PCDF/D Contamination of Foodstuffs Affected by Fumes from an Accidental Fire involving PVC

Jochen Theisen, Stephan Hamm und Armin Maulshagen, GfA - Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH, Otto-Hahn-Straße 22, D-48161 Münster, Germany

Abstract

As a consequence of a great fire accident that occurred at a factory in Lingen (Germany) and which involved approximately 10 tons of PVC-containing materials, considerable contamination with polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (PCDF/D) resulted, amongst others, in different kinds of foodstuffs and free range small animals, in a 30° lee-side sector up to a distance of approximately 2.5 km from the fire. The ITE (International Toxic Equivalents acc. to NATO/CCMS) concentrations determined for these matrices were approximately one order of magnitude higher than corresponding background levels. The elevated PCDF/D concentrations made it necessary under health precautionary aspects to carry out extensive cleaning measures, to restrict consumption of foodstuffs and to kill contaminated animals no longer fit for human consumption. The described fire damage demonstrates, among others, the influence of fire load and meteorology on the PCDF/D content in certain environmental compartments affected by fire fumes.

Introduction

On November 4, 1996, a 7000 m^2 production hall of a metal-processing plant burned down in Lingen/Ems, a town in North West Germany[1]. As sole relevant chlorine containing fire load, approximately 10 tons of Hard-PVC materials burned. By a cold, dry weather situation with high wind speeds (up to wind-force 8) from a constant direction, the fumes were driven for hours close to the ground through neighbouring residential areas, allotment gardens and farming areas. Ambient air concentrations of HCl determined during the fire showed values up to 4 ppm. The meteorological conditions were comparable to those prevailing during the large accidental fire of a plastic storage facility in the North West German city of Lengerich in October 1992, where approximately 450 tons of PVC-containing plastics as chlorine-containing material went up in flames[2]. The analysis of 11 soil samples taken immediately after the fire in Lingen provided no indication of particular PCDF/D contamination in connection with the fire damage. The high PCDF/D concentration level of a kale sample (94.8 ng ITE/kg dry mass) also taken immediately after the fire and whose PCDF/D results were first available 10 days after the incident, caused the Environmental Department of the city of Lingen to engage the GfA to further assess the impact of the fire on the environment.

Experimental Methods

All GfA sampling procedures, sample preparations, clean-ups and analyses, were carried out in accordance with the latest state-of-the-art technology. Accordingly, all PCDF/D analyses were carried out using ^{13}C-labelled standards and a HRGC/HRMS system (VG AutoSpec, GC phase: SP 2331 or DB 5). Each kale sample was freeze dried in a ready-to-eat state (i.e. washed and chopped up). When carrying out investigations with hen's eggs, the yolk and white of 5 eggs were pooled and treated as one sample, respectively.

Results and Discussion

The results of the PCDF/D analysis of the PVC-combustion residues and of the foodstuff samples with the highest PCDF/D contamination levels are listed in table 01; figure 01 shows the concentration profiles of the 2378-chlorosubstituted PCDF/D congeners for these samples. In the following text, ITE values of samples which were analysed by laboratories other than GfA have been denoted with literature references.

PVC Combustion Residues

The PCDF/D concentrations and patterns found in the combustion residues of the Hard-PVC materials are comparable to those usually observed in combustion residues of that kind [e.g. 3),4)]. A value of 117 µg/kg was determined for the total of the 17 PCDF/D congeners with 2378-chlorine substitution pattern; the 2378-TetraCDD (so-called Seveso-Dioxin) was present in the PVC-combustion residues at a concentration level of 0.14 µg/kg. Further analyses carried out with this material showed, among others, non-detectable concentrations of PCBs (< 0.3 mg/kg in total of PCBs), 21 mg/kg of Extractable Organic Halogen Compounds (EOX), 93 mg/kg of PAHs (EPA) and 23.000 mg/kg of Lead [5)].

Kale

In order to monitor the immission pollution situation, the first step of the investigations involved the collection of 9 kale samples on the lee-side of the burnt production hall, where possible, from along 3 trajectories at 3 different radii (0.2 to 2 km distance from the fire). The 9 kale samples were analysed for PCDF/Ds together with 5 further samples within the next 4 days. According to these investigations, the fire led to a particular PCDF/D affection with the consequence of restrictions being placed on consumption of special foodstuffs within a 30° sector of up to an approximate distance of 2.5 km from the fire. The following table shows the PCDF/D results of kale samples taken out of the main direction of the spread of fumes as well as reference values for classifying (all values in ng ITE per kg dry mass (m_d) or fresh mass (m_f)):

Kale	Time interval between the day of the fire and the sampling day			
	1 d		11 d	
Fire accident Lingen 1996	m_d	m_f	m_d	m_f
- 200 m lee-wards	94.8 [1)]	-	33.9	5.3
- 900 m lee-wards	-	-	11.5	1.7
- 1,300 m lee-wards	-	-	7.2	1.0
- 2,000 m lee-wards	-	-	4.6	0.4
- Regional reference values	-	-	0.9 - 2.2	0.1 - 0.3
Fire accident Lengerich 1992				
- 600 m lee-wards	33.6 [2)]	3.6 [2)]	-	-
- 2,400 m lee-wards	9.1 [2)]	1.0 [2)]	-	-
- 3,900 m lee-wards	2.1 [2)]	0.3 [2)]	-	-
- Regional reference values	0.5 [2)]	< 0.1 [2)]	-	-
Tolerance value [6)]	3.0	-	3.0	-
Intervention value	> 10.0 [6)]	> 1.0 [2)]	> 10.0 [6)]	> 1.0 [2)]

In addition, the kale sample that was most highly affected by the fumes (sample taken at 200 m lee-wards) was further analysed for PBDF/Ds, PAHs, PCBs and for the 10 elements Al, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Tl and Zn. Concerning these parameters, only the PAH and copper values of this kale sample exceeded the regional reference values and known 'normal levels' by as much as factor 3.

Cow's Milk

The following table shows the considerable PCDF/D contamination of cow's milk from a Lingen farm whose cows had received fodder grass that had been affected by the fumes; in addition comparative data are reported (all values in pg ITE/g milk fat):

Time interval between the day of the fire and the sampling day	Fire accident Lingen 1996	Fire accident Lengerich 1992
0 d	-	1.3 [2)]
7 d	-	1.7 [2)]
11 d	9.1	-
17 d	4.5	4.1 [2)]
21 d	2.6 [1)]	4.8 [2)]
24 d	2.4 [1)]	5.9 [2)]
27 d	-	3.6 [2)]
34 d	-	2.8 [2)]
62 d	-	1.8 [2)]
Background levels NRW 1994 [7)]		
- range	0.6 - 1.8	
- mean	1.0	
Intervention value I	> 3.0	
Intervention value II	> 5.0	

Intervention value I refers to a discontinuation of the direct marketing of the respective farm's milk and milk products. When exceeding intervention value II a discontinuation of any marketing of milk/milk products is recommended [8)]. The compilation of the data shows, that intervention value II was exceeded at both fire incidents. As the subsequent investigations demonstrated, the PCDF/D concentrations of the respective milk fell below intervention value I in both cases 10 days after the detection of the peak pollution and the suspension of feeding any food affected by the fumes. Consequently, the corresponding recommendation to stop the direct marketing of the respective farm's milk products could be lifted. In the case of the livestock of the dairy farm from Lengerich, the upper level of PCDF/D background concentrations in cow's milk as reported above was reached after a 6 week period of feeding animal foodstuff without particular impurities.

Hen's Eggs

PCDF/D analysis of free-range hen's eggs in the main downwind region provided the following results:

Free-range hen's eggs	pg ITE/g egg fat	Time interval between fire and sampling day
Fire Accident Lingen 1996		
- 800 m lee-wards	53.7	12 d
- 1,700 m lee-wards	9.3	12 d
- 2,300 m lee-wards	5.0	25 d
- Regional reference values	5.0 - 6.5	19 - 25 d
Fire Accident Lengerich 1992		
- 6,500 m lee-wards	4.7 [2)]	15 d
Background levels in Southern Germany [9)]		
- range	1.0 - 4.7	-
- mean	2.4	-

In accordance with the findings of the kale analyses, the PCDF/D data of the lee-side hen's eggs also showed elevated PCDF/D concentrations for the samples collected within a 2 km distance from the site of the fire. The reasons for the elevated concentrations have to be seen in an uptake of soil particles and animal foodstuffs that were contaminated by the airborne depositions caused by the fire. Even after a 4 week period without any particular surrounding-/feeding-related PCDF/D uptake no significant reduction of the ITE concentration of the eggs from a selected chicken run could be observed.

Chicken Meat

Meat samples from free-range chickens in the area of the main downwind direction also showed considerable PCDF/D contamination, as can be seen from the following table:

Chicken meat	pg ITE/g meat fat	Time interval between the day of the fire and the sampling day
Fire Accident Lingen 1996		
- 800 m lee-wards	26.0	25 d
- 1,700 m lee-wards	11.3	25 d
Local reference value	5.5	25 d
Background level [7]	0.5 - 1.1	-

As a result of the findings in the hen's eggs and chicken meat samples, a panel of experts deemed as necessary, and arranged for, the slaughter of all free-range poultry and small animals that were bred for human consumption (e.g. chickens, ducks, rabbits). This measure was taken for reasons of precautionary health protection and was restricted to the so-called Sector I (30° sector, up to a distance of 1.3 km, lee-sided of the fire site). Furthermore, large animals that had been affected (e.g. sheep, horses) were placed under official supervision until further notice.

Other PCDF/D Investigations

Elevated PCDF/D concentrations, resulting from the fire, were further detected in samples taken from the vegetation and from fodder plants (up to 58 ng ITE/kg m_d). No particular PCDF/D contamination were found in 2 beef samples (max. 2.4 pg ITE/g fat) from a slaughter animal coming from the cow-shed with the highest contaminated cow's milk. The PCDF/D analyses of 2 human milk samples gave no indications of elevated concentrations (max. 24.1 pg ITE/g fat). The most polluted lee-side soil sample showed a PCDF/D content of 3.4 ng ITE/kg m_t (the upper 5 mm of soil were taken from an exposed vegetable garden approximately 150 m from the burned production hall). No particular PCDF/D contamination could be detected after completion of cleaning measures on a lee-side playground and inside a nearby residential building.

Conclusions

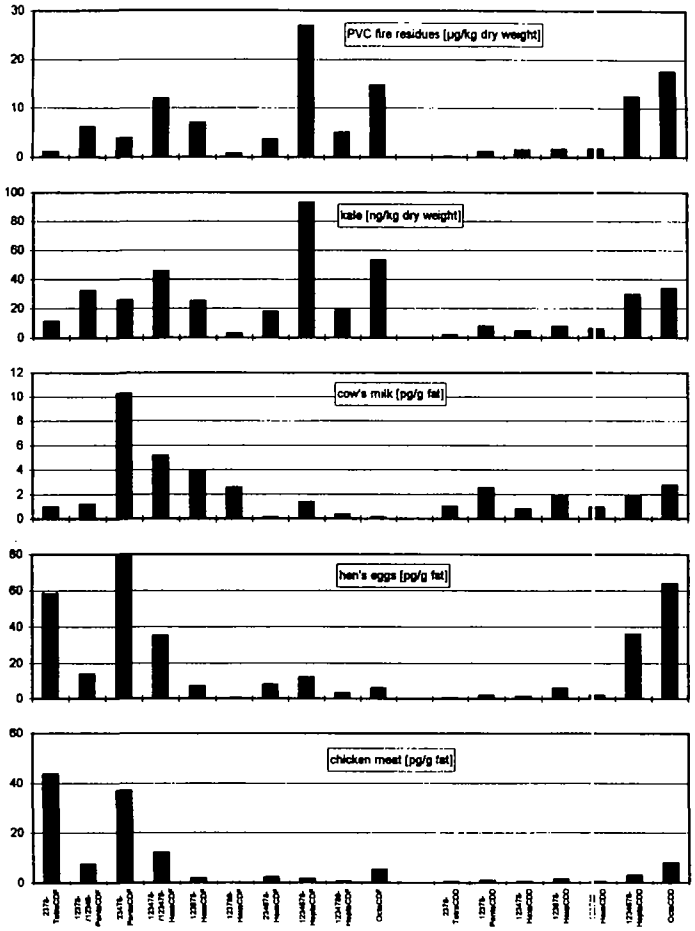
Significant contamination to certain environmental compartments, particularly through PCDF/D inputs, have to be assumed even where a few tons of PVC-containing materials - or generally chlorine containing fire loads - are involved in a fire and the resulting fumes are drifting away *close to the ground*. In order to assess the impact of a fire damage on the environment, PCDF/D soil analyses, especially those including the deeper ground layers, are not suitable; investigations of foodstuffs, vegetation or deposition samples provide better evidence in these cases.

Tab. 01: PCDF/D concentrations in PVC-combustion residues and in foodstuffs affected by the fumes of an accidental fire involving approx. 10 tons of Hard-PVC materials that occurred in Lingen/Ems (Germany) in November 1996; Analysis: GfA - Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH, FRG-48161 Münster

Matrix analysed	PVC combustion residues	Kale	Cow's milk	Hen's eggs	Chicken meat
GfA sample no.	96N152203	96N154202	96N154214	96N154502	96N165009
Dimension	µg/kg m_d	ng/kg m_d	pg/g milk fat	pg/g egg fat	pg/g meat fat
PCDFs					
Total TetraCDF	46.5	1400.8	0.97	78.4	66.6
Total PentaCDF	55.7	399.6	11.43	184.6	108.8
Total HexaCDF	65.9	288.1	11.67	118.9	27.1
Total HeptaCDF	40.1	139.4	1.73	20.6	2.7
OctaCDF	14.7	53.4	0.12	6.0	5.3
Total Tetra- through OctaCDFs	223.0	2281.2	25.92	408.5	210.5
2378-TetraCDF	1.07	11.21	0.97	58.3	43.8
12378-/12348-PentaCDF [a]	6.12	32.27	1.18	13.6	7.5
23478-PentaCDF	3.78	25.98	10.25	78.3	37.0
123478-/123479-HexaCDF [a]	11.90	45.64	5.12	35.4	12.1
123678-HexaCDF	6.93	25.01	3.87	7.0	1.8
123789-HexaCDF	0.76	2.94	2.55	0.4	0.1
234678-HexaCDF	3.54	17.71	0.11	7.9	2.2
1234678-HeptaCDF	26.98	92.78	1.36	11.7	1.6
1234789-HeptaCDF	4.97	18.96	0.37	3.1	< 0.5
PCDDs					
Total TetraCDD	7.7	473.3	1.00	2.1	1.8
Total PentaCDD	13.3	164.5	2.51	3.1	1.8
Total HexaCDD	22.2	86.8	3.67	14.1	3.7
Total HeptaCDD	22.2	60.1	1.84	39.8	4.0
OctaCDD	17.6	33.7	2.77	64.0	7.9
Total Tetra- through OctaCDDs	83.0	818.3	11.79	123.1	19.3
2378-TetraCDD	0.14	1.81	1.00	0.6	0.5
12378-PentaCDD	1.13	7.77	2.51	1.9	0.9
123478-HexaCDD	1.46	4.59	0.80	1.2	0.4
123678-HexaCDD	1.60	7.83	1.93	5.8	1.4
123789-HexaCDD	1.64	6.24	0.93	1.9	0.5
1234678-HeptaCDD	12.38	29.69	1.84	36.1	2.9
Total Tetra- through OctaCDF/Ds	305.9	3099.5	37.71	531.5	229.8
TE (BGA) excl. LD	6.34	48.3	4.06	24.2	12.3
ITE (NATO/CCMS) excl. LD	6.26	33.9	9.10	53.7	26.0
ITE (NATO/CCMS) incl. LD	6.26	33.9	9.10	53.7	26.1

a Isomers not separated on SP 2331 as GC stationary phase

Fig. 01: Concentration profiles of the 2378-chlorosubstituted PCDF/D congeners in the 5 samples of table 01



Literature Cited

1) Dokumentation Großbrand vom 04. November 1996, *eds.: Umweltamt der Stadt Lingen*, **1997**
2) Dokumentation Großbrand eines Kunststofflagers in Lengerich im Oktober 1992, *eds.: Umweltministerium des Landes Nordrhein-Westfalen (NRW)*, **1994**
3) Funcke, W.; Theisen, J.; Balfanz, E.; König, J. *Staub-Reinhaltung der Luft* **1988**, 48, 393 - 396
4) Theisen, J.; Funcke, W.; Hamm, S., *eds.: Umweltbundesamt Berlin*, Forschungsbericht 104 09 222, **1991**
5) Bericht des Chemischen Labors Dr. Wirts und Partner GmbH, Hannover, **1996**
6) Prinz, B.; Krause, G.H.M.; Radermacher, L. *Chemosphere* **1991**, 23, 1743 - 1761
7) Päpke, O.; Fürst, P. *Organohalogen Compounds* **1995**, 22, 143 - 171
8) 2. Bericht der Bund/Länder-Arbeitsgruppe DIOXINE, *eds.: Deutsches Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit*, **1993**
9) Malisch, R. *Organohalogen Compounds* **1995**, 22, 263 - 273.