

Measurement of deposition of dioxins in Flanders, Belgium

R. De Fré, M. Wevers, R. Van Cleuvenbergen and J. Schoeters

VITO, Vlaamse Instelling voor Technologisch Onderzoek, Boeretang 200, B-2400 Mol

1. Abstract

The deposition of 17 PCDD and PCDF congeners was sampled using Bergerhoff deposition gau during one month at 10 locations in Flanders, Belgium in the period from October 1993 to Janu 1994. The measured dioxin deposition ranged from 0.7 ng TEQ.m⁻².y⁻¹ to 374 ng TEQ.m⁻². Elevated dioxin depositions were measured nearby municipal waste incinerators and in an indust area. The range of the present measurements is wider than the values calculated earlier for this reg based on the 1988 dioxin emissions, the difference being assigned to the higher temporal and spa resolution of the experimental data, variations in emissions, and to weather conditions. The conge profiles in two samples with high concentrations near MSW incinerators show an increased abunda of the lower chlorinated species compared to the composition of the incinerators emissions. If the t toxic equivalency factors of these deposition samples are applied to the emissions, it is concluded t the stack measurements underestimate the TEQ emission by a factor of 3.

2. Experimental

The samples were collected in Bergerhoff deposition gauges, as described in the German VDI 211 standard. A cylindrical glass jar with 9.5 cm inner diameter, 20 cm high and a volume of 1.5 litri placed on a 1.5 m high pole for a period of at least 30 days. The Bergerhoff gauge was chosen beca it is made of glass and can be heated in a furnace to 450°C for several hours, in order to obtain blanks. Unlike the VDI standard for dustfall we added 1 cm of water in the gauges at the start of sampling period. The reason for this is that the efficiency of the gauges may be influenced by presence of water, so it is preferable to have water at all times, rather than from a random mor determined by the first rainfall in the collection period. A disinfectant was not added to the water. locations of the samples are given by the Lambert coordinates in table 1. Mol, Eksel and Moerk can be considered background sites at distances of at least 10 kilometres from MSW incinerators. samples from Menen and Melsele are strongly influenced by nearby incinerators with relatively emissions, the distances from the chimneys being 600 m and 625 m respectively. The other locat are under mixed influence from urban, industrial and waste incinerator emissions. The samples v taken during winter in order to minimize evaporation and photodecomposition of collected dioxins The wind roses for the sampling periods were drawn and show that the collectors received air me from sources in the southwest and the northeast direction for the first sampling period and in the s for the second period. In the first period from October 26th to December 2nd 1993, after collec large amounts of rain, several gauges froze and broke. At these places the samplings were repe from December 9th, 1993 to January 11th, 1994. The second sampling period was characterise unusually high amounts of precipitation, as can be seen from table 1. The annual rainfall for the re is 700 to 1000 mm. The samples from the gauges were filtered in a pre-extracted glass fibre thi which was then dried in air for 48 hours, spiked with internal ¹³C standards, and extracted

toluene by soxhlet for 24 hours. In the treatment of the wet fraction, according to Kirschmer et al. (2) evaporation losses of dioxins were avoided by replacing the water evaporation step by 3 solvent extractions with dichloromethane. The extracts from both fractions were combined, dried with anhydrous Na_2SO_4 and cleaned by column chromatography on Alumina B Super I. ^{13}C -1,2,3,4-TCDD was used as the syringe spike. The 17 congeners with 2,3,7,8-Cl-substitution were analysed by HRGC-HRMS. Gas chromatography was done on a DB-Dioxin column of 60 m x 0.25 mm x 0.25 μm and, if the 1,2,3,7,8-PeCDD or 2,3,4,7,8-PeCDF congeners were present, repeated on a CP-Sil-88 column of similar size, in order to eliminate possible co-elution of peaks on these high TEF congeners. The instruments used were a HP5890II GC with VG Autospec Q mass spectrometer.

3. Results and discussion

Table 1 shows the deposition values as TEQ on a daily and yearly basis, together with the coordinates of the locations and the rainfall during the sampling period. The deposition in mass units of the 17 individual congeners analysed at each location are given in Table 2.

Table 1: Deposition of dioxins and precipitation data at the sampling locations

Location	date	Lambert coordinates		rain mm	Deposition of dioxins, as I-TEQ	
		x, m	y, m		$\text{pg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	$\text{ng}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$
Berendrecht	26/10/93 - 02/12/93	148140	226500	48	211	77
Sint-Niklaas	26/10/93 - 02/12/93	132710	206960	51	46	17
Melsele	26/10/93 - 02/12/93	146700	210480	65	108	39
Moerkerke	26/10/93 - 02/12/93	79730	216520	40	14	5.1
Menen	28/10/93 - 02/12/93	61175	165250	32	1025	374
Eksel	09/12/93 - 11/01/94	219560	205510	206	8	2.9
Ham	09/12/93 - 11/01/94	205875	198300	179	41	15
Zelzate	09/12/93 - 11/01/94	111860	209690	154	46	17
Vilvoorde	09/12/93 - 11/01/94	154940	191390	166	37	13
Mol	09/12/93 - 11/01/94	199490	211930	184	1.9	0.7
Blank					0.13	0.05

A first point of discussion is the representativity of the sampling method. Deposition of dioxins has been measured by the Bergerhoff device (2), with snow collectors or in snow packs (3) and with frisbees (4). Tashiro et al. (5) used precipitation collectors and XAD cartridges to analyse dioxins in wet deposition. Koester and Hites (6) used wet-only collectors, inverted frisbees and flat plates covered with a mineral oil film. An analysis of the performance of these collectors for dioxins in different environments has not yet been made. Experiments with 7 types of deposition gauges in Belgium in 1979 (7) have demonstrated that the quantities of dust collected by different devices only show reasonable correlation in regions with high dustfall. For heavy metals deposition NILU and Bergerhoff gauges were tested simultaneously during 2 years at two stations. The NILU gauge, which is the standard method in Belgium, always measured higher heavy metal depositions. The 2-year average ratios of the measured depositions (NILU/Bergerhoff) for the two stations are resp. for Cd: 2 and 1.7, for Cu: 1.5 and 1.3, for Pb: 1.4 and 1.7, and for Zn: 1.2 and 1. It is concluded that the experimental method can bias deposition results by at least a factor of 2. For dioxins the net influx to the soil is

Table 2: Deposition of PCDD and PCDF congeners in $\text{pg}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$
 ("<" signs precede actual detection limit for results below D.L.)

Congener	Berendrecht	Sint Niklaas	Melsele	Moerkerke	Menen
2,3,7,8-TCDD	<17.9	<6.40	<5.90	<30.6	53.5
1,2,3,7,8-PeCDD	102	<12.6	53.3	<60.9	640
1,2,3,4,7,8-HxCDD	44.2	25.0	26.9	<75.0	396
1,2,3,6,7,8-HxCDD	78.8	23.3	51.8	<64.3	394
1,2,3,7,8,9-HxCDD	<24.9	20.5	28.1	<61.7	463
1,2,3,4,6,7,8-HpCDD	495	95.5	195	<82.6	1899
OCDD	2113	278	396	<71.9	1481
2,3,7,8-TCDF	99.0	19.9	<4.38	<18.0	190
1,2,3,7,8-PeCDF	86.0	26.2	52.5	<33.2	320
2,3,4,7,8-PeCDF	173	44.5	84.1	<2.51	579
1,2,3,4,7,8-HxCDF	115	27.8	55.2	<38.8	588
1,2,3,6,7,8-HxCDF	140	38.8	76.9	<37.4	543
2,3,4,6,7,8-HxCDF	89.8	36.7	54.4	41.5	459
1,2,3,7,8,9-HxCDF	26.5	9.63	25.5	58.2	43.9
1,2,3,4,6,7,8-HpCDF	208	77.3	152	<51.0	1517
1,2,3,4,7,8,9-HpCDF	24.3	<10.9	39.2	<82.2	172
OCDF	95.9	<13.9	136	<88.3	410
PCDD + PCDF	3890	723	1426	100	10148

Congener	Eksel	Ham	Zelzate	Vilvoorde	Mol
2,3,7,8-TCDD	<5.76	<4.48	<6.66	<4.99	<4.91
1,2,3,7,8-PeCDD	<13.0	<10.9	<16.7	10.4	<10.6
1,2,3,4,7,8-HxCDD	<11.2	<9.86	<13.5	<9.22	<9.86
1,2,3,6,7,8-HxCDD	23.9	39.7	<10.6	<8.11	<9.09
1,2,3,7,8,9-HxCDD	18.1	26.9	21.8	<7.98	<7.90
1,2,3,4,6,7,8-HpCDD	207	207	220	287	105
OCDD	598	491	615	644	324
2,3,7,8-TCDF	<4.57	<7.77	<9.69	<3.54	<2.94
1,2,3,7,8-PeCDF	<6.06	<5.93	<9.39	<5.51	<6.49
2,3,4,7,8-PeCDF	<6.70	35.1	46.1	28.0	<6.06
1,2,3,4,7,8-HxCDF	<6.66	26.7	44.0	31.7	<5.38
1,2,3,6,7,8-HxCDF	<5.80	50.4	49.5	44.8	<5.63
2,3,4,6,7,8-HxCDF	<6.06	33.9	62.3	44.0	<5.76
1,2,3,7,8,9-HxCDF	<8.32	12.3	<8.11	<6.66	<7.00
1,2,3,4,6,7,8-HpCDF	99.9	135	185	148	54.6
1,2,3,4,7,8,9-HpCDF	<9.30	27.1	30.0	31.2	<7.90
OCDF	109	102	255	126	<10.5
PCDD + PCDF	1055	1187	1528	1395	484

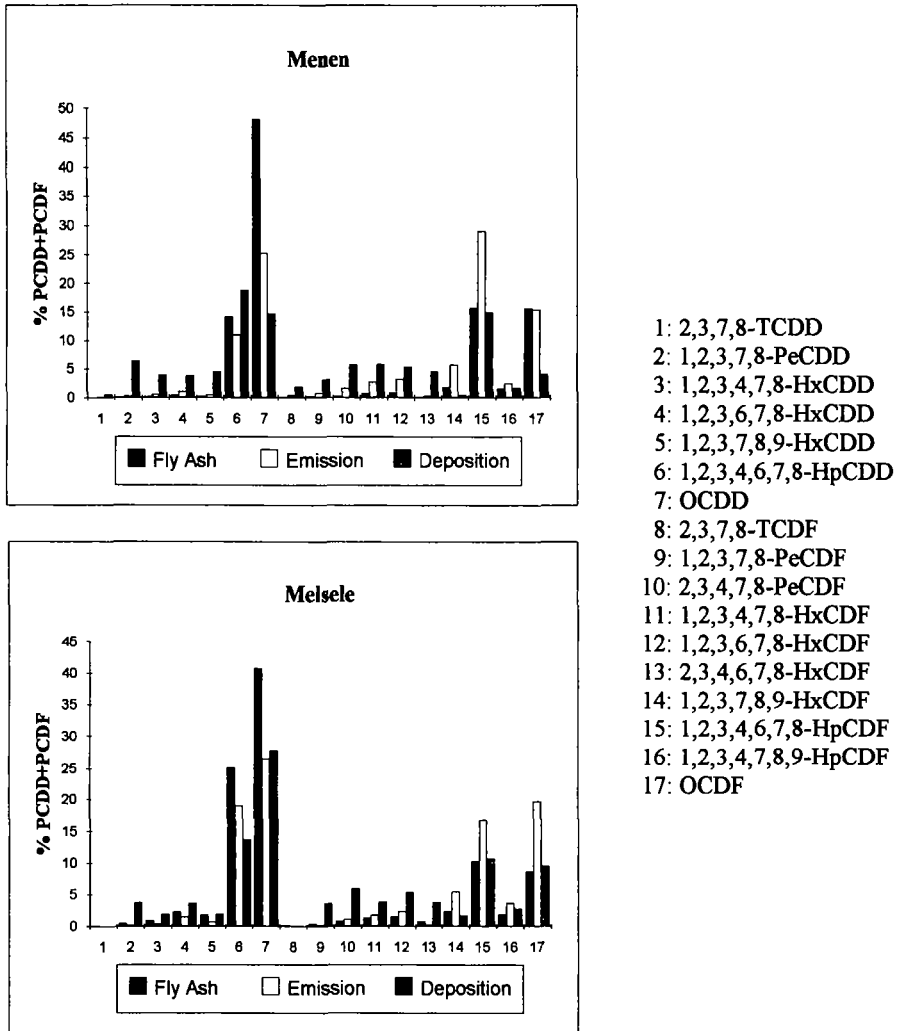
further complicated by vapour phase deposition effects. Furthermore it is known that increased deposition occurs e.g. on grassland due to a higher particle interception efficiency. It is interesting to note that the total inner surface of the gauges is about 10 times the vertical area, quite similar to grassland and crops, where the foliage surface equals 10 to 20 times the ground area.

Some caution is further required in handling the background deposition results of our background locations. As can be seen from table 2, in the low samples the most toxic congeners are below detection limit (D.L.). We consider that these samples contain a substantial concentration of the congeners below D.L. The results in TEQ are quite sensitive to this: e.g. if we assume all undetected congeners to be present at one third of D.L. level, then the results of Moerkerke, Eksel and Mol in TEQ would rise by a factor of 3, 2 and 4 respectively. The map of dioxin deposition in this part of Western Europe was calculated by Van Jaarsveld et al. with the TREND model and the emissions estimates for 1988 (8). The model calculates an average deposition of $8.7 \text{ ng I-TEQ.m}^{-2}.\text{y}^{-1}$ for Belgium. The annual averages for 30 km squares range from 3.2 to $48 \text{ ng I-TEQ.m}^{-2}.\text{y}^{-1}$. Assuming that little change to the emissions has occurred in this period, and referring to the inherent uncertainty of the method, we consider that there is a fair agreement between measured and calculated data. Our measurements show both higher maxima and lower minima. This can be explained to a large extent by the higher temporal and spatial resolution of our data, and by the variation in emissions of the sources. The two samples nearby MSW incinerators are situated in regions where a steep gradient in deposition isolines is present, and integration over larger areas yields lower average depositions. However these samples were not taken at the points with the highest expected deposition. Deposition calculations indicate that the local maxima in 100 m squares may still be 10 times higher than the reported data. The extremely wet weather in the observation period results in a higher contribution from wet deposition, and consequently increased deposition close to the source, with a smaller fraction available for long range atmospheric transport toward background areas. The extremely high value at Menen was not unexpected with respect to local milk samples of 28 pg TEQ/g fat in 1992 and 13 pg/g in 1993. Measurements at the incinerator during 6 days in 1993 however did not reveal high dioxin emissions. Fly ash from the incinerators ESP was a suspected source of dioxin contamination, since this material is transported by road, and may have had uncontrolled applications in the past, such as road hardening. Therefore the profiles of the 2,3,7,8-congeners in the incinerator emission, the fly ash and the deposition were compared (figure 1). The deposition sample shows a pattern more similar to the incinerator emissions than to fly ash, which contains a higher fraction of the less volatile octa and hepta congeners. From the similarity of their profiles the stack emissions can be indicated as the main source of deposited dioxins. However there is a systematic increase of the more volatile congeners in the deposition, and consequently the total TEF (ratio of TEQ content versus total PCDD+PCDF concentration) of the deposition mixture significantly exceeds that of emissions and of the fly ash. The same was observed in the deposition near the incinerator in Melsele, as can be seen from figure 1 and table 3. Generally an increase of OCDD is noted in remote deposition and air samples (9), which is attributed to the longer atmospheric lifetime of OCDD. The increase of the tetra through hexa 2,3,7,8-congeners close to the source could be explained by higher deposition velocities of the vapor phase congeners. Volatilization of deposited PCDDs and PCDFs has been suggested (10) as a source of increased atmospheric concentrations of lighter congeners. However, the average temperatures from 5 to 10°C during the sampling periods do not allow an appreciable fraction of dioxins in the vapor phase. Chemical changes of the PCDD/F mixture in the atmosphere or the sample involving dechlorination or rearrangement steps could be considered, but these are not likely to increase the total toxicity. In our opinion the most viable explanation is that in the emission sampling significant quantities of the lighter and more toxic congeners are lost. The emission samples referred to in table 3 were taken by a condensation and adsorption method during 5 hours each, which implies a long contact time between sample and flue gas, and therefrom a risk of degradation of less stable congeners. The first two rows of the table 3 indicate that if the emissions, at constant mass concentration of PCDD/Fs, are assigned the same TEF as the deposition samples, the actual emission measurements underestimate the TEQ output of the sources by a factor of 3 at least.

Table 3: Toxic Equivalency Factors of deposition and incinerator samples

	Menen	Melsele
TEF of deposition sample:	0.10	0.075
TEF of MSWI emissions (6 samples):	0.030	0.024
TEF of MSWI fly ash (6 samples):	0.010	0.023

Figure 1: PCDD and PCDF congener profiles in deposition, fly ash and incinerator emissions



4. References

- 1) Atkinson R.
Atmospheric lifetimes of dibenzo-p-dioxins and dibenzofurans
Sci. Total Environ., 104(1-2), 17-33, 1991
- 2) Kirschmer P., Muelder W., Eynck P.
Comparison of sample preparation and extraction procedure for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans in deposited particulate matter and bulk deposition
Chemosphere, 24(5), 575-80, 1992
- 3) Marklund S., Tysklind M., Andersson R., Ljung K., Rappe C.
Environmental deposition of PCDDs and PCDFs as determined by the analysis of snow samples from northern Sweden
Chemosphere, 23(8-10), 1359-64, 1991
- 4) Fernandes A. R., Bushby B. R., Faulkner J. E., Wallace D. S., Clayton P., Davis B. J.
The analysis of toxic organic micropollutants (PCDDs, PCDFs, PCBs, and PAHs) in ambient air and atmospheric deposition
Chemosphere, 25(7-10), 1311-16, 1992
- 5) Tashiro C. H. M., Steer P. J., Shackleton M. N., Reid N. W., Clement R. E.
Dioxins and furans in wet and dry deposition in Ontario
Proc., Annu. Meet. - Air Waste Manage. Assoc., 84th(Vol. 6A), Paper 91/76.7, 1991
- 6) Koester C. J., Hites R. A.
Wet and dry deposition of chlorinated dioxins and furans
Environ. Sci. Technol., 26(7), 1375-82, 1992
- 7) Thiessen L. Personal communication on comparison of deposition gauges in the Belgian monitoring network, 1994
- 8) Van Jaarsveld J. A., Schutter M. A. A.
Modeling the long-range transport and deposition of dioxins, first results for NW Europe
Chemosphere, 27(1-3), 131-9, 1993
- 9) Eitzer B. D., Hites R. A.
Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans
Environ. Sci. Technol., 23(11), 1396-401, 1989
- 10) Goldfarb T. D., Harrad, S. J.
Consideration of the environmental impact of the volatilization of PCDDs and PCDFs
Chemosphere, 23(11-12), 1669-74, 1991