A COMPARISON OF PCDD/F PROFILES IN COMBUSTION RESIDUES

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Abstract
PCDD/F isomer profiles (26 individual PCDD and 46 PCDF; P = 4 to 8) are established for four different filter dust samples, derived from 2 selected incinerator plants. The plants are selected because of their specific emission profiles: a fluid bed unit having had high I-TEQ emissions, despite a highly chlorinated PCDD/F-profile, and a mechanical grate unit with a PCDD dominated profile. The resulting fingerprints are examined with respect to distribution of isomer groups, PCDD/PCDF-ratio, weight average level of chlorination, I-TEF part of 2,3,4,7,8-PeCDF and inverted toxicity ratio (PCDD/F to I-TEQ). The relative importance of 2,3,7,8-congeners and other isomers is evaluated and compared to results from a conventional plant and two round robin testing samples, analysed under similar conditions, and to data from selected literature references.

Introduction
Dioxin fingerprints have been identified in numerous media, in emissions from chemical sources (e.g. electrode sludge, pentachlorophenol), thermal and metallurgical plant, air, depositions, river sediment and sewage sludge[1]. Dioxin analysis often only centers on I-TEQ-values and *dirty 17* profiles, possibly supplemented with data on PCDD/F isomer groups (P = 4-8). Relatively few authors studied complete fingerprints, sometimes including low-chlorinated congeners. Alternative PCDD/F formation routes result in different distributions of PCDD/F isomers, suggesting that measured PCDD/F isomer distributions provide clues on how formation occurred[2]. Some authors present profiles[2], obtained from experiments involving chlorophenol precursors[3], or in chlorinating DD, DF, active carbon, and de-chlorinating OCDD and OCDF[4, 5] or in fly ash desorption[6].
Several authors studied thermodynamic equilibrium relationships of PCDD/F isomers. Fly ash isomer patterns and relative Gibbs free energy of formation show similarities, but also differences[5]. The experimental distribution of mono-chlorinated isomers was used to predict isomer distributions, formed by chlorination of DD and DF. Agreement between predicted and measured PCDF isomer distributions supports the hypothesis that DF chlorination plays an important role in PCDF formation[2]. However, DD chlorination is not a dominant PCDD formation mechanism[2]. PCDD isomers with a chlorination pattern at alternating carbon sites, e.g. 1368-and 1379-TCDD, are favoured due to the abundance of 246-chlorinated phenol precursors. OCDD and OCDF produced by de novo synthesis can undergo catalytic de-chlorination producing a broad distribution of PCDD/F products in which 1,4,6,9 isomers are favoured, as follows from an excellent review[2].

Materials and Methods
Analytical procedure. The samples are analysed at the University of Amsterdam: 5 g of fly ash is first treated with 3% HCl. After washing with water two neutral ^{13}C labelled internal standards are added. The sample is extracted with toluene in a soxhlet apparatus for 24 hours or more. The extract is cleaned with a carbon column. The extract is further purified using acid, base and silver nitrate modified silica gel, and aluminium oxide.
Quantification was done with a Kratos Concept High-resolution mass spectrometer and the separation of isomers is performed with a 60m highly polar Supelco 2331 column.
Samples. Plant A features an internally circulating fluidised bed combustor, burning Municipal Solid Waste (MSW), commercial and industrial waste, hospital waste, sewage sludge, as well as leachate. A boiler, featuring 2 radiation-passes and 1 convection-pass, a cyclone pre-separator, a neutraliser with turbine injecting lime slurry, an in-line activated carbon injection and a baghouse filter follow the fluid bed. This plant attracted much attention in 2005, when one line reached an emission level of almost 700 ng I-TEQ/Nm^3!

The now obsolete **plant B** features a reverse reciprocating grate furnace, surmounted by a cooling tower, and followed by an electrofilter ESP, in-line injection of activated carbon, a lime slurry neutraliser reactor and a baghouse filter. It burns MSW and is always low in PCDD/F. These feature an exceptionally high PCDD to PCDF ratio, which is possibly due to the high moisture content (typically 35 vol.%) of flue gases.
Samples are taken in the course of dioxin abatement studies relating to both plants. The samples have been studied thoroughly and more info is presented in parallel papers. Sample **plant C** is from a conventional mechanical grate incinerator in the Netherlands.

Results and Discussion
Isomer Profiles and derived parameters. PCDD/F levels in **plant A** (Table 1) rapidly rise in a sequence: boiler, cyclone, baghouse BH. Compared to the BH-values boiler dust only reaches 0.33% (PCDD), 0.42% (PCDF), or 0.34% (I-TEQ), whereas the relatively coarse cyclone dust already attains 26.7% (PCDD), 43.6% (PCDF) or 53.6% (I-TEQ). Weight average level of chlorination values are unexpectedly high, probably related to the very high Cu-content (0.6-2 wt.%!) of fluid bed fly ash. **Plant B** has an unusually high PCDD to PCDF ratio and its ESP-dust is selected for that purpose. Remarkably, PCDF are higher chlorinated than the PCDD. Earlier sample analyses from **Plant C** and the 2 **Round Robin** samples are used as a reference and for comparison. **I-TEQ values** are very low for samples A-Boiler and B-ESP. In all analyses considered the contribution of 2,3,4,7,8-PeCDF to I-TEF is very low (16-27%, against a more usual 35-40%); the inverted toxicity ratio (PCDD/F to I-TEQ), usually in a range of 35 to 50, is exceptionally high for all four A –B samples studied, which indicates that a 2378 substitution is not favoured for these samples and/or that chlorination levels are elevated (Table 2).
PCDD and PCDF isomer profiles. In PCDD distributions few peaks (Table 4) represent the bulk of their respective isomer groups. PCDF are rather evenly distributed.
TCDD. The most important isomers are 1368 and 1379, their sum averaging 49% for all 6 samples studied, yet totalling 89 and 88% for B-ESP and A-BH, which is unusually high. Thus, this TCDD distribution provides a formidable discriminator, with the sum of 2 peaks totalling between a low 9.4% for a round robin sample and almost 90% for two samples. Literature figures are respectively 13 and 9%[2] and 14.5-42.3 and 13.2-32.6%[6], confirming a wide spread between different plants (cf. Table 4). A third large peak is being disregarded in this analysis, since it groups 5 different isomers.
PeCDD. The sum of three peaks {12368, 12379 and (12479 + 12468)} averages 73.5% for all samples, yet totals 95 and 91.5% for B-ESP and A-BH. All remaining isomers attain only a few % of the PeCDD total.
HxCDD. Two composite peaks dominate: (124679+124689+123468; 23679+123679). The first peak represents 90% of the total for the A-BH sample.
HpCDD. Both **1234678** and 1234679 are of comparable importance.
PCDF. The 38 **TCDF** isomers are spread over 25 peaks, with 2467 as largest individual peak, yet only showing 7.3% (range 3.3-11.9%)! The 28 **PeCDF** isomers are rather well separated (23 peaks), with 23467 as largest peak (16.3%; range 7.8-29%)! The main other peaks are 23468 (8.2%; range 4.7-11%) and **23478** (7.5%; range 4.1-9.7%)**.** **HxCDF** has 3 important single-isomer peaks: 123467 (13%; range 6.3-16%), **123478** (12.8%; range 9-17.8%)**,** **123678** (12%; range 8.8-14.3%)**.**
Based on both internal variability and relative size the following peaks are selected as suitable candidates for fingerprint discrimination exercices: 1368, 1379, **2378,** 1478, 12369, 12389 for **PCDD** and 3467, 1289, 23467, 234678, 1234678 for **PCDF.**

Conclusions
A large number of isomers has been analysed individually and the results are compared with various literature data. Not all individual isomers are separated and isomers identified in literature vary in number and kind (Table 3a/b), limiting possibilities for a direct comparison. Nevertheless, no disparities within PCDF were identified with the various references studied, whereas PCDD is sample-specific. It follows that TCDD and PeCDD profiles are excellent choices for screening samples.

Sample B-ESP, with high PCDD to PCDF ratio, is quite exceptional. Sample A-BH also markedly diverges in fingerprint, e.g. when compared to the upstream boiler and cyclone separator samples from the same plant. The question is raised whether this strong modification in profile is a consequence of lime dechlorination.

Table 1. PCDD/F Isomer groups and derived parameters

	A-Boiler	**A-Cyclone**	**A-Baghouse**	**B - ESP**	**C**	**RR**	**RR1**
T4CDD,% of PCDD	0.3	0.5	3.6	11.1	3.4	5.6	3.4
T5CDD,% of PCDD	1.5	2.0	7.3	25.1	21.1	12.1	6.3
T6CDD,% of PCDD	18.3	11.2	39.2	38.9	16.9	18.4	18.3
T7CDD,% of PCDD	24.7	26.4	16.1	14.2	22.7	27.2	23.5
T8CDD,% of PCDD	55.2	59.9	33.8	10.8	35.9	36.7	48.5
PCDD, ng/g	**0.81**	**65.94**	**247.36**	**3.12**	**24.31**	**32.95**	**7.05**
T4CDF,% of PCDF	1.5	3.9	6.8	22.1	27.8	19.3	18.0
T5CDF,% of PCDF	5.3	9.9	11.1	18.7	33.5	20.1	22.3
T6CDF,% of PCDF	13.3	18.2	17.9	17.0	11.0	28.8	17.5
T7CDF,% of PCDF	41.2	38.7	34.1	20.6	24.0	22.8	24.2
T8CDF,% of PCDF	38.7	29.3	30.1	21.6	3.8	9.1	18.0
PCDF, ng/g	**0.85**	**88.24**	**202.12**	**0.53**	**18.47**	**36.23**	**11.33**
PCDD/F, ng/g	**1.65**	**154.17**	**449.49**	**3.65**	**42.77**	**69.18**	**18.39**
I-TEQ, ng/g	0.011	1.73	3.23	0.030	0.63	1.39	0.38
Toxic. Ratio, -	149.6	89.1	139.2	120.4	68.0	49.7	48.9
Cl-PCDD, -	7.33	7.43	6.69	5.88	6.67	6.77	7.08
Cl-PCDF, -	7.10	6.79	6.70	6.01	5.42	5.82	6.02
PCDD/PCDF, -	0.96	0.75	1.22	5.89	1.32	0.91	0.62

Table 2. Ratio of the 2,3,7,8 substituted congeners to their own isomer group

Isomers	**Congener**	**A-Boil**	**A-Cycl**	**A-BH**	**B - ESP**	**C**	**RR**	**RR1**	**Ref 2**	**Ref 6**
TCDD	**2,3,7,8**	2.18	1.84	0.20	0.14	2.39	3.7	13.5	4	0.12-9.2
PeCDD	**1,2,3,7,8**	2.42	3.71	0.91	0.76	4.41	8.4	16.3	8	1.2-8.6
HxCDD	**1,2,3,4,7,8**	1.01	2.86	0.58	0.79	5.75	6.8	4.1	6	1.7-3.4
	1,2,3,6,7,8	2.49	8.39	1.45	4.20	6.65	10.6	6.5	9	6.9-8.7
	1,2,3,7,8,9	1.48	5.32	1.15	3.46	5.16	9.2	7.1	9	4.1-4.7
HpCDD	**1,2,3,4,6,7,8**	56.5	57.6	58.6	54.9	47.8	55.9	54.8	52	51.2-61.6
TCDF	**2378**	5.4	3.1	1.9	6.7	3.2	6.6	3.2	3	_
PeCDF	**12378**	9.1	13.6	5.1	9.7	11.3	8.1	11.3	< 9	5-10.3
	23478	8.8	7.4	5.7	9.8	4.2	8.5	4.2	7	7.7-10.2
HxCDF	**123478**	15.2	13.0	9.0	17.7	12.2	10.7	12.2	< 13	6.6-8.8
	123678	14.3	12.6	8.8	13.3	12.9	9.7	12.9	< 19	7-10.1
	123789	5.1	4.2	2.8	2.5	1.3	1.4	1.3	1	1.35-2.8
	234678	3.0	20.4	18.3	15.5	10.3	11.3	10.3	10	7-13.3
HpCDF	**1234678**	52.9	58.1	35.8	73.8	76.2	60.6	76.2	73	36.7-69.7
	1234789	12.6	14.3	17.2	4.4	5.1	10.6	5.1	6	7.4-14.6

Ref. 2: all values were read from Figures; < means that there are 2 isomers under the same peak.

Table 3a. Number of peaks separated (denoted as single/twin/triple… isomer peaks)

	MCDD	DiCDD	TrCDD	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Number	2	10	14	22	14	10	2	1
This work	-	-	-	10/4/3/5	8/6	5/2/3	2	1
Ref. 6	-	-	-	9/6/3/4	5/6/3	6/4	2	1

Table 3b. Number of peaks separated for various analyses

	MCDF	DiCDF	TrCDF	TCDF	PeCDF	HxCDF	HpCDF	OCDF
Number	4	16	28	38	28	16	4	1
This work	-	-	-	18/12/8	18/10	10/6	4	1
Ref. 6	2/2	4/-/6/5	5/6/6/_/5	10/4/3/4/5/12	12/2/3/4/5	12/4	4	1

Table 4. Main TCDD, PeCDD and HxCDD-peaks, as a % of the isomer group's total

Sum of the Main peaks	**A-Boil**	**A-Cycl**	**A-BH**	**B - ESP**	**C**	**RR**	**RR1**	**Ref 2**	**Ref 6**
1368 + 1379	88.4	88.7	53.9	40.8	27.5	34.9	9.4	21	28
12368 + 12379	55.4	68.3	44.1	56.7	34.5	33.9	24.4	27	33
Id. + 3rd peak	95	91.5	74.8	83.3	69.8	58.5	41.8	48	68
2 HxCDD peaks	90.8	96.2	79.2	94.6	76.2	65.1	76.3	67	64

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