Source Identification by Congener-specific PCDF/D Complete Analysis Taking Real Fire Damage Samples as an Example

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The investigation of samples for polychlorinated dibenzofurans and dibenzo-p-dioxins (PCDF/D) is being increasingly reduced to the analysis of the 17 PCDF/Ds with 2378-chlorine substitution patterns for various reasons. This severely restricts or even excludes the following possibilities, for example:

- identification of PCDF/D sources
- interpretation of process parameter changes
- plausibility/quality control of the analysis results by pattern comparisons
- re-calculation/assessment of the toxic potential of a sample considering congeners without 2378-chlorine substitution pattern.

Such drawbacks can, however, be avoided when performing a congener-specific PCDF/D complete analysis (comprising the analysis data of all Tetra- to OctaCDF/Ds in electronically processable form); the extra evaluation time involved is approx. 30 to 45 minutes per sample for an experienced analyst. The PCDF/D complete analysis is performed interactively (it is therefore not fully automatic) using self-developed software.

Table 01 illustrates by way of example such a complete analysis for a soot wipe sample which was taken from a small school library after a fire. The unexpectedly high ITE area load of 900 ng/m^2 (ITE calculated according to the NATO/CCMS toxicity equivalent model) has already been clearly traced to the thermal loading of a PCB-containing source on account of the specific TetraCDF congener distribution which can only be recognised in complete analysis (cf. Fig. 01 and Fig. 03); PCB follow-up investigations in this case traced special sound insulation panels as the source of PCDF/D, the coating of which contained up to 18 % PCB, type Clophen A60. Procurement of the analysis data of all Tetra- to OctaCDF/Ds closes the gap of cluster analyses from reduced PCDF/D investigations; the latter patterns are presented in Fig. 02 taking the specified damage as an example.

Finally, Fig. 03 shows examples of similar and different TetraCDF distributions which were recorded by GfA in congener-specific complete analysis of samples from real fires, incorporating different fire loads.

Combining all the presented fingerprint-analysis possibilities of evaluation (possibly adding homologue totals of the Mono- to TriCDF/Ds and certain quotient ratios, e.g. total PCDFs/total PCDDs), databases can be built up with current analyses or previous analyses evaluated at a later date, with the aid of which main sources of PCDF/D can be identified quickly, unambiguously and at reasonable cost, as and when required.

Tab. 01: Congener-specific complete analysis of Tetra- to OctaCDF/Ds, taking a fire soot wipe sample as an example; all area loads in ng/m^2

	Polychlorinated Dibenzofurans (PCDFs)[a]							
	Total TetraCDF	10533.0		**Total PentaCDF**	6209.0		**Total HexaCDF**	1361.0
1	1368-TetraCDF	56.9	*1*	13468-PentaCDF	85.7	*1*	123468-HexaCDF	34.5
2	1379/1378-TetraCDF	267.1	*2*	12468-PentaCDF	129.9	*2*	134678-HexaCDF	218.3
3	1347-TetraCDF	75.8	*3*	23479-PentaCDF	65.8	*3*	134679-HexaCDF	0.0
4	1468-TetraCDF	194.0	*4*	13479-PentaCDF	7.8	*4*	124678-HexaCDF	242.1
5	1247/1367-TetraCDF	248.4	*5*	13478/12368-PentaCDF	544.5	*5*	124679-HexaCDF	38.5
6	1348-TetraCDF	194.2	*6*	12478-PentaCDF	817.9	*6*	123478/123479-HexaCDF	248.2
7	1346/1248-TetraCDF	497.2	*7*	12479/13467-PentaCDF	247.4	*7*	123678-HexaCDF	129.2
8	1246/1268-TetraCDF	355.3	*8*	12467-PentaCDF	485.1	*8*	124689-HexaCDF	29.4
9	1237/1478/1369-TetraCDF	887.8	*9*	12347/23469-PentaCDF	341.4	*9*	123467-HexaCDF	161.1
10	2349/1234-TetraCDF	95.1	*10*	13469-PentaCDF	34.7	*10*	123679-HexaCDF	24.9
11	2468/1238/1467/1236-TetraCDF	635.4	*11*	12378/12348-PentaCDF	520.1	*11*	123469/123689-HexaCDF	52.5
12	1349-TetraCDF	9.6	*12*	12346-PentaCDF	36.2	*12*	123789-HexaCDF	9.3
13	1278-TetraCDF	1052.6	*13*	12379-PentaCDF	0.0	*13*	123489-HexaCDF	18.6
14	1267/1279-TetraCDF	236.7	*14*	12367-PentaCDF	199.1	*14*	234678-HexaCDF	153.8
15	1469-TetraCDF	41.6	*15*	12469/23489-PentaCDF	463.0			
16	2368/1249-TetraCDF	704.3	*16*	13489-PentaCDF	60.8		**Total HeptaCDF**	130.0
17	2467-TetraCDF	311.3	*17*	12369-PentaCDF	26.0	*1*	1234678-HeptaCDF	64.8
18	1239/2347-TetraCDF	213.8	*18*	23468-PentaCDF	198.8	*2*	1234679-HeptaCDF	8.8
19	1269-TetraCDF	90.1	*19*	12349-PentaCDF	2.8	*3*	1234689-HeptaCDF	44.6
20	2378-TetraCDF	1783.0	*20*	12489-PentaCDF	77.8	*4*	1234789-HeptaCDF	11.5
21	2348-TetraCDF	622.1	*21*	23478-PentaCDF	1259.0			
22	2346-TetraCDF	172.4	*22*	12389-PentaCDF	37.3	*1*	**OctaCDF**	51.9
23	2367-TetraCDF	1488.7	*23*	23467-PentaCDF	567.5			
24	3467-TetraCDF	240.1						
25	1289-TetraCDF	59.9						
	Polychlorinated Dibenzo-p-dioxins (PCDDs)[a]							
	Total TetraCDD	29.0		**Total PentaCDD**	44.0		**Total HexaCDD**	77.0
1	1368-TetraCDD	1.3	*1*	12479/12468-PentaCDD	4.1	*1*	124679/124689/123468-HexaCDD	13.0
2	1379-TetraCDD	0.9	*2*	12368-PentaCDD	4.1	*2*	123679/123689-HexaCDD	37.3
3	1378-TetraCDD	3.0	*3*	12478-PentaCDD	9.0	*3*	123478-HexaCDD	3.7
4	1369/1247/1248-TetraCDD	4.7	*4*	12379-PentaCDD	2.0	*4*	123678-HexaCDD	13.6
5	1268-TetraCDD	1.1	*5*	12469/12347-PentaCDD	3.6	*5*	123469-HexaCDD	1.0
6	1478-TetraCDD	3.0	*6*	12378-PentaCDD	7.8	*6*	123789-HexaCDD	5.9
7	2378-TetraCDD	3.7	*7*	12369-PentaCDD	2.5	*7*	123467-HexaCDD	2.5
8	1237-TetraCDD	3.6	*8*	12467-PentaCDD	1.8			
9	1234/1246/1249/1238-TetraCDD	0.0	*9*	12489-PentaCDD	2.8		**Total HeptaCDD**	260.0
10	1236/1279-TetraCDD	1.7	*10*	12346-PentaCDD	2.2	*1*	1234679-HeptaCDD	88.9
11	1278/1469-TetraCDD	5.7	*11*	12367-PentaCDD	2.2	*2*	1234678-HeptaCDD	171.1
12	1239-TetraCDD	0.6	*12*	12389-PentaCDD	2.2			
13	1269-TetraCDD	0.0				*1*	**OctaCDD**	508.1
14	1267-TetraCDD	0.0						
15	1289-TetraCDD	0.0						
Total Tetra- to OctaCDF/Ds								**19203**
Total 17 PCDF/Ds with 2378-chlorine substitution								**4945**
International toxic equivalents (ITE acc. to NATO/CCMS)								**901**

a within the corresponding homologue group the elution sequence of the congeners at the GC-phase SP 2331 is given as peak number sequence (italicized numbers); the identification of the congeners was done on the basis of a publication from Ryan et al., Journal of Chromatography, 541 (1991) 131 - 183

Fig. 01: Concentration distributions of all Tetra- to HeptaCDF/Ds as a percentage of the respective homologue total (PCDF/D fingerprint) for the fire soot wipe sample presented in Tab. 01; for congener identification compare the peak number with the peak numbers in italics within the homologue groups in Tab. 01 and the congeners listed there

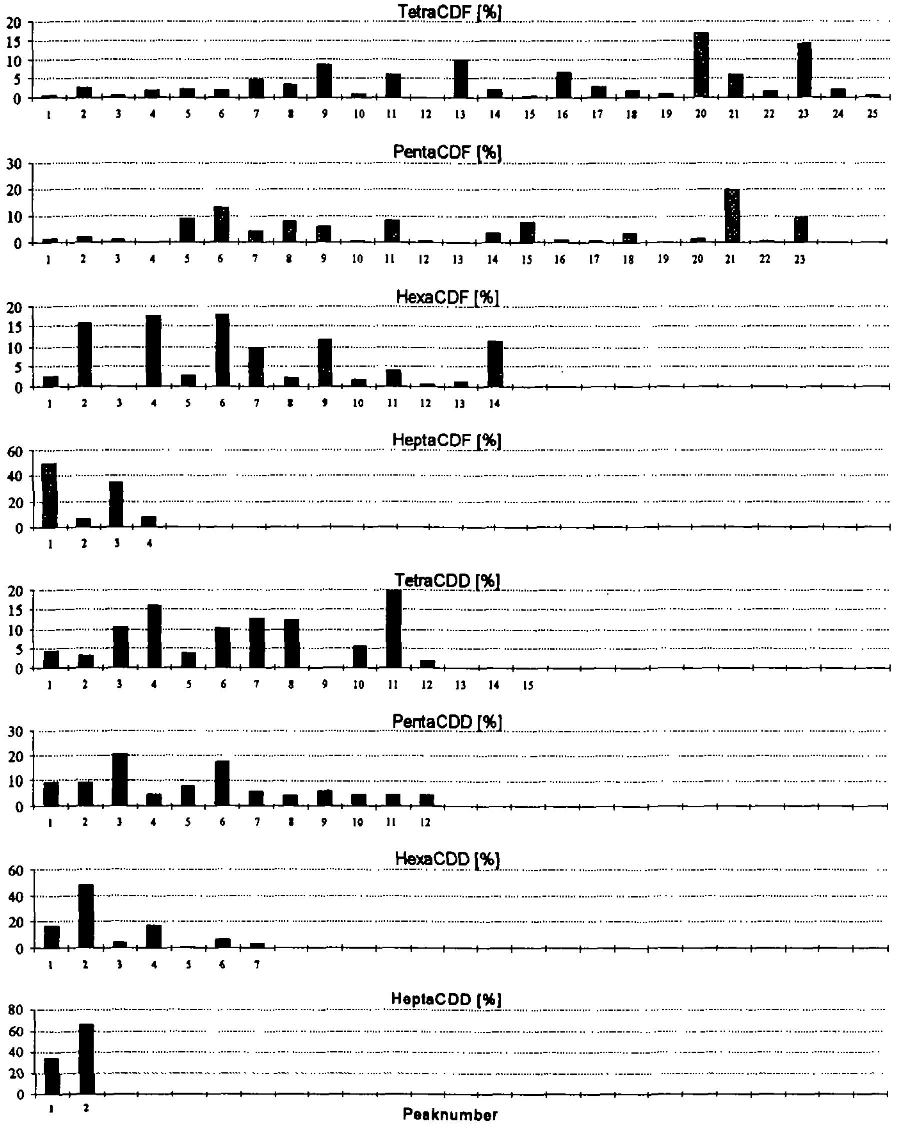


Fig. 02: PCDF/D distributions for the fire soot wipe sample presented in Tab. 01;
- A Part-concentrations of the 2378-chlorine substituted PCDF/Ds as a percentage of the total 17 PCDF/Ds
- B ITE portions of the 2378- chlorine substituted PCDF/Ds as a percentage of ITE total
- C Homologue concentrations as a percentage of the total of all Tetra- to OctaCDF/Ds
- D Part-concentrations of the 2378- chlorine substituted PCDF/Ds as a percentage of the respective homologue total

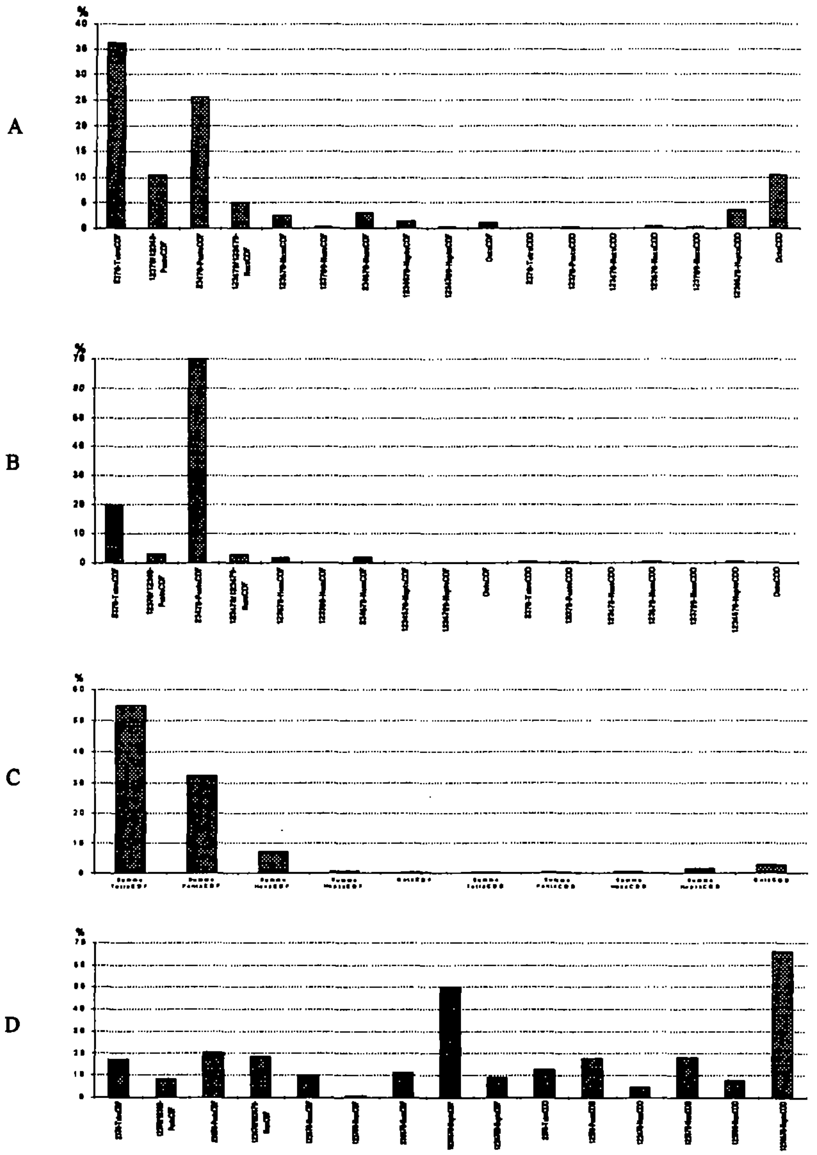
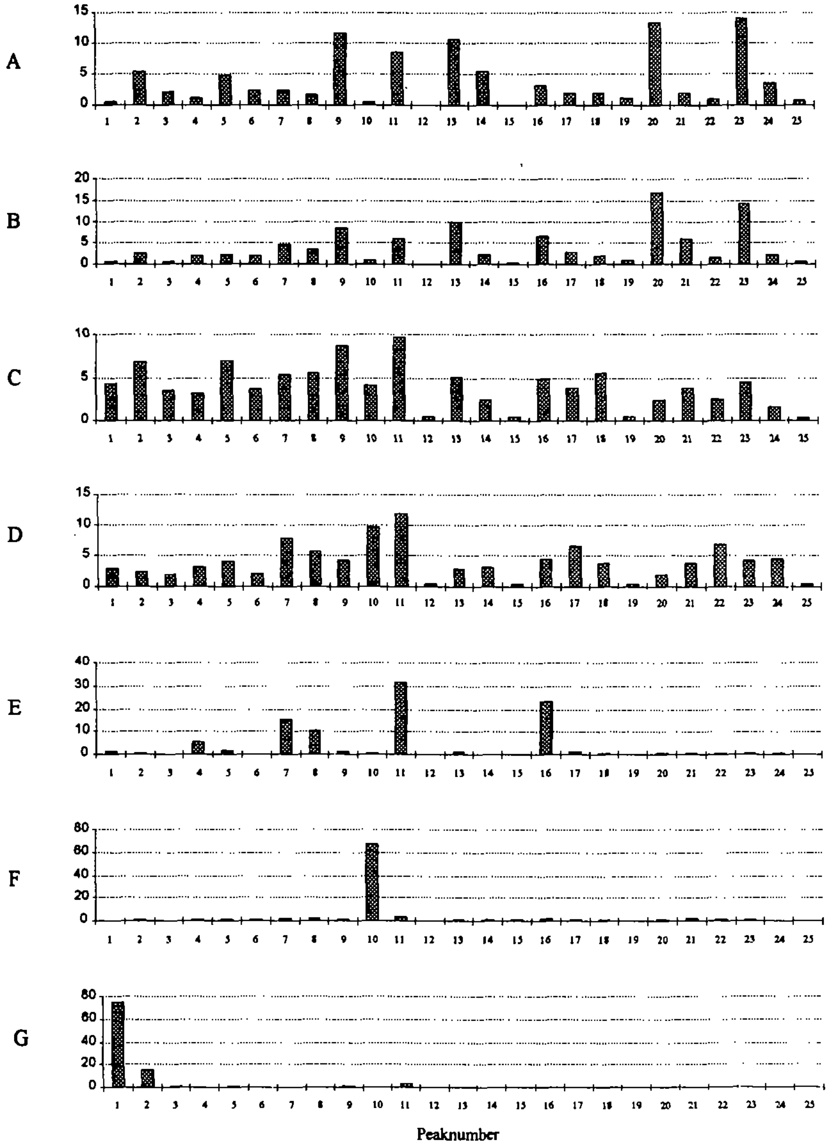


Fig. 03: Examples of TetraCDF congener distributions (presented as a percentage of the respective homologue concentration) in soot samples from various real fires, incorporating defined fire loads;

Fire load A	PCB mixture, type Clophen A40
Fire load B	PCB mixture, type Clophen A60
Fire load C	PVC
Fire load D	PVC and copper (electric cable)
Fire load E	PVC, copper, carbon and calcium chloride
Fire load F	Wood preserved with chlorphenol
Fire load G	Chlorinated aromatic industrial chemical



(for congener identification compare to Fig. 01 resp. Tab. 01)