

PCDD/F and PBDD/F Concentrations in the Air of Working Places of a MSWI-Plant in Germany

H.-J. MOSCHE, N. BUCHHOLZ, M. VOLLE, ST. AHLBRAND, J. WIECHENS

CHEMISCHES LABORATORIUM DR. E. WESSLING GmbH
Oststraße 6, 48341 Altenberge, Germany

With simultaneous air sampling for PCDD/F and PBDD/F at 14 different spots at a MSWI-plant, a collection of datapoints was obtained for the rating of workers health situation. As a base for the rating the German TRK-value for the PCDD/F's, which sets a limit at 50 pg/m³ I-TE for industrial working areas, was used to interpret the results.

The occurrence and correlation of PCDD/F and PBDD/F is discussed. The results show, that although the TRK-limit was not reached in this example, the PBDD/F can add a significant value of toxicity to that of the PCDD/F in some areas.

MSWI-plants in Germany are under the strict observation of the public, because of their real or perceived emission of PCDD/F in the environment in the past and until today. Since 1990 the emission of PCDD/F in outstream is limited to 0.1 ng/m³ I-TE (17. BImSchV) to all new plants being built or planned. All older plants have to be modernised until 1995. This step leads to a very effective filtration of fine dust and adsorption of gaseous compounds out of the waste gas and on the other hand to more toxic residue waste collected out of gas cleaning steps of the plant. Workers involved in activities at 'hot spots' in MWI-plants so still may be exposed to a higher risk, although PCDD/F concentrations will decrease due to better combustion technologies and waste gas cleaning technics in the future. To have more knowlegde about this risk and to get control for steps that minimise that risk, working place analysis of PCDD/F and their related compounds PBDD/F can be used.

Project Design:

In this example known and supposed 'hot spots' are compared with places that were not supposed to be involved in the PCDD/F and PBDD/F immission (new machine building) caused by the technical installations. The sampling was carried out from October 1993 - March 1994.

Those 'hot spots' were: P 1 - P 3 municipal waste handling area
P 4 - P 9 combustion area with higher temperature surrounding
P10 - P12 residue waste handling area

As reference points P 13 and P 14 were selected. For location of this points see scheme 3.

HUTOX

All sampling spots except the reference point P 14 were working places with longer stay of the exposed persons. The samplers were collected on a filter system consisting of a glass fibre filter followed by two PU-foam pieces.

The sampling was carried out during 16 h with a speed of 3 m³/h. The sampling speed for P 11 was 22 m³/h carried out for 1.5 h (a high volume sampler was used). The procedure follows the German ZH 1/120.47²⁾ and BIA 6880³⁾ sampling and analysis procedures.

The table 1 shows the monitored components for this project:

2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD	TCDD PeCDD HxCDD HpCDD OCDD	2,3,7,8-TBDD 1,2,3,7,8-PeBDD 1,2,3,4,7,8-HxBDD incl. 1,2,3,6,7,8-HxBDD 1,2,3,7,8,9-HxBDD 1,2,3,4,6,7,8-HpBDD	TBDD PeBDD HxBDD HpBDD
2,3,7,8-TCDF 1,2,3,7,8-PeCDF + 1,3,4,6,9-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF	TCDF PeCDF HxCDF HpCDF OCDF	2,3,7,8-TBDF 1,2,3,7,8-PeBDF 2,3,4,7,8-PeBDF 1,2,3,4,7,8-HxBDF 1,2,3,6,7,8-HxBDF 2,3,4,6,7,8-HxBDF 1,2,3,7,8,9-HxBDF 1,2,3,4,6,7,8-HpBDF 1,2,3,4,7,8,9-HpBDF	TBDF PeBDF HxBDF HpBDF
		Included in the totals Coelution with other PBDD/F-congeners are possible	

Table 1

The analysis was carried out by intensive soxhlet extraction, extract fine cleaning procedures under elimination of daylight and HRGC/HRMS measurement. (see figure 3: analysis scheme)

The sampling efficiency, the reproducibility and the cross contamination was controlled by quality assurance steps.

The limit of determination could be calculated from statistic data as 0.14 pg/m³ I-TE for the PCDD/F.

Results:

Comparison between I-T E and the measured dust and temperature values

Location	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14
dust (mg/m ³)	0.70	8.00	18.50	0.96	0.90	0.64	0.08	<0.01	<0.01	1.3	3.00	0.31	0.13	0.30
temperature (°C)	14.9	11.0	13.0	13.4	29.8	30.7	15.0	25.0	25.0	16.0	12.0	14.0	22.8	10.5
I-TE (pg/m ³)	0.4	0.6	1.7	8.9	5.6	14.5	2.4	1.7	2.1	0.3	0.3	1.0	0.2	0.7

no correlation

Table 2

Waste handling area P 1 - P 3

PCDD/F :

The values for the waste supply are 0.4 and 0.6 pg/m^3 I-TE. These amounts are quite low and caused by dust of the waste supplying. This waste was not dried.

A significant higher value of 1.7 pg/m^3 I-TE in the waste bunker is caused by dryer waste being handled by a crane in the housed waste bunker.

PBDD/F:

In all spots the PBDF's dominate. The value for the waste supply show a strong variation between 100 pg/m^3 and 6.3 pg/m^3 for the tetra-hepta-BDD/F. For P 1 this amount is more than 3 times higher as for the PCDD/F. P 3 shows a good correlation to the PCDD/F (325 pg/m^3 PBDD/F to 315 pg/m^3 for PCDD/F) with similar amounts of the totals.

Combustion area with higher temperature surroundings P 4 - P 9.

PCDD/F:

The points P 4, P 5, P 6 show a 10- 20 times higher PCDD/F concentration compared with spots of the waste handling area. These spots around the older combustion chambers (K 1, K 2 and K 3) produce a higher temperature surrounding niveau due to wore insulation and more leakstreaming as the K 4 which is a later design. The value of 14.5 pg/m^3 I-TE for P 6 was measured in 15 m high near the ventilatore system.

P 7, P 8, P 9 show significant lower values for the I-TEs at K 4.

PBDD/F:

The values correlate quite good with the PCDD/F except for the higher amounts for the PBDD/F at K 4 - combustion chamber. Values from 156 pg/m^3 to 607 pg/m^3 add a significant amount to the PCDD/F toxic potential. Because no OBDD and OBDF was analysed, and three of the four 2, 3, 7, 8 - HxBDF cannot be identified on the used GC-column, yet a calculation of a TE for the PBDD/F is quite inaccurate.

A part of 15 - 50 % added for the PBDD/F in a PCDD/F-PBDD/F- I-TE value is possible for this examples.

Residue waste handling areas:

PCDD/F:

All spots show low values from 0.3 - 1.0 pg/m^3 I-TE. Specially the low PCDD/F amount at the flyash shift station was surprising.

HUTOX

PBDD/F:

A good correlation to the PCDD/F amount is given at the washer building and the ash running belt. A poor correlation to the PCDD/F at the flyash shift station was obtained.

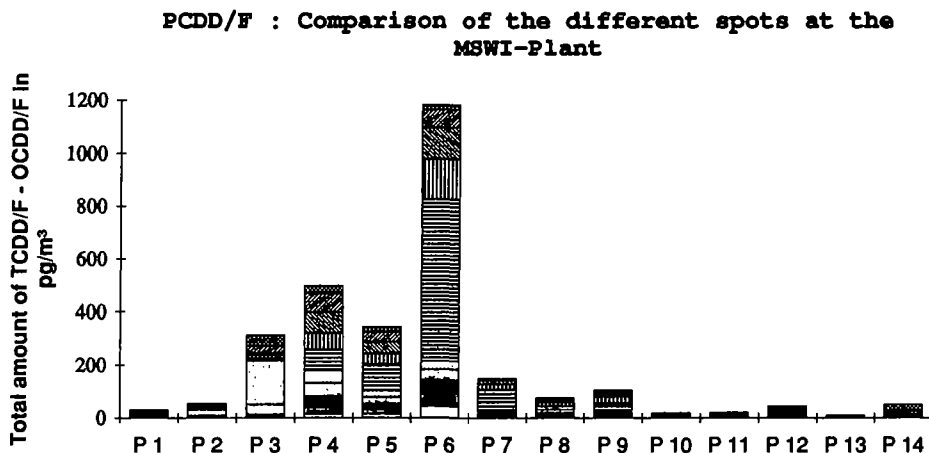


Figure 1a :

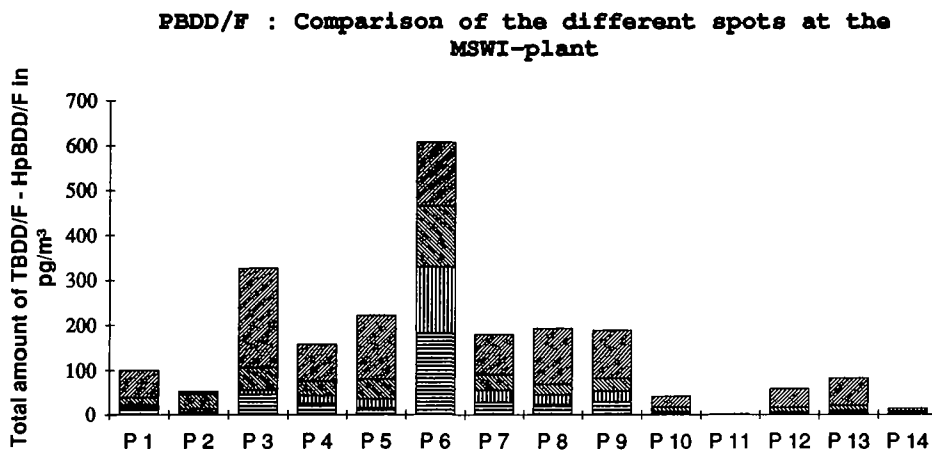


Figure 1b :

Summary:

The results show a good correlation between the PCDD/F and PBDD/F for the most analysed samples. A significant value of toxic potential considering of the PBDD/F (10 - 256 % of the amount from tetra- to hepta-BDD/F) is added to the PCDD/F's.

The I-TE values for the PCDD/F are increasing by the consideration of the PBDD/F by estimated 15 - 50 % for the most spots in this example. Therefore the PBDD/F should be considered in further analysis to get more and better data to precise this early results.

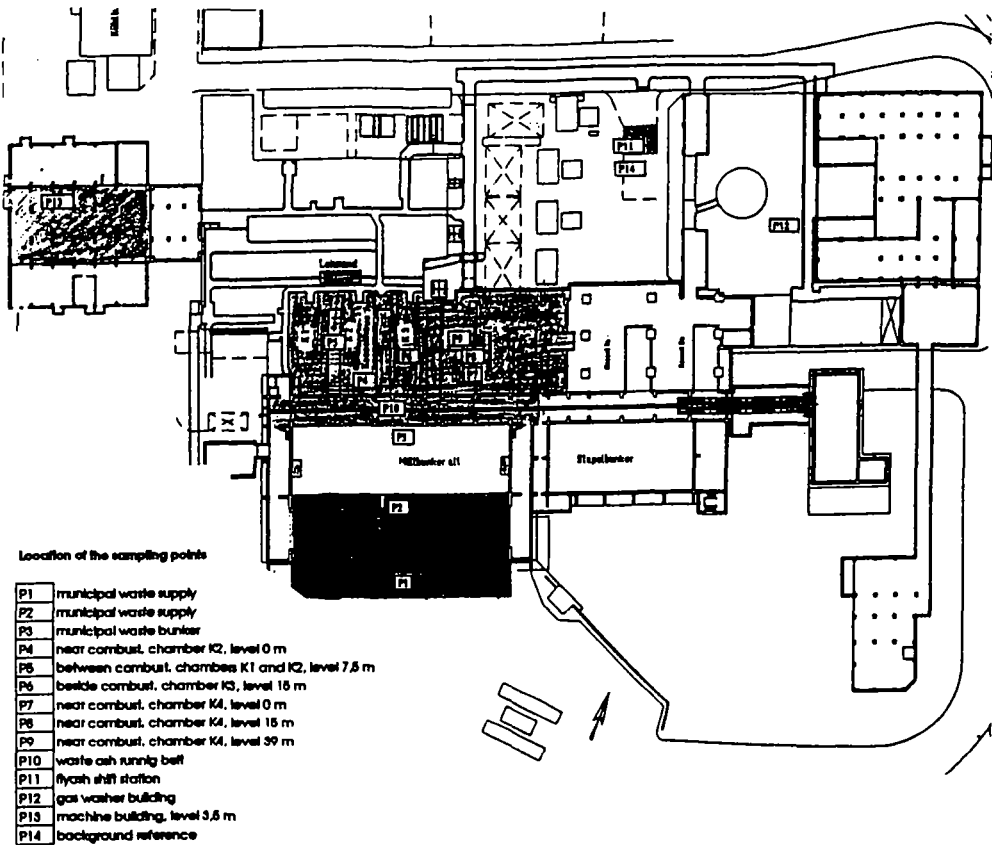


Figure 2: Location of the sampling points

HUTOX

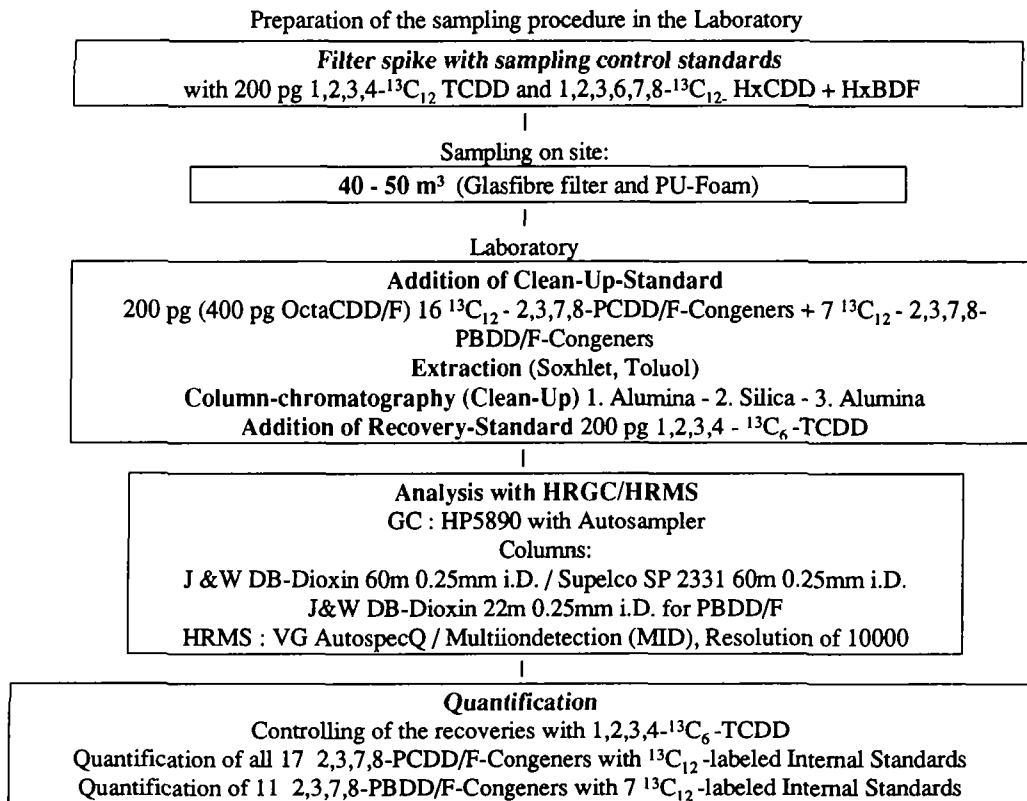


Figure 3 : Scheme of PCDD/F-, PBDD/F-analysis of workplaces

Literature:

- 1.) R. Stockmann, J.U. Hahn: Polychlorierte Dibenzodioxine und -furane an Arbeitsplätzen, Staub-Reinhaltung der Luft 53 (1993)
- 2.) Verfahren zur Bestimmung von 2,3,7,8-Tetrachlordibenzo-p-dioxin und anderen in 2,3,7,8-Stellung chlorierter PCDD und PCDF (ZH/120.47) Carl Heymanns Verlag, Cologne Germany ('91)
- 3.) BIA-Arbeitsmappe 10 Lfg. IV/93, Methode 6880
Erich Schmidt Verlag, Germany (1993)
- 4.) M. Neupert, A. Grupe, H. Weis: Stability of polybrominated dibenzo-p-dioxins and dibenzofurans under laboratory handling conditions, Chemosphere Vol.17 No. 6 1089-1097 (1988)
- 5.) U. Lahl, M. Wilken, A. Wiebe: Polybromierte Diphenylether in der Müllverbrennung Müll und Abfall 2/91 (1991)
- 6.) J. Wiechens: Entwicklung eines Probenvorbereitungsverfahrens für die gaschromatographische Bestimmung von polybromierten Dibenzo-p-dioxinen und polybromierten Dibenzofuranen in unterschiedlichen Matrices, diploma (1993), E. Krahe', Fachhochschule Münster, Chem. Labor. Dr. Weßling GmbH Altenberge, Germany