degree of Chlorination. The ratio of the total PCDD and PCDF concentrations (the D/F ratio) is commonly used as a homologue pattern indicator. The average D/F ratios and the average degree of chlorination (the average number of chlorine atoms in each molecule) in the stack gas samples from the four incinerators were calculated and are presented in Table 2.

It can be seen from Table 2 that all of the D/F ratios were below 1, indicating that PCDFs dominated the homologues of PCDD/Fs in stack gas samples. The total D/F ratios (i.e., for the Mo-to OCDD/Fs) were 0.13−0.22, so the PCDF concentrations were 3.5−6.7 times higher than the PCDD concentrations. The D/F ratios for the Mo- to Tr-CDD/Fs were much lower (about 6−12 times) than the ratios for the Te- to OCDD/Fs. A clear discrepancy could be seen between the PCDD and PCDF degrees of chlorination, the PCDF homologues being less chlorinated (with an average degree of chlorination of between 1.95 and 2.64) and the PCDD homologues being more chlorinated (with an average degree of chlorination of 3.59−4.46). This is because the less chlorinated PCDFs contributed relatively high proportions of the total PCDF concentrations, as seen in the "ladder-shaped" profile in Figure 1, but the less chlorinated PCDDs were not very abundant.

As mentioned above, MA and MB are MSWIs and MC and MD are MWIs. There was an obvious difference between the two MSWIs, which can be seen in Table 2, with lower D/F ratios being found in the MA than in the MB samples. This trend was consistent for both the Mo- to Tr-CDD/Fs and the Te- to OCDD/Fs. The degrees of chlorination were also lower in the MA samples than in the MB samples. It has previously been found that different combustion parameters and APCSs can lead to different PCDD/F homologue profiles.[24,25] The different PCDD/F congeners have different boiling points and

volatilities,[26] and the more chlorinated congeners are more likely to bind to particles, while the less chlorinated congeners can partition more into the gas phase.[16,27,28] It is, therefore, reasonable to suppose that an incinerator equipped with a good APCS will emit PCDD/Fs with a lower level of chlorination than one equipped with a poor APCS, because most of the more chlorinated PCDD/Fs will be bound to particles that are removed by the APCS. Furthermore, the MSWIs with effective APCSs would have lower D/F ratios because the D/F ratios are smaller for the Mo- to Tr-CDD/Fs than for the Te- to OCDD/Fs, and because most Te- to OCDD/Fs, sorbed to particles, are removed. Similar comparisons could be drawn between the MWIs, MC, and MD, the MD samples having higher TEQs, and having higher D/F ratios and degrees of chlorination, than the MC samples. We therefore speculated that the TEQ was positively related to the D/F ratio and the degree of chlorination and that a higher degree of chlorination or D/F ratio in the stack gas would imply higher PCDD/F emissions.

Correlations among TEQs, Congeners, and Homologues. TEQ indicators are necessary for the real-time monitoring of PCDD/F emissions from waste incinerators. Previous studies have shown that the Te- to OCDD/F congeners are not suitable for many online monitoring technologies, such as REMPI-TOFMS,[29] but some Mo- to Tr-CDD/F congeners have been shown to be effective toxicity indicators. It has been reported that 2,3,7-TrCDD concentrations correlate well with TEQs,[30,13] and good correlations have also been found between 1,2,3-TrCDF and TEQs in several MSWIs.[31] However, it has been observed in other studies that the less chlorinated isomers only weakly correlate with TEQ and, therefore, cannot be used to predict total dioxin-like toxicity.[32] Therefore, we performed statistical analyses to examine the correlations between individual congener concentrations and TEQs, and the correlation coefficients between the TEQs, the congeners, and the homologues are given in Tables S4 and S5.

It can be seen from Table S4 that 13 of the 27 measured PCDD/F congeners showed good positive correlations with the TEQ ($R^2 > 0.9$, $p < 0.05$). Of the tetra- to octa-chlorinated congeners, six PCDF and three PCDD congeners correlated well with the TEQs. Of the Mo- to Tr-CDD/Fs, except for 2,3,7-TrCDD (which was found to correlate with the TEQ in previous studies[30,13]), we found that 2,8-DiCDF, 2,4,8-TrCDF, and 2,3-DiCDD had good positive correlations with the TEQs. However, compared with 2,3-DiCDD and 2,3,7-TrCDD, the concentrations of 2,8-DiCDF and 2,4,8-TrCDF were relatively high, and they were detected in all of the samples. The 2,8-DiCDF concentration was, on average, 5.87 times the 2,3-DiCDD concentration, and the 2,4,8-TrCDF concentration was, on average, 3.89 times the 2,3,7-TrCDD concentration. 2,8-DiCDF and 2,4,8-TrCDF were, therefore, more suitable as TEQ indicators for the incinerators studied. Interestingly, there was a strong correlation ($R^2 = 0.962$) between 2,4,8-TrCDF and 2,3,4,7,8-PeCDF, the latter being widely accepted as the
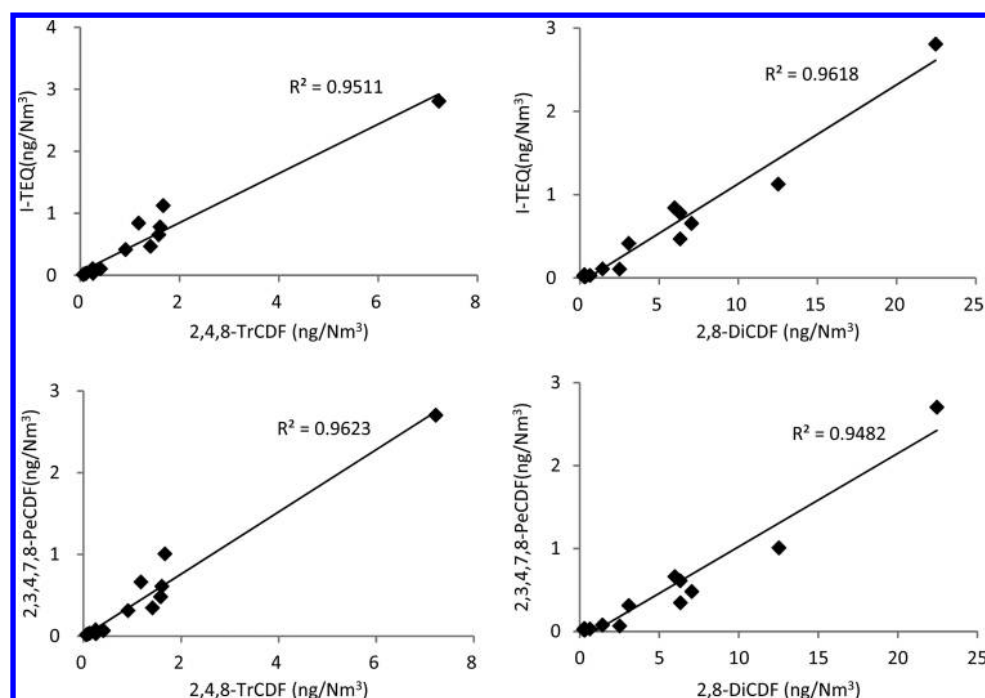
Figure 2. Correlations among 2,8-DiCDF, 2,4,8-TrCDF concentrations and the TEQs, and the 2,3,4,7,8-PeCDF concentrations.

Table 3. Average Ratios between the Concentrations of Some PCDF Congeners and the TEQs

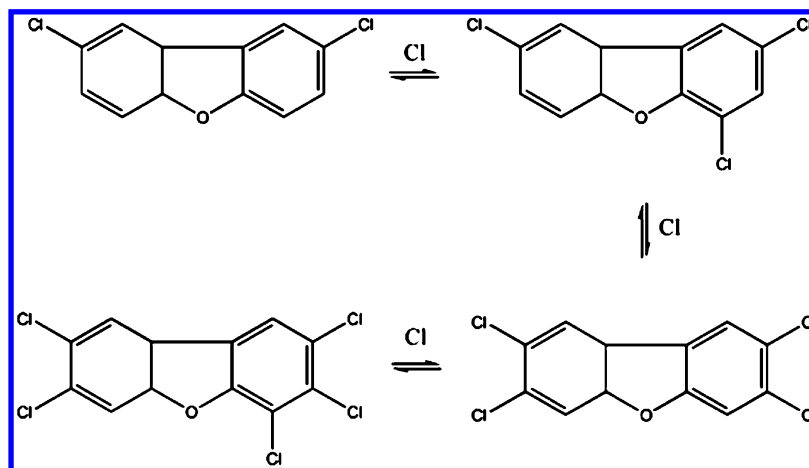|	MA	MB	MC	MD
2,8-DiCDF/2,4,8-TrCDF	3.65 ± 1.41	4.14 ± 1.12	6.48 ± 0.91	3.47 ± 0.42
2,4,8-TrCDF/2,3,4,7,8-PeCDF	3.70 ± 0.23	4.47 ± 2.99	3.70 ± 2.30	2.74 ± 0.16
2,8-DiCDF/2,3,4,7,8-PeCDF	13.57 ± 5.58	15.99 ± 5.50	23.10 ± 13.37	9.50 ± 1.07
2,8-DiCDF/I-TEQ	13.79 ± 8.12	12.90 ± 5.56	15.86 ± 6.52	7.83 ± 0.38
2,4,8-TrCDF/I-TEQ	3.60 ± 0.71	3.71 ± 2.96	2.52 ± 1.17	2.27 ± 0.27
2,3,4,7,8-PeCDF/I-TEQ	0.97 ± 0.16	0.79 ± 0.09	0.74 ± 0.14	0.83 ± 0.11

Figure 3. Possible formation pathway for 2,8-DiCDF, 2,4,8-TrCDF, 2,3,7,8-TeCDF, and 2,3,4,7,8-PeCDF.

most important contributor to the TEQ. 2,8-DiCDF also strongly correlated with 2,3,4,7,8-PeCDF ($R^2 = 0.948$). Some of the linear relationships found for 2,8-DiCDF and 2,4,8-TrCDF are shown in Figure 2.

To quantify and further assess this phenomenon, the ratios between the TEQs and the 2,8-DiCDF, 2,4,8-TrCDF, and 2,3,4,7,8-PeCDF concentrations were calculated and are shown in Table 3. It can be seen from Table 3 that there were a number of correlations between the TEQs and the individual

congener concentrations in both of the stack gas samples, and the standard deviations are relatively low. It has been suggested in previous publications that TEQ indicators are not applicable to all facilities,[30] and we propose, from the results of this study, that indicator compounds might be effectively used for incinerators with relatively stable operating conditions. Relatively constant ratios between the different congener concentrations and the TEQs were found in this study. Although the ratios shown in Table 3 were not consistent

between the four incinerators, they were stable for the samples from each individual incinerator. These ratios can be further quantified through repeat measurement, and they can be used as surrogate indicators in future assessments. The more stable the incinerator operation, the more effective these TEQ indicators will be.

There were fairly strong linear relationships between 2,8-DiCDF, 2,4,8-TrCDF, and 2,3,4,7,8-PeCDF (see the ratios and standard deviations in Table 3), and the concentrations decreased considerably with increasing chlorination level. Because these three congeners are structurally similar and strongly correlated, it appears possible that their formation mechanisms are related (see Figure 3). A chlorination pathway could cause the linear correlations and the lower concentrations of the more chlorinated congeners and might explain why 2,8-DiCDF and 2,4,8-TrCDF are potential TEQ indicators. The intermediate 2,3,7,8-TeCDF was not assessed because it was found at low concentrations and was not detected at all in several samples.

New online monitoring technologies have made it possible to predict TEQ from homologue concentrations. Although it was not accurate, PeCDF was used as a TEQ indicator in a study using vacuum ultraviolet single-photon ionization ion trap TOFMS as an online monitoring method.[21] The potential for using other PCDD/F homologues as TEQ indicators was tested in our study, and it can be seen, from Table S5, that many homologues had good correlations with the TEQs ($R^2 > 0.9$, $p < 0.05$), suggesting that some homologues could also be used as TEQ indicators. The DiCDF homologue concentration correlated well with the 2,8-DiCDF concentration ($R^2 > 0.97$, $p < 0.05$), meaning that 2,8-DiCDF is an excellent surrogate for the DiCDF homologue. A similar relationship was found between 2,4,8-TrCDF and the TrCDF homologue. In summary, 2,8-DiCDF and 2,4,8-TrCDF, DiCDF, and TrCDF can be used as TEQ indicators when monitoring PCDD/Fs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Tables S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Olie, K. Chlorodibenzo-p-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere* 1977, 6, 455−459.

(2) Hutzinger, O.; Choudhry, G. G.; Chittim, B. G.; Johnston, L. E. Formation of polychlorinated dibenzofurans and dioxins during combustion, electrical equipment fires and PCB incineration. *Environ. Health Perspect.* 1985, 60, 3−9.

(3) Liu, W.; Tao, F.; Zhang, W.; Li, S.; Zheng, M. Contamination and emission factors of PCDD/Fs, unintentional PCBs, HxCBz, PeCBz and polychlorophenols in chloranil in China. *Chemosphere* 2012, 86, 248−251.

(4) Anderson, D. R.; Fisher, R. Sources of dioxins in the United Kingdom: the steel industry and other sources. *Chemosphere* 2002, 46, 371−381.

(5) Wang, X.; Ni, Y.; Zhang, H.; Zhang, X.; Chen, J. Formation and emission of PCDD/Fs in Chinese non-wood pulp and paper mills. *Environ. Sci. Technol.* 2012, 46, 12234−12240.

(6) Buekens, A.; Cornelis, E.; Huang, H.; Dewettinck, T. Fingerprints of dioxin from thermal industrial processes. *Chemosphere* 2000, 40, 1021−1024.

(7) Gullett, B. K.; Ryan, J. V.; Tabor, D. Inclusion of $^{13}C_{12}$-labelled mono-, di-, and tri-chlorinated dibenzo-p-dioxin and dibenzofuran standards in US EPA methods 0023A/8290. *Chemosphere* 2001, 43, 403−406.

(8) Bacher, R.; Swerev, M.; Ballschmiter, K. Profile and pattern of monochloro-through octachlorodibenzodioxins and-dibenzofurans in chimney deposits from wood burning. *Environ. Sci. Technol.* 1992, 26, 1649−1655.

(9) Osera, H.; Thannera, R.; Grotheera, H. H.; Gullettb, B.; Natschkec, D.; Raghunathanc, K. Lowly chlorinated dibenzodioxins as TEQ indicators. A combined approach using spectroscopic measurements with DLR jet-REMPI and statistical correlations with waste combustor emissions. *Combust. Sci. Technol.* 1998, 134, 201−220.

(10) Wikström, E.; Tysklind, M.; Marklund, S. Influence of variation in combustion conditions on the primary formation of chlorinated organic micropollutants during municipal solid waste combustion. *Environ. Sci. Technol.* 1999, 33, 4263−4269.

(11) Gullett, B. K.; Dunn, J. E.; Raghunathan, K. Effect of cofiring coal on formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste combustion. *Environ. Sci. Technol.* 2000, 34, 282−290.

(12) Lundin, L.; Aurell, J.; Marklund, S. The behavior of PCDD and PCDF during thermal treatment of waste incineration ash. *Chemosphere* 2011, 84, 305−310.

(13) Ryu, J.-Y.; Mulholland, J. A.; Dunn, J. E.; Iino, F.; Gullett, B. K. Potential role of chlorination pathways in PCDD/F formation in a municipal waste incinerator. *Environ. Sci. Technol.* 2004, 38, 5112−5119.

(14) Usami, M.; Sakemi, K.; Tabata, H.; Kawashima, K.; Takanaka, A. Developmental toxicity of 2-chlorodibenzofuran in cultured post-implantation rat embryos. *Toxicol. In Vitro* 1993, 7, 259−264.

(15) Park, H.; Kim, J.; Chang, Y.-S. Prevalence of low chlorinated dibenzo-p-dioxin/dibenzofurans in human serum. *Chemosphere* 2013, 90, 1658−1663.

(16) Hites, R. A. Environmental behavior of chlorinated dioxins and furans. *Acc. Chem. Res.* 1990, 23, 194−201.

(17) Rordorf, B. F. Prediction of vapor pressures, boiling points and enthalpies of fusion for twenty-nine halogenated dibenzo-p-dioxins and fifty-five dibenzofurans by a vapor pressure correlation method. *Chemosphere* 1989, 18, 783−788.

(18) Liu, G.; Zheng, M.; Liu, W.; Wang, C.; Zhang, B.; Gao, L.; Su, G.; Xiao, K.; Lv, P. Atmospheric emission of PCDD/Fs, PCBs, hexachlorobenzene, and pentachlorobenzene from the coking industry. *Environ. Sci. Technol.* 2009, 43, 9196−9201.

(19) Ba, T.; Zheng, M.; Zhang, B.; Liu, W.; Xiao, K.; Zhang, L. Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. *Chemosphere* 2009, 75, 1173−1178.

(20) Nose, K.; Falandysz, J.; Wyrzykowska, B.; Orlikowska, A.; Noma, Y. By-side PCDD/Fs in technical PCB formulations of Kanechlor series. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* 2009, 44, 1528−1537.

(21) Tsuruga, S.; Suzuki, T.; Takatsudo, Y.; Seki, K.; Yamauchi, S.; Kuribayashi, S.; Morii, S. On-line monitoring system of P_5CDF

homologues in waste incineration plants using VUV-SPI-IT-TOFMS. *Environ. Sci. Technol.* **2007**, *41*, 3684−3688.

(22) Gao, H.; Ni, Y.; Zhang, H.; Zhao, L.; Zhang, N.; Zhang, X.; Zhang, Q.; Chen, J. Stack gas emissions of PCDD/Fs from hospital waste incinerators in China. *Chemosphere* **2009**, *77*, 634−639.

(23) Lundin, L.; Marklund, S. Distribution of mono to octa-chlorinated PCDD/Fs in fly ash from a municipal solid-waste incinerator. *Environ. Sci. Technol.* **2008**, *42*, 1245−1250.

(24) Gullett, B.; Dunn, J.; Bae, S.-K.; Raghunathan, K. Effects of combustion parameters on polychlorinated dibenzodioxin and dibenzofuran homologue profiles from municipal waste and coal co-combustion. *Waste Manage.* **1998**, *18*, 473−483.

(25) Wang, L.-C.; Lee, W.-J.; Tsai, P.-J.; Lee, W.-S.; Chang-Chien, G.-P. Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from stack flue gases of sinter plants. *Chemosphere* **2003**, *50*, 1123−1129.

(26) Li, X.-W.; Shibata, E.; Nakamura, T. Theoretical calculation of thermodynamic properties of polybrominated dibenzo-p-dioxins. *J. Chem. Eng. Data* **2003**, *48*, 727−735.

(27) Lohmann, R.; Jones, K. C. Dioxins and furans in air and deposition: a review of levels, behaviour and processes. *Sci. Total Environ.* **1998**, *219*, 53−81.

(28) Wyrzykowska-Ceradini, B.; Gullett, B. K.; Tabor, D.; Touati, A. PBDDs/Fs and PCDDs/Fs in the raw and clean flue gas during steady state and transient operation of a municipal waste combustor. *Environ. Sci. Technol.* **2011**, *45*, 5853−5860.

(29) Blumenstock, M.; Zimmermann, R.; Schramm, K.-W.; Kaune, A.; Nikolai, U.; Lenoir, D.; Kettrup, A. Estimation of the dioxin emission (PCDD/FI-TEQ) from the concentration of low chlorinated aromatic compounds in the flue and stack gas of a hazardous waste incinerator. *J. Anal. Appl. Pyrolysis* **1999**, *49*, 179−190.

(30) Oh, J. E.; Touati, A.; Gullett, B. K.; Mulholland, J. A. PCDD/F TEQ indicators and their mechanistic implications. *Environ. Sci. Technol.* **2004**, *38*, 4694−4700.

(31) Gullett, B. K.; Wikström, E. 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. *Chemosphere* **2000**, *40*, 1015−1019.

(32) Blumenstock, M.; Zimmermann, R.; Schramm, K. W.; Kettrup, A. Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line real-time detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry. *Chemosphere* **2001**, *42*, 507−518.