

THERMAL BEHAVIOR OF PCDD/PCDF IN FLY ASH FROM
MUNICIPAL INCINERATORS

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Abstract

The effect of thermal treatment of fly ash on the behaviour of PCDD/PCDF was studied in the range between 120 and 600° C. Annealing at 300° C (2 hrs) resulted in an increase of PCDD/PCDF concentration by a factor of 10 to 15. At 600° C degradation to concentrations below 0.1 ng/g is observed.

Introduction

Following the discovery of polychlordibenzodioxins, PCDD, and polychlordibenzofurans, PCDF, in fly ash of municipal waste incinerators by K. Olie et al. (1), their confirmation and first quantitative determination by H.R. Buser et al. (2), the phenomenon was investigated in various aspects. Attempts to correlate the formation of PCDD/PCDF with the composition of the input refuse failed. Neither could the emission of PCDD/PCDF be correlated with the emission of HCl (3) or with that of HCl, SO₂, NO_x and CO (4). To date formation mechanisms are discussed on basis of laboratory experiments (5). The debate of alternative formation paths (via chlorinated precursor compounds or via de novo synthesis from organics with natural chlorine donors) is still going on.

An answer to these questions might be obtained by investigation of thermal reactions of the fly ash itself. The possibility of gas-phase-particulate interaction was studied by Eiceman and Rghei, and dechlorination of TCDD on fly ash reported (6,7).

In our experiments the thermal behavior of PCDD/PCDF on fly ash was investigated between 120° C and 600° C as a direct contribution to the chemistry of incinerator processes.

Experimental

Materials: A large quantity of fly ash, obtained from the electrofilter system of a municipal incinerator was thoroughly homogenized and divided into identical fractions.

Annealing experiments: The homogeneous fly ash samples (20 g) were placed in a crucible and heated in a furnace for two hours at temperatures of 120, 200, 300, 400, 500, and 600° C respectively. The furnace temperature was controlled to $\pm 4^\circ$ C. During the annealing a stream of air (40 l/h) was passed through the furnace and - at the gas outlet of the furnace - through a condensation equipment consisting of a 70 cm long quartz tube and two washing bottles in series, each containing 50 ml toluene. After the experiment the quartz tube was rinsed with 2 x 10 ml toluene.

The annealing experiment was carried out for each temperature in duplicate. The residues from the two experiments were combined; representative samples for analysis were obtained by milling, dividing and mixing. The toluene solutions from the washing bottles were also combined, mixed and divided to give an average sample. The same treatment was carried out with the rinsing solutions.

Analysis: 10 g of the solid was digested with 60 ml 4 N HCl, the residue centrifuged, freeze dried and extracted by refluxing with toluene. After addition of 50 ng of C-13 labeled 2,3,7,8 T4CDD and OCDD the extracts were cleaned up using a combination column of 2 g silica gel and 4 g Florisil (1% water). For details of the analytical procedure see reference (8). The toluene solutions from the quartz tube rinsing and from the washing bottles were treated by the same procedures after addition of the C-13 labeled internal standards. The respective toluene-diethylether (90:10) eluates were concentrated and analyzed by GC/MS.

Gaschromatography was performed on a Hewlett-Packard Mod. 5780 with splitless on column injection on an uncoated precolumn (3 m length) which was coupled to a DB-5 column (30 m length, 0,32 mm i.d.). The temperature program was: 3 min isothermal at 105° C, 20°/min to 200°, 5°/min to 275° C. Helium was used as carrier gas.

Mass spectrometry: A mass selective detector Mod. 5970 (Hewlett-Packard) with a workstation was operated in multi-detection mode (1 cycle/sec). Selected masses for the respective compounds monitored were: T4CDD 319.9; 321.9; P5CDD 353.9; 357.9; H6CDD 389.8, 391.8; H7CDD 423.8, 425.8; OCDD 457.7, 459.7; T4CDF 305.9, 307.9; P5CDF 339.8, 341.8; H6CDF 373.8, 375.8; H7CDF 407.8, 409.8; OCDF 441.7, 443.7. The two C-13 labeled internal standards were monitored by 331.9, 333.9 and 469.7, 471.7 respectively. The congeners were identified on basis of their correct isotope mass ratios and their retention times. The concentrations were evaluated via experimentally determined substance specific response factors and the two internal standards. At PCDD/PCDF concentrations of 40 to 120 ng/g the confidence limits (95% probability) are $\pm 10\%$ for triple measurements.

Results and Discussions

The data for the behavior of PCDD/PCDF during 2 hrs isothermal annealing at 120, 200, 300, 400, 500 and 600° respectively are shown in table 1 and table 2. In part A of the tables the concentrations in the fly ash are listed. Part B contains the concentrations of compounds which had been vaporized during the experiment and recovered in the quartz tube and in the washing bottles. These values relate to the sum of vaporized congeners (in ng) per gram initial fly ash. On the last line of each table the total sum (A+B) of analyzed PCDD/PCDF is evaluated.

Behavior of PCDD: The non-treated sample has a total PCDD concentration of 395 ppb. The pattern shows a maximum with OCDD and H7CDD with a distinct decrease towards the lower chlorinated compounds. The concentration range and the compound pattern remain practically unchanged up to 200° C. At 300° C an overall increase of the total PCDD up to 3915 ppb takes place. The individual congeners are increased to a different extent: The OCDD is increased from 120 to 640 ppb, i.e. by a factor of 5. The corresponding factors are for the H7CDD ~10, for the H6CDD ~20, for P5CDD ~15 and for T4CDD ~4. The fraction vaporized at this temperature is negligible (table 1B). By annealing at 400° C a complete different picture is obtained: The sum of PCDD in the residue is 90 ppb, the vaporized fraction is 280 ppb. In comparison with the non-treated sample the concentration in the fly ash has been reduced to 23%. Besides the concentration maximum in the residue has been shifted to the P5CDD and in the vaporized amounts as well. At 500° C a further degradation takes place resulting in a concentration of ca. 4 ppb. Finally at 600° C the PCDD are decreased below 0.1 ppb both in fly ash and in the collecting solutions.

Behavior of PCDF: In the non treated sample the total PCDF is comparable with the PCDD, however, in a reversed pattern the maximum of the concentration is with compounds containing 4 and 5 chlorine atoms (table 2). In the annealing experiments the behavior of PCDF is similar to the PCDD: Practically no effect is noticed up to 200° C. At 300° C PCDF is additionally formed to give a total concentration of 4577 ppb, an enhancement by a factor of ~15. The congeners with 5 to 7 chlorine atoms are preferably formed with a maximum concentration of 1570 ppb P5CDF. As may be seen from table 2 B the vaporization at 300° C is negligible. At 400° C the formation processes are superimposed by degradation and volatilization. Compared with the non-treated sample the sum of residual and volatilized PCDF (total ca. 1600 ppb) is still higher by a factor of ~4; more than 70%, however, are released to the gas phase. In comparison with the PCDD, the PCDF show a higher chemical stability against thermal degradation. This is further confirmed by the results from the 500 and 600° experiments. In total at 500° C 256 ppb PCDF survive the 2 hrs thermal treatment, with 93% being released into the gas phase. At 600° C low, but still measurable concentrations (0.4 ppb) of PCDF remain in the residue.

Table 1: Thermal Behavior of PCDD in Fly Ash
(Concentration ng/g fly ash)

	non treated	120	200	temperature (°C)			
				300	400	500	600
A. FLY ASH							
O8CDD	120	120	90	640	6	0.2	<0.1
H7CDD	125	90	100	1000	15	0.2	<0.1
H6CDD	85	65	65	1640	22	1.	<0.1
P5CDD	45	35	40	570	35	1.	<0.1
T4CDD	20	15	15	65	13	2.	<0.1
sum (solid)	395	325	310	3915	91	4.4	<0.1
B. VAPORIZED							
O8CDD	-	-	-	0.2	9	0.3	≤0.1
H7CDD	-	-	-	0.4	45	0.8	≤0.1
H6CDD	-	-	-	0.8	88	2.	≤0.1
P5CDD	-	-	-	0.15	100	3.	≤0.1
T4CDD	-	-	-	0.1	37	3.	≤0.1
sum (vaporized)	-	-	-	1.6	280	9.	<0.1
total sum (A+B)	395	325	310	3916	370	13.5	<0.1

Table 2: Thermal Behavior of PCDF in Fly Ash
(Concentration ng/g fly ash)

	non treated	120	200	temperature (°C)			
				300	400	500	600
A. FLY ASH							
O8CDF	12	11	12	218	4	0.1	0.04
H7CDF	48	42	48	1030	37	0.4	0.1
H6CDF	56	51	61	1253	80	1.4	0.1
P5CDF	129	119	129	1570	187	8.	0.2
T4CDF	113	95	122	506	140	8	0.1
sum (solid)	358	318	372	4577	448	18	0.4
B. VAPORIZED							
O8CDF	-	-	-	<0.1	8	1.5	<0.1
H7CDF	-	-	-	0.4	75	15	1.
H6CDF	-	-	-	1.8	180	34	2.
P5CDF	-	-	-	1.	500	93	9.
T4CDF	-	-	-	1.	390	95	15.
sum (vaporized)	358	318	372	4.	1153	238	27
total sum (A+B)	358	318	372	4581	1603	256	27

The difference in the behavior of PCDD/PCDF may be explained by higher volatility and chemical stability of PCDF due to the molecular structure. Assuming that decomposition starts as unimolecular reaction by simple bond rupture, in the dioxin molecules the cleavage may occur at two centers containing carbon oxygen bonds, whereas with furans only one site with a C-O-C bond is available.

Conclusions

From the data the following conclusions may be arrived at.

1. Besides the already present dioxins and furans in particulates from waste incinerations, there is also a potential of additional PCDD/PCDF formation due to the presence of precursor compounds. This potential is activated by longer thermal treatment at a temperature range around 300° C.
2. Applying the results from our laboratory experiments to the processes in waste incinerators we must consider the possibility that at least part of the PCDD/PCDF is not formed directly in the combustion chamber but on the deposits of the inner surface of the boiler, preferably at the boiler off gas exit where the temperature is between 300 and 400° C. Also dioxin and furan formation on the dust filters which are often operated at temperatures around 250° C cannot be excluded.
3. The fact of additional PCDD/PCDF formation is directly related to the question of sampling conditions of the fly dusts. Direct sampling from off gas channels may be critical in cases where due to sampling techniques used, the dust samples are exposed to temperatures above 200° for a prolonged time, since the dioxin/furan content may change during the sampling process.
4. In a speculative interpretation the effect reported may also be used to explain the great variation of PCDD concentration as reported by Lustenhouwer et al. (9) in an overview on 25 incinerators. In the literature cited the data are divided into three groups with regard to PCDD:
 - low, total PCDD 532 ppb, the congeners ranging from 5 ppb (T4CDD) to 226 ppb (OCDD), the pattern maximum with H7CDD and OCDD.
 - medium, total PCDD 956 ppb, with a distinct concentration maximum for the H6CDD (326 ppb).
 - high, total PCDD 2810 ppb, also with the maximum with the H6CDD (1200 ppb). The data of the low concentration range correspond to our data of untreated fly ash with regard to concentration range and pattern. The data with medium and high concentrations might be explained if they were obtained from incinerators where the fly ash had been exposed to temperatures around 300° C for a longer time either during the sampling or due to a longer residence time in the electrostatic filters. The fact that the maximum of concentration is with the H6CDD - as also in our annealing experiment - is very much in favor of this assumption.

5. Dioxin decomposition can occur on the fly ash already at medium temperatures. With residence times in the range of hours nearly quantitative decomposition may be achieved at 600° C.

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