COMPARISON OF DIFFERENT COMBUSTION FACILITIES ACCORDING TO THEIR EMISSION PROFILES OF POLYCHLORINATED COMPOUNDS

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Introduction

Since several years profiles and patterns of various polychlorinated compounds such as benzenes (PCBz), biphenyls (PCB) and dibenzo-*p*-dioxins/furans (PCDD/F) in different combustion facilities have been studied in order to explain the formation processes of these highly toxic substances. First Ballschmiter et al. (1) mentioned two different patterns for PCDD/F and suggested to classify them in a high temperature („2,6-pattern") and a low temperature pattern („2,3-pattern"). In the work of Wehrmeier et al (2) different sample types (e.g. fly ash, flue gas samples) were statistical analysed, using principal component analysis (PCA) to show the dominant „2,6-pattern" (explained variance: 78%) for TCDD. But on the other side, also the „2,3-pattern" was observed (explained variance: 13%) and preliminary explained as a result of formation and destruction processes of PCDD/F. Furthermore the relative occurrence of the isomers were explained by their thermodynamic stability (Gibbs free energies calculated with semiempirical methods) and their reactivity (HOMO-LUMO), which could confirm the „2,6-pattern". For PCB Bavel et al. (3) showed that in laboratory scale combustion of PCB mixtures the typical congener pattern, as observed in municipal waste incinerators, is obtained. Upon this, a reliable model was calculated with partial least square regression (PLS) using physio-chemical properties of the congeners (e.g. UV-spectra, log K_{ow} etc.) to predict the experimental patterns.

However, the clue for the decoding of the polychlorinated aromatic formation mechanisms is most probably hidden in the observed homologue and isomer patterns. Therefore it is of particular importance to study the pattern as a function of the combustion conditions. In case, that PCB may act as precursors for the PCDF formation (4) the generally resulting PCDF pattern will be strongly influenced by the original PCB pattern. Further on someone could propose that PCDF or PCB may also be possible „precursors" for the PCDD formation and could affect the pattern of the emitted PCDD. All the resulting patterns, at last, will be influenced by physio-chemical properties of the different isomers, e.g. their thermodynamic stability, kinetic aspects of the reactions, etc.

The aim of this study is to show, whether different combustion facilities turn out a uniform isomer pattern for one degree of chlorination for PCDD/F and PCB, or not, using PCA as a statistical tool.

Materials and Methods

Table 1: Brief description of the plant under investigation

Plant Sample number	*Type Flue gas cleaning*	*Thermal power (MW)*	*Sampling point(s)*	*Fueltype*
Plant 1 (9samples; C1-C9)	Pilot scale plant with a retrograde stoker and a post combustion chamber/active coke filter and bagfilter house	0.5	End of the post combustion chamber; Temperaturerange: 600°C-900°C	Wood, spatially contaminated wood
Plant 2 (12samples; P1-P12)	Full scale industrial wood combustion plant with a foreward moving stoker and a second post combustion chamber /multicyclone	14	After the multicyclone, before the stack; Temperaturerange: 210°C-230°C	Natural wood, medium density fibreboards, lignite, railroad sleepers
Plant 3 (20 samples; 10 samples from the flue gas and 10 samples from the stack gas; G1-G20)	Full scale hazourdous waste incinerator/ electrostatic precipitator and various wet scrubbers	22	Two sampling points: Flue gas at the end of the heat recovery zone (Temperature 350°C) and stack gas (Temperature 70°C)	Hazardous waste: liquid, pasteous and solid

For sampling setup, cleanup procedure and HRGC/HRMS conditions see elsewhere (5,6). It should be not added that the sample cleanup of PCB is very sophisticated due to observed losses of several isomers. Therefore the solvent mixtures for the eluation of the acidified Silica- and Alox-column were changed and a GPC (Gelpermeation chromatography) cleanup step was added to purify the sample, furthermore the measurements were performed on a HRGC/HRMS (MAT 95) (6). For the 209 PCB congeners 102 peaks (coeluting are included) were detected, which is a quite high value for PCB analysis by HRGC (7). The concentrations were normalized to 1013mbar, 273K and 11%O_2.

For statistical calculation the STASTICA package version 5.0 was used. To reduce the information and to group the variables/cases of the data set PCA analysis was used. This method gives the possibility to detect internal structures and substructures of the investigated data and to obtain a simplified and reduced overview of the data. For further information of PCA see (8). To carry out PCA analysis, normal distribution of the data is necessary. Therefore we transformed all the data to

a logarithmic scale. Normal distribution was tested with a overall F-Test on a significance level of $p<0.1$. All variables showed normal distribution under the previous described test conditions.
A further statistical problem is the treatment of missing values for variables. In literature different possibilities for that problem were described (9,10). In Ref. 10 it was suggested to take the detection limit or the half of the detection limit for the missing data. Subsequently all regressions, normal distribution or other statistical values have to be checked for significant changes and compared with the results obtained before replacing the missing data. Setting missing data to zero also makes it impossible to carry out logarithmic normal distribution calculations.
In this work the hexa- and pentachlorinated compounds were investigated. Within this homologues we achieved the most complete data set under the investigated samples. For missing data we exclude not the complete variable(s) from the correlation matrix (same number of cases for all variables), but we deleted pairs of missing data from the correlation matrix calculation of the PCA. Thus for individual variables in the PCA plot the number n of cases is reduced.

Results and Discussion

Figure 1 shows the homologue profiles of TCDD/F to OCDD/F for the three plants for two cases respectively. It can be observed from this Figure that the proportion between PCDD and PCDF is different for different plants and also different for different cases in one plant (e.g. G1 and G2). Furthermore it is also obvious that the distribution of the homologues can be different in one plant under similar plant conditions (e.g. P1 and P2). This result show that no generally valid homologue profiles exist for the selected incinerators.

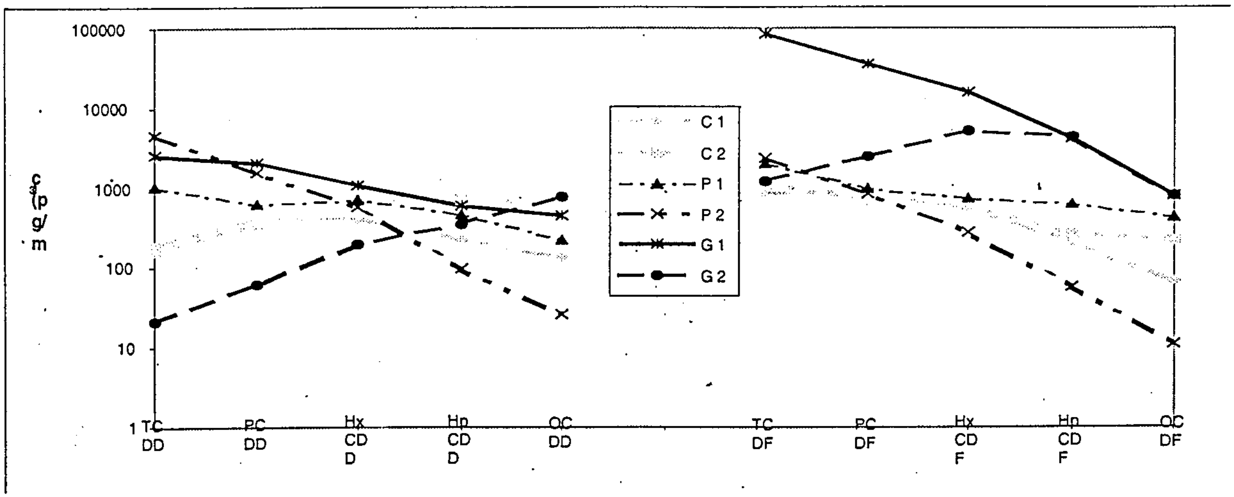


Figure 1: Homologue profiles (logarithmic concentrations of the homologues in pg/m^3) of the three different incineration plants., each facility is represented with two cases (e.g. C1 and C2).

In Table 2 an overview for the observed isomers for each class of compounds is given and their abbreviations in the statistical analysis. For the PCB, 25 of 41 hexachlorinated isomers could be identified, which were also the most intensive peaks observed in the chromatograms. PCDD/F isomers occurred in a concentration range 10 up to 1000 pg/m^3, while for PCB a concentration range of 100 up to 10000 pg/m^3 was observed.

Table 1: Hexachlorinated isomers of PCDD/F and PCB and their systematic numbering according to Ballschmiter et al. (11) and the corresponding abbreviations in the PCA analysis.

PCDD	Ballschmiter	Abbreviations	PCB	Ballschmiter	Abbreviations
1,2,3,4,7,8-HxCDD	#66	DD1	2,2',3,3',6,6'-HxCB	#136	CB1
1,2,3,6,7,8-HxCDD	#67	DD2	2,2',3,5,5',6-HxCB	#151	CB2
1,2,3,7,8,9-HxCDD	#70	DD3	2,2',3,3',5,6'- + 2,2',3,4,5',6- + 2,2',3,4',5,6'-HxCB	#135,#144,#147	CB3
1,2,4,6,7,9/1,2,4,6,8,9/1,2,3,4,6,8-HxCDD	#71/72/64	DD4	2,2',3,4',5',6-HxCB	#149	CB4
1,2,3,6,7,9/1,2,3,6,8,9-HxCDD	#68/69	DD5	2,2',3,3',5,6-HxCB	#134	CB5
1,2,3,4,6,9-HxCDD	#65	DD6	2,2',3,3',4,6-HxCB	#131	CB6
1,2,3,4,6,7-HxCDD	#63	DD7	2,2',3,3',4,6'- + 2,2',3,4',5,5'-HxCB	#132,#146	CB7
PCDF			2,2',4,4',5,5'-HxCB	#153	CB8
1,2,3,4,7,8-HxCDF	#118	DF1	2,2',3,4,5,5'-HxCB	#141	CB9
1,2,3,6,7,8-HxCDF	#121	DF2	2,2',3,4,4',5-HxCB	#137	CB10
1,2,3,7,8,9-HxCDF	#124	DF3	2,2',3,3',4,5'-HxCB	#130	CB11.
2,3,4,6,7,8-HxCDF	#130	DF4	2,3,3',4,5,6- + 2,3,3',4',5,6-HxCB	#160,#163	CB12
1,2,3,4,6,8-HxCDF	#116	DF5	2,2',3,4,4',5'-HxCB	#138	CB13
1,3,4,6,7,8/1,3,4,6,7,9-HxCDF	#128/129	DF6	2,2',3,3',4,5- + 2,2',3,4',5',6-HxCB	#129,#158	CB14
1,2,4,6,7,8-HxCDF	#125	DF7	2,3'4,4'5,5'-HxCB	#167	CB15
1,2,4,6,7,9-HxCDF	#126	DF8	2,2',3,3',4,4'- + 2,2',3,4,5,5'-HxCB	#128,#159	CB16
1,2,4,6,8,9-HxCDF	#127	DF9	2,3,3',4,4',5-HxCB	#156	CB17
1,2,3,4,6,7-HxCDF	#115	DF10	2,3,3',4,4',5'-HxCB	#157	CB18
1,2,3,6,7,9-HxCDF	#122	DF11	3,3'4,4'5,5'-HxCB	#169	CB19
1,2,3,4,6,9/1,2,3,6,8,9-HxCDF	#117/120	DF12			
1,2,3,4,8,9-HxCDF	#119	DF13			

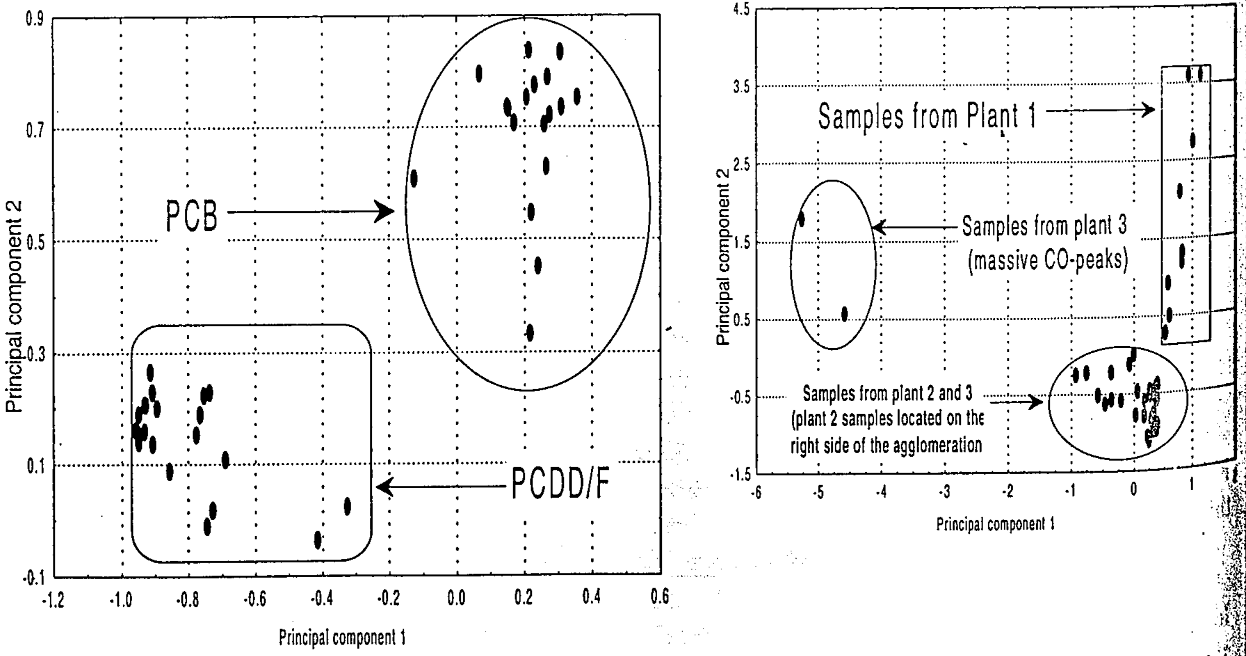
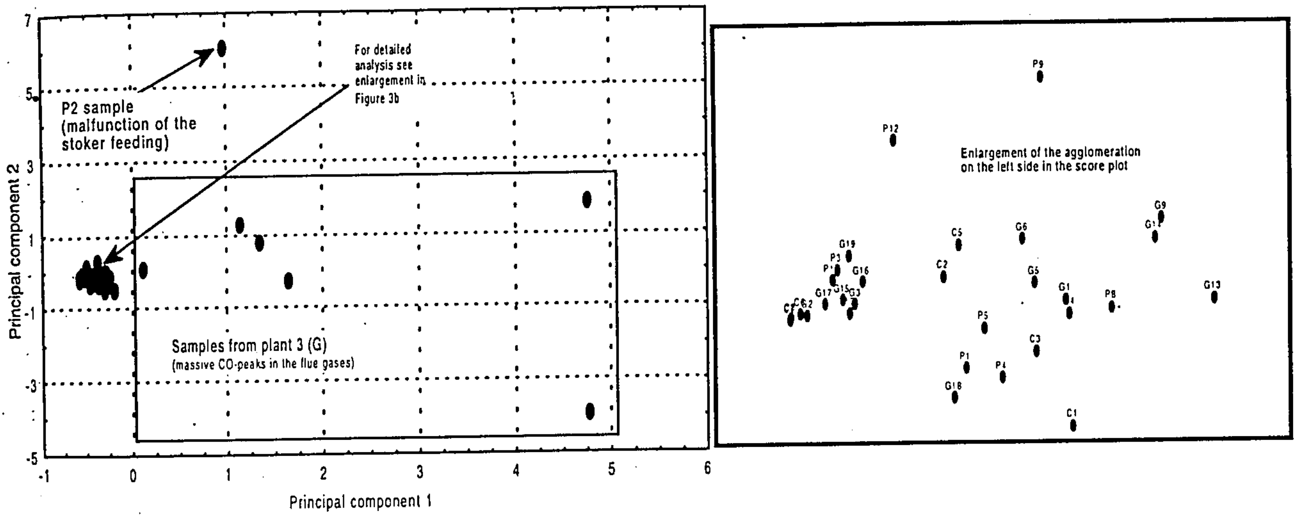


Figure 2: PCA analysis for the investigated compound classes (loading plot: left side; score plot: right side). Explained variance is 39% for PC1 and 24% for PC2.

In the first PCA in Figure 2 all variables (hexachlorinated isomers of PCDD/F and PCB) were analysed to figure out differences between the three classes of compounds.
The loading plot of the PCA depicts clearly that the PCDD/F and PCB were separated from each other (explained variance on the PC 1 and PC 2 are both below 40%). Therefore no uniform combustion pattern for the classes of compounds could be observed. The score plot of the PCA (on the right side of Figure 2) shows that the cases are according to plant conditions (e.g. massive CO-peaks in plant 3) and typical facilities (e.g. samples from plant 1) separated by the PCB patterns (according to the loading plot on the left side of Figure 2).
In addition a further PCA (Figure 3) was carried out to investigate HxCDD pattern of the combustion samples.



Figures 3a and 3b: Score plot for the HxCDD (Figure 3a; left side). Explained variance is 78% for PC1 and 12% for PC2. Figure 3b (right side) depicts an enlargement from the agglomeration of cases in Figure 3a.

In this PCA analysis the explained variance is in a similar range as reported by A. Wehrmeier et al. (4) for tetrachlorinated isomers. However, in the score plot (Figure 3a) some cases are clearly separated from the others, which indicates changes in the emitted isomer patterns. All these cases are due to experiments on the different plants, where disturbances in the combustion conditions (e.g. malfunction of the stoker feeding = P2) occurred. In summary this means, that combustion conditions could influence the pattern of emitted PCDD, which was not mentioned in literature before. But on the other hand, the PCDD pattern seems to be more or less stable over a great range if different plants are investigated, which is shown in Figure 3b with the enlargement of the agglomeration of cases from Figure 3a. In this Figure no clear structure of the cases (different plants) could be observed.
The loading plot (not shown in this contribution) exhibits that the two „pure“ 2,3 HxCDD isomers (DD1 and DD3) are grouped together, while the greatest number of the isomers are chlorinated in the 2,3,6 position and form also a group on themselves. Possibly this spatial separation of the different substituted isomer groups may give a hint of the formation pathways due to their thermodynamic stability mentioned in the introduction (1).

Figure 4 shows the PCA score plot for the hexahchlorinated dibenzofurans (HxCDF).

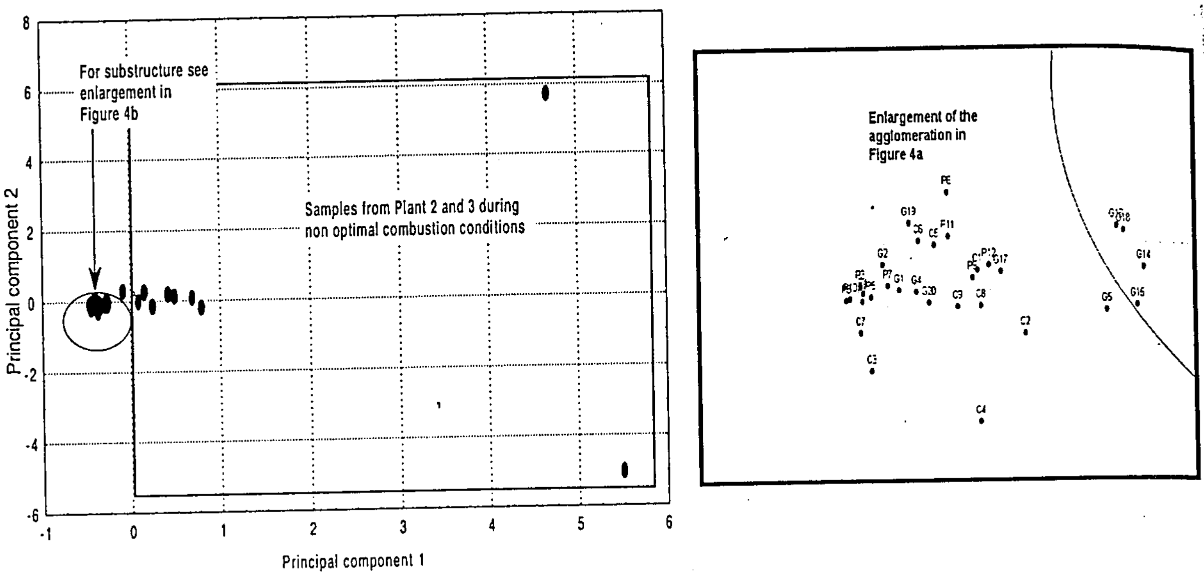


Figure 4a and 4b: Score plot for HxCDF (Figure 4a; left side). Explained variance is 69% for PC1 and 16% for PC2. Figure 4b (right side) depicts an enlargement of agglomeration from cases in Figure 4a.

Like in Figure 3a the cases which are according to non optimal combustion conditions were clearly separated from the agglomeration on the left side in the plot (Figure 4a). Furthermore the explained variance for the first two principal components is lower than for the HxCDD, which also is in accordance with the results from Wehrmeier et al. (4). The enlargement of the agglomeration of the cases (Figure 4b) proves that the cases form plant 1 (C label) and most of the cases form plant 2 (P label) were separated from the cases form plant 3 (G label). This substructure indicates that there were plant specific emission patterns for the HxCDF. Further the loading plot (not shown here) depicts a widespread behaviour of the individual isomers and therefore no clearly defined 2,3 or 2,6 pattern in contrast to the HxCDD could be observed.

In Figure 5 the loading plot of the PCA analysis for PCB is shown.

The explained variance is quite low in comparison with the values for PCDD or PCDF and turns out that there is no typical isomer pattern obtained from the PCB samples. This result is in contrast to the results from Bavel et al. (6), which suggested a uniform combustion pattern for the PCB due to his results from laboratory scale experiments. Although the pattern is not uniform, a group of hexachlorinated biphenyl isomers, which exhibits two ortho chlorine substitutents, could be identified. Especially the cases from plant 1 and 2 were separated in the score plot (not shown here) from the cases from plant 3, this information already appeared in Figure 2. A similar result was found also for cases received from a singular plant, where plant specific conditions influenced the isomer pattern of the emitted PCB (12)

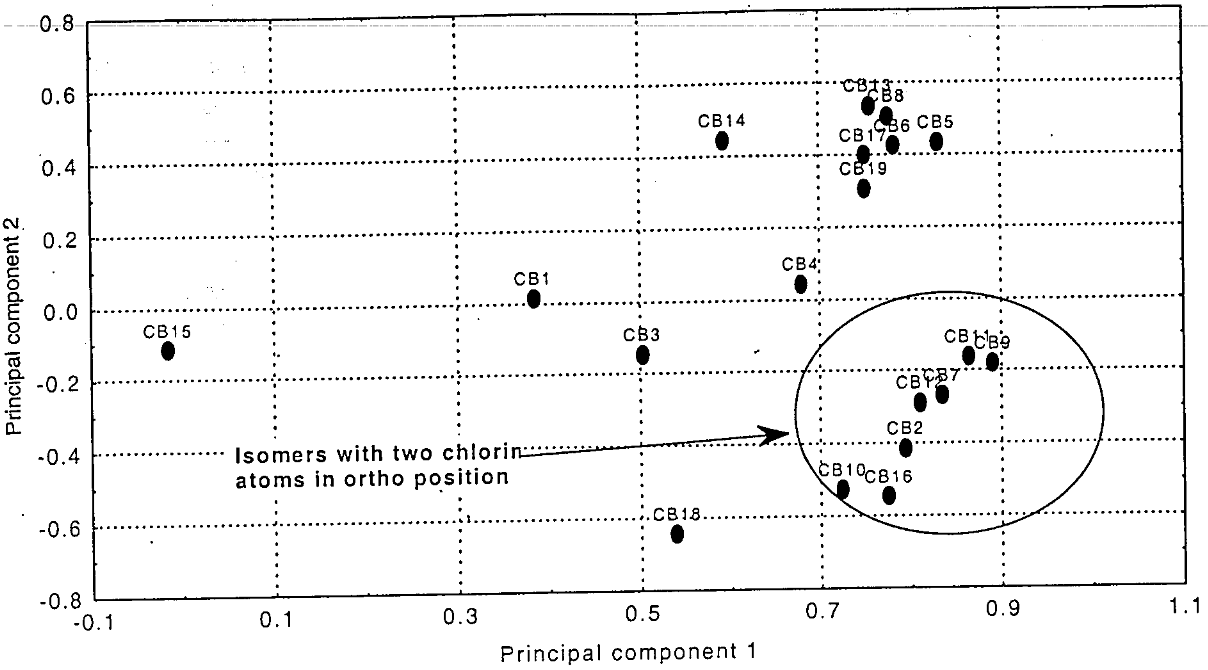


Figure 5: Loading plot from PCA analysis for HxCB. Explained variance is 51% for PC 1 and 15% for PC2.

This different behaviour for PCB in comparison with the PCDD/F may be due to the strong influence of the chlorine substitutent position on the molecular structure in the case of the PCB (13). For example the highly resolved UV-spectra (REMPI) of dichlorinated biphenyl isomers with chlorine atom in ortho position are very different form those without a chlorine atom in ortho position.
In Table 3 the results for the PCA analysis of hexa- and pentachlorinated PCDD/F and PCB were summarized.

Table 3: Values for the explained variance for the first two principal components of the PCA analysis for hexa (Hx)- and pentachlorinated (Pe) PCDD/F and PCB

Explained variance (%)	HxCDD	HxCDF	HxCB	PeCDD	PeCDF	PeCB
Principal component 1	78	69	51	76	70	48
Principal component 2	12	16	15	9	11	14

Hexa- and pentachlorinated compounds show a similar behaviour in the PCA analysis. This result is a hint on different formation/degradation pathways of these compounds in combustion processes either under thermodynamic or kinetic control. In literature it is reported that PCDF are formed in higher temperature windows and in greater amounts than PCDD during incineration (14). Further Blumenstock et al. (15) found that a high percentage of the PCDF, PCB and PCBz are formed in the high temperature range of about 700°C-800°C during combustion processes at the post

combustion chamber outlet. These products of incomplete combustion were then able to react in further pathways like it is described in Choudry G. G. and Hutzinger O. (16). The early occurrence in the flue gas stream and therefore the possibilities for reactions of PCB (precursors for PCDF, see Ref. 4) and PCDF could explain their non uniform behaviour in the PCA analysis. However, the presented results and the previous observations in the high temperature window of incinerators could help to explain why PCB or PCBz act as reliable surrogates for the emitted amount of PCDD/F (5,17).
For further explanation and understanding of the processes semiempirical molecular orbital calculations (e.g. AM1 or PM3) and additional statistical works for all classes of compounds are necessary to elucidate any relationship between the results of multivariate statistics and thermodynamic calculations.

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