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## The Formation of PCB on Fly Ash and Conversion to PCDD/PCDF

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### Abstract

Thermal experiments with fly ash in the temperature range from 300-400°C (reaction time 2hrs.) show the formation of up to 1660 ng/g PCB. In fly ash with  $^{13}\text{C}/^{12}\text{C}$  labelled carbon only pure  $^{12}\text{C}$  or  $^{13}\text{C}$  labelled PCB are detected, no mixed  $^{12}\text{C}_6$ - $^{13}\text{C}_6$  structures are found. This indicates that one-ring aromatic compounds are not precursors for PCB. Once formed from carbon PCB may act as precursors for PCDF, not, however, for PCDD.

### Introduction

In a series of investigations it has been shown that fly ash of municipal waste incineration plants acts as a source of a variety of halogenated aromatic compounds<sup>1-4</sup>). These compounds are formed in heterogeneous reactions on the fly ash surface from the residual carbon of incomplete combustion. This so called de-novo-synthesis includes the metal ion-catalyzed transfer of chloride to the carbon lattice with the formation of carbon-chlorine bonds, and the subsequent oxidation, also metal catalyzed, of the carbon lattice, which leads to the release of thermodynamically stable halogenated aromatic compounds<sup>5,6</sup>). Most investigations dealt with the polychlorodibenzodioxins (PCDD) and -furans (PCDF), but polychlorinated biphenyls are formed, too<sup>2,7,8</sup>). There are two ways for the formation of the biphenyl structure: 1) Via the release of the preformed biphenyl substructures from the carbon lattice, or 2) via the condensation of two phenyl rings. To get a closer look at the mechanistic aspects of the formation of PCB, experiments with carbon isotopes have been carried out. The results are presented here. Another point of interest are the reactions of PCB on fly ash. The ability to act as precursors in PCDF formation has been shown earlier, but only under pyrolytic conditions without fly ash<sup>9-11</sup>). By spiking fly ash or model mixtures with different PCB congeners, their influence in the formation of chloroorganics, especially PCDF, has been investigated.

### Experimental Methods

**Materials:** For the formation studies fly ash from a municipal waste incinerator was used as received. For the isotope experiments carbon-free fly ash was spiked with  $^{12}\text{C}$ -carbon (amorphous, 99,95%, Cambridge Isotope Laboratories) and  $^{13}\text{C}$ -enriched carbon (amorphous, 99%, Cambridge Isotope Laboratories). Three different mixtures were prepared: Mixture A with 40 mg  $^{12}\text{C}/\text{g}$  fly ash; mixture B with 43,4 mg  $^{13}\text{C}/\text{g}$  fly ash; mixture C with 20 mg  $^{12}\text{C}$  and 21,7 mg  $^{13}\text{C}$ , corresponding to a carbon ratio  $^{12}\text{C}/^{13}\text{C} = 1:1$ . For the experiments with PCB, fly ash (4% carbon) purified by extraction was spiked with decachlorobiphenyl (22 nmol/g FA), 2,3,4,4',5,5'-hexachlorobiphenyl (19,9 nmol/g FA) or 3,3',4,4',5,5'-hexachlorobiphenyl (13,2 nmol/g FA). Not spiked fly ash served as reference. In the experiments with model mixtures Florisil (Al-silicate) with 7% KCl and 0.4%  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was used.

# FORMATION

**Thermal Treatment and Analysis:** The mixtures were heated at 300°C for 2 hrs. in an apparatus described earlier with an air flow of 50 ml/min containing 150 mg water vapor /l. Volatile compounds were sampled by passing the gas stream through an XAD-2 resin trap. After the thermal treatment the fly ash sample and the resin were extracted by toluene. Clean-up and fractionation were performed with an alumina column using hexane, hexane:dichloromethane (95:5) and hexane:dichloromethane (1:1) as eluents. In the three isotope experiments  $^{13}\text{C}$ -decachlorobiphenyl was added as internal standard since this compound is not formed in measurable quantities. Both fractions of each sample, one including the PCB, and one including the PCDD/F, were measured by HRGC-HRMS (HP5890-Fisons Autospec) with a 50 m SP-2331 column in the multi detection mode at a resolution of 10000. Two masses characteristic for the  $^{12}\text{C}_{12}$ -,  $^{13}\text{C}_{12}$ -, and  $^{12}\text{C}_6\text{ }^{13}\text{C}_6$ -labelled PCDD, PCDF and PCB species were recorded. Quantification was achieved by the  $^{13}\text{C}$ -decachlorobiphenyl via substance specific factors for PCDD/PCDF and PCB. For the samples of the experiments with PCB spiked fly ash a mixture of  $^{13}\text{C}$ -PCB standards (Promochem) containing tri- to decachlorobiphenyl was used. These samples were measured by HRGC-MSD (HP5890-HP5970MSD) with a 30 m DB-5 column also in the multi detection mode by recording two masses.

## Results and Discussion

The thermal experiments with genuine fly ash show that as with PCDD/PCDF also PCB are formed from particulate carbon via the de-novo-synthesis. Average concentrations in ng/g obtained by annealing in air at 300°C are 200 mono-CIBP, 230 di-CIBP, 280 tri-CIBP, 380 tetra-CIBP, 390 penta-CIBP, 130 hexa-CIBP, 40 hepta-CIBP, 10 octa-CIBP, the nona- and decachloro congeners being below 2 ng/g in confirmation with results reported earlier <sup>2)</sup>. With an increase of the temperature to 350°C the formation drops from 1660 ng/g to 1050 ng/g total (60%), a further temperature increase to 400°C results in an additional decrease by 40% to 400 ng/g.

In order to contribute to the elucidation of the formation mechanism experiments with  $^{12}\text{C}$ - $^{13}\text{C}$  spiked fly ash were performed. Table 1 shows the results of the experiments.  $^{12}\text{C}_{12}$  and  $^{13}\text{C}_{12}$  means that all 12 carbon atoms of the biphenyl structure are either  $^{12}\text{C}$  or  $^{13}\text{C}$ ,  $^{13}\text{C}_6\text{-}^{13}\text{C}_6$  indicates that one ring contains 6  $^{12}\text{C}$  and the other 6  $^{13}\text{C}$ .

Table 1: Formation of PCB (concentrations in pmol/g fly ash)

compound	Mixture A	Mixture B	Mixture C	
	$^{12}\text{C}$ : 40 mg/g FA	$^{13}\text{C}$ :43,4 mg/g FA	$^{12}\text{C}/^{13}\text{C}=1$	
	$^{12}\text{C}_{12}$	$^{13}\text{C}_{12}$	$^{12}\text{C}_{12}$	$^{13}\text{C}_{12}$
monoCB	<0,1	<0,1	<0,1	<0,1
diCB	8	3	9	2
triCB	44	<0,1	128	<0,1
tetraCB	32	6	103	5
pentaCB	56	7	178	7
hexaCB	41	5	132	7
heptaCB	16	10	32	5
octaCB	4	14	3	6
nonaC-B	1	28	0,2	13
decaCB	0,1	<0,1	0,2	<0,1
PCB sum	201,1	73	585,4	45

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In the isotopically pure systems only the corresponding carbon labelled compounds could be detected. There is a difference in the reactivity of the carbon isotopes.  $^{12}\text{C}_{12}$  compounds are formed in a concentration higher by a factor of 2.7 than  $^{13}\text{C}_{12}$ . Whereas in the  $^{12}\text{C}$ -system the species with lower chlorination degree dominate, there is a trend to the higher chlorinated compounds in the  $^{13}\text{C}$ -system. In the mixed system the  $^{12}\text{C}_{12}$  and  $^{13}\text{C}_{12}$  compounds are not formed in comparable concentrations. We found 13 times more  $^{12}\text{C}_{12}$  than  $^{13}\text{C}_{12}$  compounds. But the decisive result is that no mixed  $^{12}\text{C}_6^{13}\text{C}_6$  compounds were detected. Consequently it must be assumed that in the PCB formation on fly ash intermediate reactions of one-ring-compounds such as chlorobenzenes and -phenoles are not involved. *Preformed biphenyl structures in the carbon lattice undergo catalyzed chlorination and oxidation rather than the formation of a C-C-bonds between two aromatic rings.*

**Formation of PCDD/PCDF on PCB spiked fly ash:** For the experiments with PCB spiked fly ash we chose the above mentioned congeners with different ortho chlorination patterns: decachlorobiphenyl (Ballschmitter#209) with 4 ortho-Cl, 2,3,4,4',5,5'-hexachlorobiphenyl (#167) with one ortho-Cl and 3,3',4,4',5,5'-hexachlorobiphenyl (#169) without any ortho-Cl. Because of the potential for a de-novo synthesis of PCDF of the fly ash itself we had to correlate the results of the spiked fly ash to experiments with fly ash not spiked. In all experiments the PCDD concentrations formed in the spiked system were identical to the concentrations in the blank samples, so under the experimental conditions PCB are no precursor for PCDD. Table 2 shows the results for PCDF for 2 h experiments at 300°C.

Table 2: Concentrations of PCDF in experiments with PCB spiked fly ash

compound	concentration PCB, spiked nmol/g FA	PCDF concentration formed nmol/g FA	
		in spiked sample	in blank sample
deca-CIBP, #209	22	12,0	13,3
hexa-CIBP, #167	19,9	16,0	13,3
hexa-CIBP. # 169	13,2	15,4	13,3

Compared with the non-spiked sample there is an increase in the formation of PCDF in the presence of the hexachlorobiphenyls for about 15-20%. In the presence of decachlorobiphenyl the PCDF concentration is within experimental error in the same level as in the non spiked sample. So the decachlorobiphenyl seems not to be a remarkable precursor for the PCDF. The reasons for the different behaviour of the PCB congeners may be in the difference of the structure: With deca-CIBP the two phenyl rings are twisted out of the plane, additionally the ortho-chlorines highly protect the ortho sites of the rings. In the case of the hexachlorobiphenyls there is only a small protecting effect, and the one without ortho-chlorine has the possibility of a planar conformation. The one with one ortho-chlorine has a smaller twisted angle than decachlorobiphenyl. The spiking concentration of the two hexachlorobiphenyls differs: For #167 with 19,9 nmol/g fly ash it is about 52% higher than for #169 with 13,2 pmol/g fly ash. In spite of this, the concentrations after the experiments are similar. This shows the much higher tendency of the non-ortho-hexachlorobiphenyl #169 to form a dibenzofuran structure. No increased PCDD concentrations were found, indicating that PCB do not present precursor models for PCDD. These results could be confirmed in experiments with a model mixture spiked with the hexachlorobiphenyl (#167, ) as the only source of carbon. Although we used the hexachlorobiphenyl #167 with one ortho-chlorine, two hexachlorodibenzofurans have the highest yields: 134678- and 234678-H6CDF. Together their part is over 96% of the whole H6CDF concentration. The H6CDF in sum are 72% of all detected PCDF. This shows that the ortho-chlorine is not necessary for the formation of a oxygen bridge that leads to the dibenzofuran structure. Of stronger

influence seems to be the presence of a planar structure. Table 3 shows the results from experiments at different temperatures.

Table 3: Concentrations of PCDF (nmol/g) in PCB spiked model mixture at various temperatures

concentration in pmol/g	250°C	300°C	350°C	400°C
PCDF sum	0,16	2,4	13,4	0,8

These data again confirm the role of PCB as precursors of PCDF. We found a strong increase in PCDF concentrations with increasing temperature. The maximum is at 350°C. At higher temperatures the degradation is the main reaction. The yields of PCDF from the educt biphenyl which has reacted are: 0.6% at 250°C, 10.3% at 300°C, 56.3% at 350°C and 6.0% at 400°C. The distribution of the sum concentration of the homologues is presented in table 4.

Table 4: Distribution of the homologues of the PCDF in percent

% distribution	250°C	300°C	350°C	400°C
T4CDF	0	3.9	2.1	12.7
P5CDF	22	7.4	1.9	15.9
H6CDF	77.8	72	87.4	25.7
H7CDF	0	15	7.9	45.6
OCDF	0	1.6	0.6	0

Up to 350°C the H6CDF are the main dibenzofuran product, but H7CDF is the second important one at 300°C and 350°C. At 400°C it is the main product, but here we have to consider that also enhanced degradation takes place yielding lower chlorinated species. Consequently besides the ring closure from PCB also chlorination and dechlorination takes place.

In conclusion we could prove that carbonaceous material from fly ash may be degraded to yield PCB. In this reaction no scrambling of the phenyl rings takes place. In a further reaction the PCB produced may undergo a ring closure to yield PCDF, however not PCDD.

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