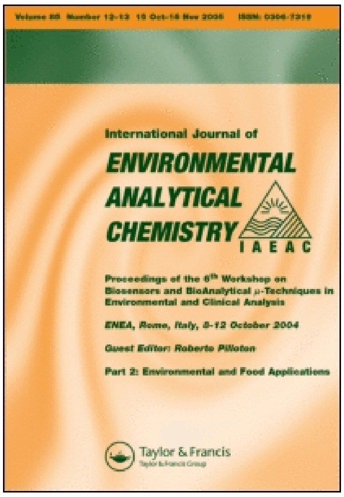

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Thermal Degradation of Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans on Fly Ash from a Municipal Incinerator

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Heating fly ash from a municipal incinerator under oxygen deficient conditions in the temperature range from 200 to 470 °C caused dechlorination of the PCDDs and PCDFs present in the matrix. The isomeric and congeneric composition of PCDDs and PCDFs was qualitatively and quantitatively determined by using GC/MS analysis. TCDD, TCDF, PnCDD and PnCDF concentrations increased in the temperature range from 200 to 370 °C followed by a decrease at higher temperatures. The higher chlorinated compounds showed no distinct concentration maximum and

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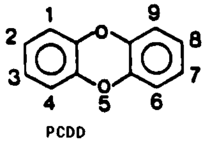
decreasing concentrations were observed starting in the 300 to 350 °C range. The 2,3,7,8-Cl substituted congeners were the most stable PCDDs and PCDFs in the fly ash matrix. Decomposition of all PCDDs and PCDFs was almost complete at 470 °C. OCDD and OCDF were added to hydrochloric acid-treated fly ash, which was preheated at 550 °C, thus purified from extractable PCDDs and PCDFs. Heating of this matrix in the same temperature range with pure OCDD and OCDF caused dechlorination of OCDD and OCDF to lower chlorinated congeners. The isomeric patterns found within each PCDD and PCDF group were different from those present in the original fly ash matrix. Within the tetra-, penta- and hexa-chlorinated PCDD and PCDF groups those isomers with two, three or four adjacent chlorine atoms were the least stable towards heating.

KEY WORDS: PCDDs, PCDFs, thermal degradation, fly ash, municipal incinerator.

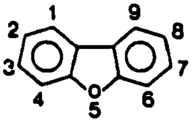
INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been found in flue gas as well as on fly ash from municipal incinerators since 1977.[1-7]

Some of these PCDDs and PCDFs show high toxic and persistent properties in the environment. However, the most toxic, 2,3,7,8-chlorine substituted congeners are usually found in minor concentrations on fly ash and in flue gas.[8,9]



PCDD



PCDF

Considering the emissions of PCCDs and PCDFs from flue gas into the environment and their potential health hazard it is important to know more about formation, adsorption, desorption and degradation processes of these compounds during the incineration.

It is proved that polychlorinated biphenyls (PCBs), chlorinated benzenes and chlorinated phenols are important intermediates in the formation of PCDDs and PCDFs during incineration processes.[10,11,22]

When fly ash was heated at a temperature of 300 °C under oxygen deficient conditions, a loss of about 90–90% of the total PCDD contents occured.[12] Recently thermal desorption losses of about 80% of the originally present PCDDs from fly ash have been reported.

The percentage lost was found to be independent of heating time and temperature.[13]

In contrast, another thermal treatment of fly ash at 300 °C, in the presence of air, showed an increase of PCCD and PCDF concentration by a factor 10.[14] Since further information on desorption and dechlorination processes of PCDDs and PCDFs from heated fly ash is very limited, more research in these areas has to be done to understand the chemistry of these incineration processes.

This paper reports the results from experiments where fly ash was heated under oxygen deficient conditions, with emphasis on the change in isomeric composition of the PCDDs and PCDFs. In the first series of heating experiments a quantitation was made of the change in PCDD- and PCDF-isomers, while in the second series the dechlorination and formation of lower chlorinated PCDDs and PCDFs from OCDD and OCDF was studied after addition to purified and HCl-treated fly ash. With the results of both experiments an attempt was made to describe thermal dechlorination mechanisms of PCDDs and PCDFs on fly ash after heating.

MATERIALS

Fly ash from a municipal incinerator (Zaanstad, the Netherlands) has been used in both the experiments. Purified fly ash was obtained by Soxhlet-extraction with toluene for 48 hours after hydrochloric acid treatment of the fly ash and heated at 550 °C for 2 hours.[15] No PCDDs and PCDFs have been detected on this fly ash after prolonged Soxhlet-extraction. Detection limits of TCDD and OCDD were 0.1 ng/g fly ash.

All solvents used were nanograde or HPLC-grade (Mallinckrodt).

A Pyrex tube 30 cm × 4 cm ID has been used to carry out the heating experiments. Glassware was thoroughly cleaned with a mild detergent and after rinsing with deionized water dried overnight at 300 °C. Before use glassware was rinsed with solvent.

As internal standard 1 or 2 ml of a mixture of ^{13}C-labeled 2,3,7,8-TCDD (27.9 ng/ml), 1,2,3,7,8-PnCDD (22.3 ng/ml), 1,2,3,4,7,8-HxCDF (26.3 ng/ml) and OCDD (24.5 ng/ml) has been added to the fly ash before Soxhlet-extraction. These compounds were obtained from Cambridge Isotope Laboratories (Woburn, USA).

Silicagel and basic alumina were purchased from Merck (Darmstadt). The silicagel has been treated with H_2SO_4, NaOH and $AgNO_3$ as described previously.[10,15,16]

OCDD and OCDF were synthesized as described earlier[17] and dissolved in toluene at concentrations of 31.5 mg/ml and 24.0 mg/ml respectively.

TEMPERATURE STUDIES

The pyrex tube was filled for about 30% with approximately 25 g of fly ash was kept at that temperature for 1 hour. The temperature was tube and its contents were purged with high grade helium (Hoekloos, Amsterdam, the Netherlands). A cold trap (CO_2/acetone) containing *n*-hexane was attached to the downstream end of the tube outside the oven. This was done to trap any desorbed organic material. The fly ash was quickly heated under a constant helium flow of 30 ml/min, until the desired temperature was reached. The fly ash was kept at that temperature for 1 hour. The temperature was measured with a calibrated thermocouple. The experiments with OCDD and OCDF, added to purified fly ash were carried out in the same way as described above. Only in these experiments 15 g purified fly ash with 6 μg OCDD and 5 μg OCDF was heated.

EXTRACTION PROCEDURE

The heated fly ash was stirred in 1 N hydrochloric acid for 1 hour. The acid treated fly ash was washed with deionized water on a Buchner funnel and freeze-dried. Extractions were carried out with toluene during 24 hours and in the dark to minimize the formation of foto-oxidation products from toluene. This method was reported to be the most efficient extraction procedure.[15] Since the purified fly ash already had pretreatment with HCl this was not applied after heating with OCDD and OCDF. The Soxhlet-extract was reduced to a few ml, transferred with hexane into a pear-shaped flask and then concentrated under a gentle stream of purified nitrogen.

RESULTS AND DISCUSSION

When fly ash from a municipal incinerator was heated at different temperatures under oxygen deficient conditions, changes in total concentrations of PCDDs and PCDFs occurred as shown in Table 1.

Table 1 Concentration of PCDDs and PCDFs on heated fly ash (ng/g)

Congener	*Heating temperature (°C)*											
	not	*200*	*215*	*250*	*290*	*300*	*350*	*370*	*400*	*420*	*450*	*470*
TCDF	266	243	214	230	219	241	281	232	178	79	18	6
PnCDF	252	459	456	524	536	539	251	162	133	50	17	2
HxCDF	292	275	296	284	290	215	95	67	54	16	7	2
HpCDF	195	n.a.	227	147	156	83	47	32	26	11	5	2
OCDF	54	n.a.	21	30	4	1	2	1.3	1.5	1	0.3	n.d.
Total	1059		1214	1215	1205	1079	676	494	393	157	30	19
TCDD	146	117	126	129	120	167	269	243	173	75	19	6
PnCDD	195	375	367	n.a.	477	478	308	180	160	57	19	8
HxCDD	360	388	353	386	393	330	140	109	76	20	9	3
HpCDD	421	n.a.	455	423	376	185	97	53	46	14	8	3
OCDD	257	n.a.	311	378	169	162	77	51	38	19	9	4
Total	1379		1612		1535	1322	891	636	493	185	64	24

n.a. = not analyzed.
n.d. = not detectable.

The observed variation in concentration is not equal for each congener-group. While the amounts of OCDD, OCDF, HpCDD and HpCDF are slightly increased at lower heating temperatures, a decrease in concentration was found at temperatures of 250 °C and higher. HxCDD and HxCDF concentrations remain constant up to 300 °C and above this temperature strongly decrease.

PnCDD and PnCDF concentrations increase dignificantly between 200 and 350 °C but above 350 °C a strong decrease is observed.

The concentrations of TCDDs and TCDFs show an increase at temperatures between 300 ° and 350 °C. This increase is most distinct for the TCDD-isomers. Above 370 °C the concentrations of TCDDs and TCDFs decrease strongly.

When the fly ash was heated at a temperature of 470 °C only 1–2 % of the originally present PCDDs and PCDFs has been detected. Until now these compounds were found to be thermally very stable with decomposition not found below 700 °C.[20] However thermal degradation and formation of PCDDs and PCDFs on fly ash in the presence of oxygen has been reported in the temperature range from

300 to 600 °C.[14] As our experiments were carried out under oxygen deficient conditions, it can be concluded that oxygen does not play a key role in this degradation process, which is in agreement with recently published results.[22]

As we clearly found a shift in contribution for each congener group to the total sum of PCDDs and PCDFs, it can be postulated that this is the result of thermal dechlorination of the higher chlorinated congeners (see Table 1). Dechlorination within this temperature range is most likely due to a catalyzed reaction within or on the fly ash particles.

Considering the toxic effects of the 2,3,7,8-chlorine substituted congeners, it is important to know whether or not these congeners show a similar shift in distribution pattern as the otherwise substituted isomers.

PURIFICATION AND ISOMERSPECIFIC ANALYSIS OF PCDDs AND PCDFs

Purification of the Soxhlet-extract was obtained by column chromatography as described earlier.[10,15,16,18] The extract from heated fly ash with OCDD and OCDF had no further clean-up and was analyzed directly on GC/MS. The dichloromethane-extract from the heated fly ash samples had an additional clean-up by means of fractionated HPLC. A Zorbax octadecylsilane column, 25 cm × 9.4 mm ID was used with methanol as eluent. PCDDs and PCDFs from the collected fractions were extracted with hexane, concentrated and then analyzed on GC/MS.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GC/MS analyses were carried out on a Hewlett-Packard 5984 GC/MS system, using the Selected Ion Monitoring (SIM) mode scanning the $M^+ + 2$ or $M^+ + 4$ masses with a dwell time of 100 ms.

Chromatographic conditions were as follows: GC column: fused silica, 60 m × 0.32 mm ID column with 0.2 μm SP 2331 stationary phase (Supelco). Helium carrier gas inlet pressure was 15 psi. Temperature programming: $T_1 = 140$ °C 2 min, 32 °C/min, $T_2 =$

Table 2 Relative isomeric composition of PCDD and PCDF congeners on fly ash when heated under oxygen deficient conditions (%)

Congener	*Isomer*	*Heating temperature (°C)*						
		not	*200*	*250*	*300*	*350*	*400*	*450*
TCDF	1,3,7,9 + 1,3,7,8	6	4.8	5.2	7.0	14.3	15.1	14.1
	1,3,6,8	4.2	3.0	2.9	4.2	9.8	11.2	10.2
	1,4,6,9	4.7	4.4	4.4	4.9	6.4	6.8	7.5
	1,2,7,8	7.5	7.1	7.4	6.0	5.4	5.2	5.4
	1,2,4,9	4.5	4.0	3.8	3.8	2.7	2.8	2.9
	2,3,4,7 + 1,2,3,9	6.5	6.5	6.8	5.9	3.7	3.2	3.4
	1,2,6,9	4.3	4.6	4.6	3.7	2.0	1.6	2.2
	2,3,4,6	5.2	5.6	5.8	3.7	1.6	1.2	1.3
	2,3,6,7	6.5	7.2	7.7	7.2	4.2	3.8	3.5
	3,4,6,7	5.6	6.7	6.9	3.4	1.7	1.8	1.1
TCDD	1,3,7,8	13.1	12	10.9	15.8	24.8	25.2	23.0
	2,3,7,8	1.4	1.4	1.4	2.6	9.2	8.9	11.2
	1,2,7,8 + 1,4,6,9	2.6	3.2	3.5	4.9	5.5	5.2	5.9
	1,3,6,8	27.3	20.6	22.6	16.5	15.6	16	15.7
	1,3,7,9	21.7	19.1	20.4	16.5	16.1	16.1	16.2
PnCDF	1,2,4,6,8	5.9	5.6		6.3	7.9	9.5	9.5
	1,3,4,7,9 + 1,2,3,6,8	10.5	9.3		11.4	14.5	14.3	13.1
	1,2,4,7,8	6.3	6.4		7.8	11.3	11.2	10.3
	2,3,4,8,9	6.2	6.6		5.9	4.8	3.9	4.1
	2,3,4,7,8	7.0	7.4		7.2	5.7	5.3	5.1
	2,3,4,6,7	12.0	12.6		10.1	6.1	5.6	5.4
PnCDD	1,2,4,7,8	7.4	7.3		9.1	11.6	12.7	11.3
	1,2,3,7,8	7.6	8.0		10.1	12.5	12.4	10.3
	1,2,4,8,9 + 1,2,4,6,7	4.3	7.2		7.7	6.7	5.5	7.8
	1,2,3,4,6 + 1,2,3,6,7	3.3	4.5		5.1	4.1	3.0	2.3
	1,2,4,7,9 + 1,2,4,6,8	32.5	28.0		24.8	28.3	29.1	26.7
	1,2,3,6,8	19.7	18.1		17.0	14.9	15.4	12.7
HxCDF	1,3,4,6,7,8	14.7	14.4	17.5	17.7	12.4	18.4	19.9
	1,2,3,6,7,8	12.3	12.7	13.2	16.7	11.5	16.7	15.7
HxCDD	1,2,3,6,7,9 + 1,2,3,6,8,9	32.2	32.1	32.4	35.4	36.1	37.2	33.5

250 °C. Injection port temperature: 250 °C.

For this column the eluting order of the various PCDD and PCDF isomers has been reported.[8,19]

Assuming that GC/MS response is equal for compounds with the same number of chlorine atoms quantitation was carried out with the internal ^{13}C-standards. The amount of HpCDDs and HpCDFs was calculated by intrapolation between ^{13}C-HxCDF and ^{13}C-OCDD.

Therefore, the concentrations of the 2,3,7,8-chlorine substituted isomers were compared with the sum of the other isomers of each congener-group. Results are graphically represented in Figures 1 to 5.

From these figures it can be concluded that the 2,3,7,8-chlorine substituted congeners are the most stable PCDDs and PCDFs in the thermal dechlorination process. The only exception was found for HpCDD as 1,2,3,4,6,7,9-HpCDD seems to be more stable towards heating than the 1,2,3,4,6,7,8-isomer.

Based on the isomeric distribution pattern it was examined whether a chlorine-substitution pattern exists, that leads to thermal less stable isomers. All isomers that show a different contribution in concentration within an isomer group compared to the original fly ash-extract are given in Table 2.

From this table and Figures 1 to 5, it can be concluded that the higher chlorine-substituted congeners show no or very little difference in isomeric composition. Some lower chlorinated isomers, however, show significant differences in distribution within one isomer group. Generally it is found that the tetra-, penta- and hexachlorinated PCDDs and PCDFs with two, three or four adjacent chlorine atoms were less stable than otherwise substituted congeners.

When purified, acid-treated fly ash was heated with OCDD and OCDF under oxygen deficient conditions a distinct difference in PCDD and PCDF distribution patterns was found, if compared with the first fly ash experiment. The results of these experiments are given in Table 3 and Figures 6 to 9.

From these experiments it can be concluded that OCDD and OCDF are thermally dechlorinated into lower chlorinated PCDDs and PCDFs. At first OCDD and OCDF are dechlorinated into HpCDDs and HpCDFs even at heating temperatures below 300 °C.

Formation of HpCDDs and HpCDFs show a maximum around 300 °C, and at higher temperatures these compounds decrease easily.

Formation of HxCDDs, HxCDFs, PnCDDs and PnCDFs starts

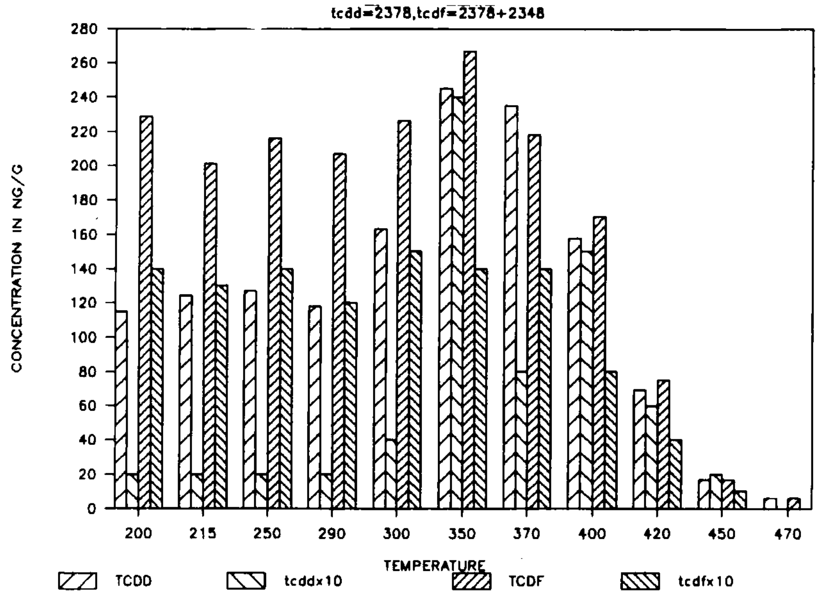


Figure 1 Thermal degradation of TCDDs and TCDFs on fly ash.

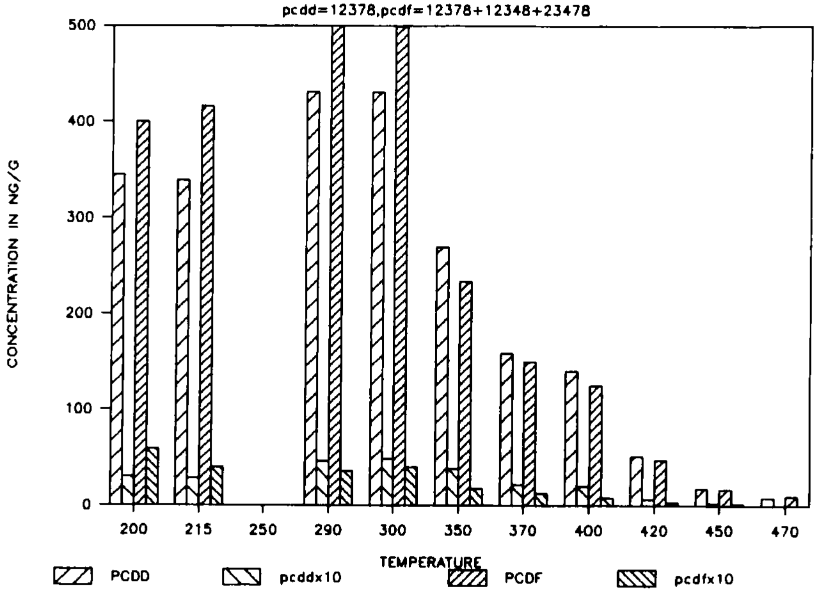


Figure 2 Thermal degradation of PnCDDs and PnCDFs on fly ash.

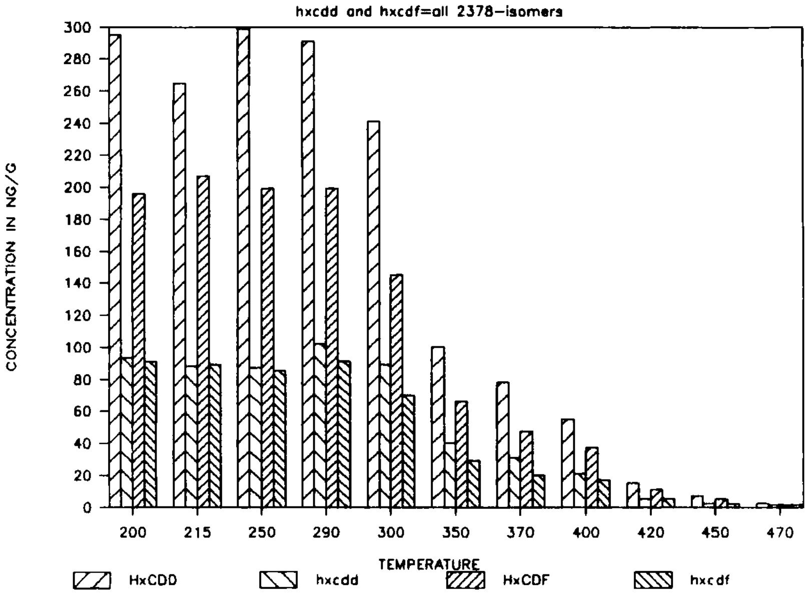


Figure 3 Thermal degradation of HxCDDs and HxCDFs on fly ash.

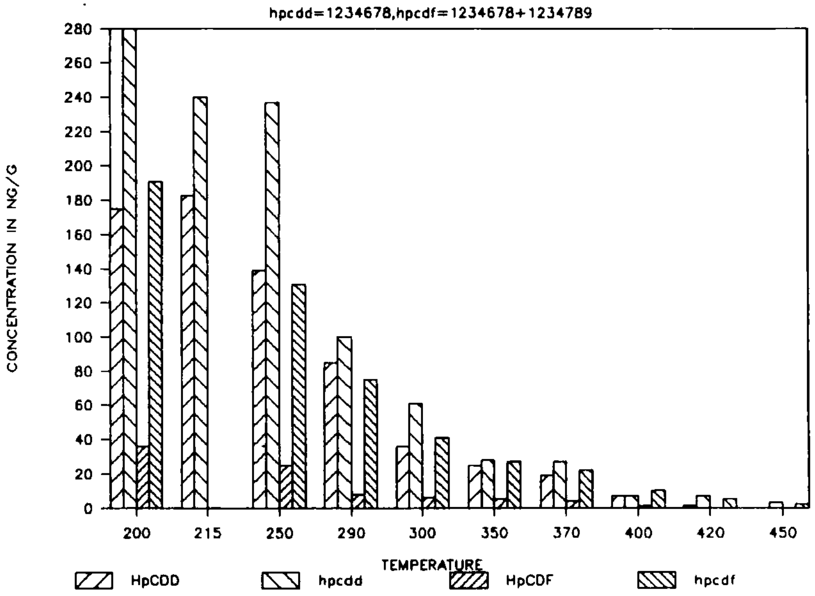


Figure 4 Thermal degradation of HpCDDs and HpCDFs on fly ash.

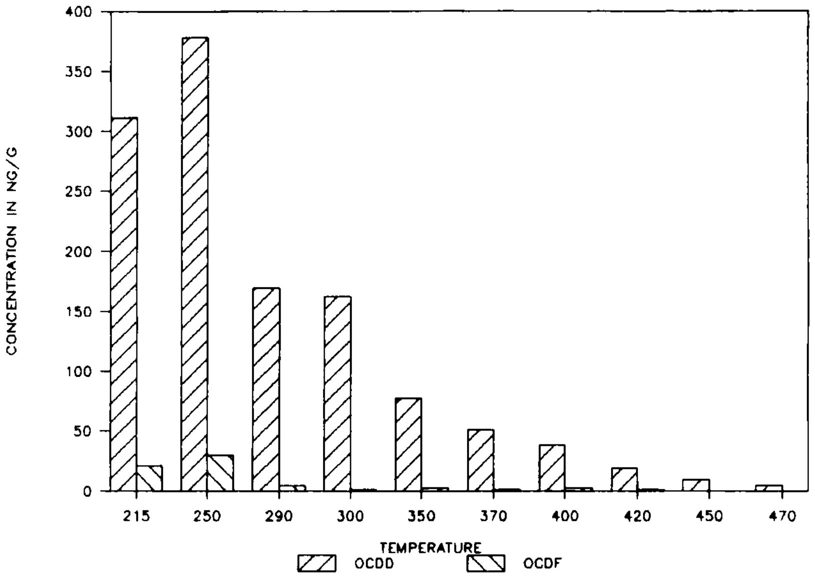
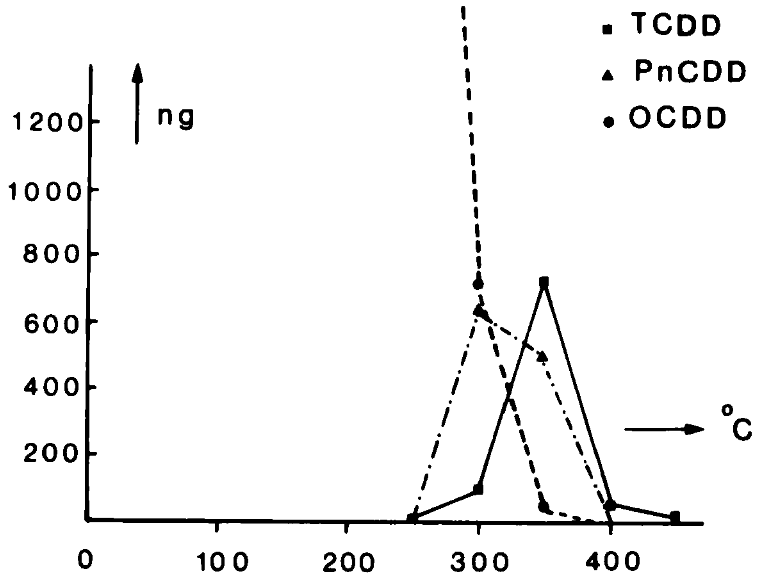


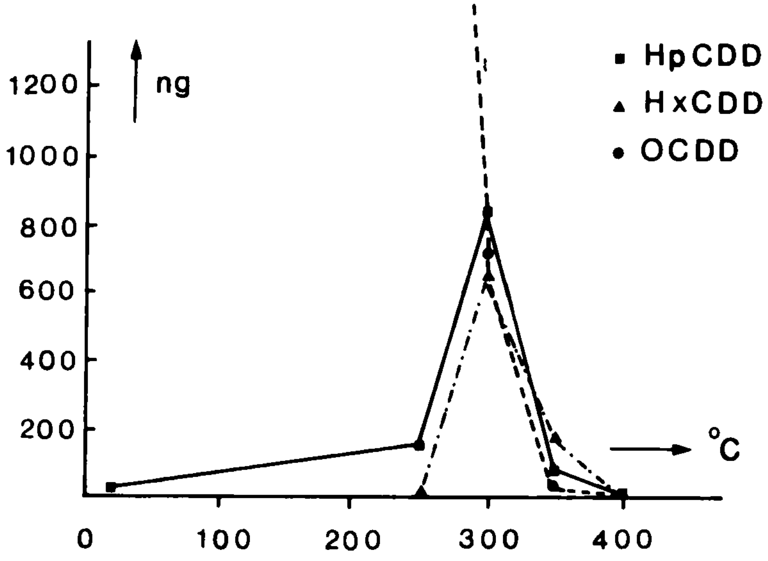
Figure 5 Thermal degradation of OCDD and OCDF on fly ash.

Table 3 Decomposition of OCDD and OCDF on acid-treated fly ash when heated under oxygen deficient conditions (ng)

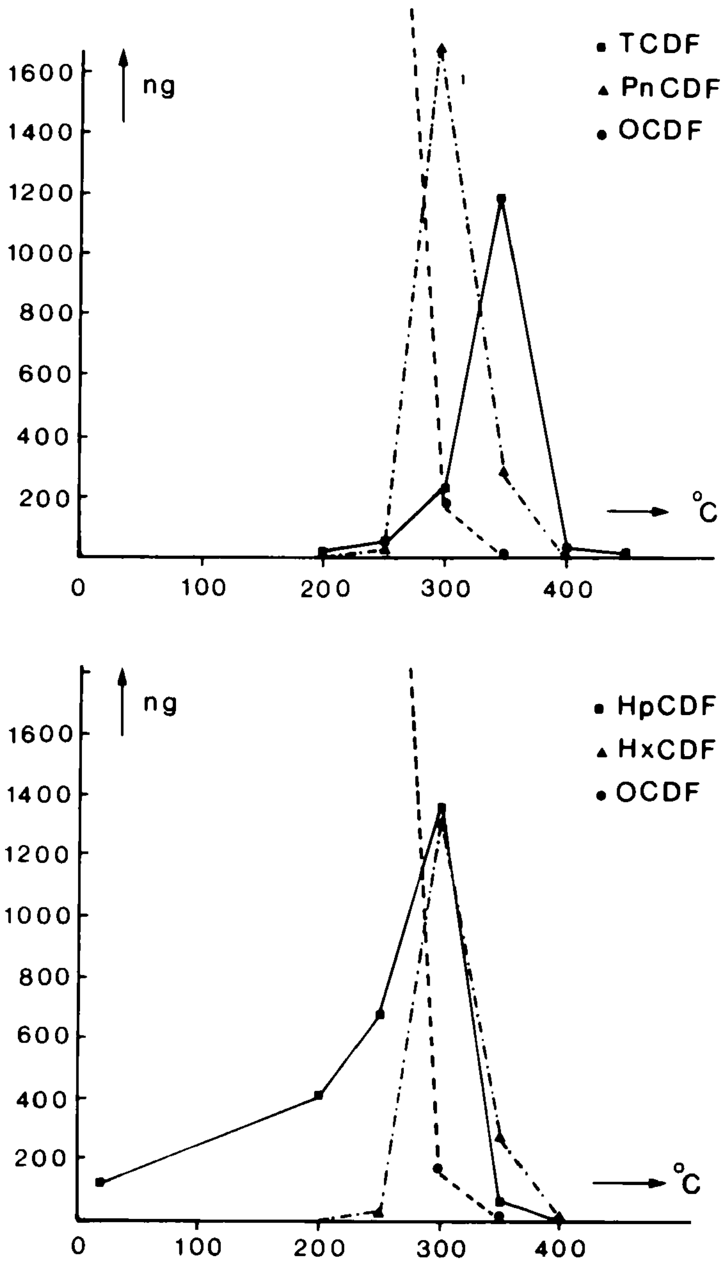
Congener	*Not heated*	*Heating temperature (°C)*						
		200	*250*	*300*	*350*	*400*	*450*	*added*
TCDF	n.d.	10	39	220	1183	26	12	n.d.
PnCDF	44	12	17	1670	1209	16	8	n.d.
HxCDF	9	4	31	1320	286	7	n.d.	2
HpCDF	300	420	688	1365	74	4	n.d.	123
OCDF	4647	4809	3399	182	10	15	6	4861
Total	5000	5255	4174	4757	2762	68	26	4986
TCDD	n.d.	n.d.	n.d.	152	724	11	n.d.	n.d.
PnCDD	n.d.	n.d.	n.d.	761	586	n.d.	n.d.	n.d.
HxCDD	n.d.	n.d.	3	649	176	n.d.	n.d.	n.d.
HpCDD	n.d.	n.d.	153	827	72	n.d.	n.d.	17
OCDD	6273	6047	4225	711	35	17	15	6291
Total	6273	6047	4381	3100	1591	28	15	6308

n.d. = not detectable





Figures 6 and 7 Thermal formation and degradation of lower chlorinated PCDDs from OCDD on acid treated, purified fly ash.



Figures 8 and 9 Thermal formation and degradation of lower chlorinated PCDFs from OCDF on acid treated, purified fly ash.

in the temperature range of 250 to 300 °C, with maximum concentrations between 300 and 325 °C.

TCDD and TCDF are formed highest around 350 °C.

At 450 °C more than 99% of the original amount of OCDD and OCDF added to the fly ash was decomposed. Based on these results it has to be assumed that the acid treatment of fly ash did not remove the catalyst responsible for the dechlorination and degradation process. This is in contrast with other experiments where no thermal degradation of OCDD on acid treated fly ash was found.[21]

Some remarkable differences between degradation of OCDD and OCDF have been observed. At first, the amount of the PCDF-congeners is much higher than that of the PCDD-congeners. The reason for this phenomena is not clearly understood. It can be suggested that some chlorine substitution positions in the dibenzofuran molecule are less stable towards heating than the corresponding positions in the dioxin molecule. This is supported by the fact that the formation of HpCDFs starts at very low temperature and probably also during Soxhlet-extraction at about 100 °C.

As a consequence TCDF formation already starts at 200 °C which is in contrast to the TCDD formation starting around 280 °C. The maximum formation of the tetra- and penta-chlorinated congeners is preceded by a strong decrease of HpCDDs and HpCDFs. This indicates clearly formation of lower chlorinated PCDDS and PCDFs by dechlorination of the higher chlorinated congeners.

It is valuable to know if the isomeric patterns of PCDDs and PCDFs are similar in both types of experiments. This can elucidate the importance of the catalyzed thermal dechlorination of OCDD and OCDF in the original fly ash experiments and also possible involvement of other formation mechanisms from precursors like chlorinated phenols and benzenes. If the isomeric distribution patterns at temperatures of 300 °C and 350 °C are compared, some important differences are noticed. Most of the PCDDs and PCDFs found in the experiments with OCDD and OCDF on purified fly ash are present in the same relative amounts as found in the experiments with the heated original fly ash.

For some individual PCDDs and PCDFs, however, a change in relative contribution was observed. These differences are shown in Table 4.

Table 4 Differences in relative contribution of PCDDs and PCDFs on purified fly ash with OCDD and OCDF, compared to the original fly ash, heated at 300 °C and 350 °C

Congener	*Isomer*	
TCDF	1,3,7,9 + 1,3,7,8	2 × higher
	1,3,6,8	1.5 × higher
	1,4,6,9	2 × higher
	1,2,4,9	not detected
	2,3,4,7 + 1,2,3,9	2.5 × lower
	2,3,4,6	not detected
	2,3,6,7	3 × lower
	3,4,6,7	not detected
TCDD	1,3,6,8	2 × lower
	1,3,7,9	1.5 × lower
	2,3,7,8	1.5–2 × higher, up to 20% at 400 °C
	1,2,7,8 + 1,4,6,9	1.5 × higher
PnCDF	1,2,4,6,8	2 × higher
	1,2,4,7,8	2 × higher
	2,3,4,7,8	2 × lower
	2,3,4,6,7	5 × lower
PnCDD	1,2,3,6,8	1.5 × higher
	1,2,4,7,8	1.4 × higher
	1,2,3,7,8	1.5 × higher
	1,2,4,8,9 + 1,2,4,6,7	1.3 × higher
HxCDF	1,3,4,6,7,8	1.7 × higher
	1,2,3,6,7,8	1.5 × higher
	1,2,3,4,6,7	3 × lower

It cannot be concluded that the formation of lower chlorinated PCDDs and PCDFs by heating the fly ash is uniquely caused by the stepwise dechlorination of OCDD and OCDF, also other formation mechanisms might be involved. New formation of PCDDs and PCDFs from precursors present in the fly ash has been reported after heating in the presence of oxygen [14] and very recently it has been shown that formation of PCDDs from polychlorinated phenols occurs on fly ash at 300 °C under oxygen deficient conditions.[22]

CONCLUSIONS

A catalyzed thermal dechlorination reaction of PCDDs and PCDFs occurs in or on fly ash particles from a municipal incinerator between 200 °C and 470 °C, under oxygen deficient conditions.

Pretreatment of the fly ash with hydrochloric acid does not diminish this catalytic activity in or on the fly ash.

The toxic 2,3,7,8-chlorine substituted PCDDs and PCDFs present on the fly ash are more stable towards heating than otherwise substituted congeners.

It is found that tetra-, penta- and hexa-chlorinated PCDDs and PCDFs with two, three or four adjacent chlorine atoms are less stable than otherwise substituted congeners.

Although dechlorination of the highest chlorinated PCDDs and PCDFs to lower chlorinated congeners appears to be the major pathway, other thermal formation mechanisms, e.g. from polychlorinated phenols and benzenes, are also involved.

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