Concentrations of PCDDs and PCDFs in ambient air at selected locations in Flanders.

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ABSTRACT.
Air samples were collected to estimate PCDD and PCDF concentrations in ambient air in Flanders at typical locations including rural sites, the largest industrial areas and urban locations. Two different high volume sampling techniques were used: a Ströhlein high volume sampler, collecting the particles at a rate of 75 m^3/h and a two phase samlper, equipped with a filter and a polyurethane foam (PUF) absorbent to collect the gas phase as well as the particulates at a rate of 24 m^3/h.
Ambient air concentrations between 17,5 and 587 fg TEQ/m^3 were analyzed with a PCDD contribution of 54 % ± 18 % to the total TEQ content, whereas the dioxins accounted for 80 % to 98 % of the total mass of all 2,3,7,8 chlorinated dioxins and dibenzofurans.
Since the high volume sampler collects more PCDDs and PCDFs than the two phase sampler for all congeners and at all temperatures of our measurements (4°C - 20°C), it is concluded that the sampling efficiency of the aerosol has a dominant effect on the dioxin concentrations measured in ambient air.

SAMPLING LOCATIONS.
Six sampling locations were selected, geographically spread over Flanders and in the neighbourhood of (a) typical emission source(s).
- Mol: this station was located in a rural area with a coal fired power station at 1 - 4 km from the sampling site.
- Moerkerke: a rural location with a large municipal waste incinerator (175000 ton/yr) at about 10 km W from the sampling site as the nearest known source.
- Berendrecht: is situated in the Antwerp harbour area, with industry stretching out 2 - 15 km SE to SW from the sampling site and the city of Antwerp at 15 km SE.
- Zelzate: this sampling site is situated in the vicinity of metalurgical and chemical industry at the Gent-Terneuzen canal, with a highway at 1 - 15 km SW from the sampling site and the city of Gent at 20 km SW.
- Ham: a location characterized by chemical industry and a highway at 2 - 7 km SE to W from the sampling site.
- Vilvoorde: situated at about 15 km NE from the Brussels metropolitan centre, characterized in addition by a coal fired power station at 1 km W and industry extending 1 - 7 km SW - W, including a MWI at about 6 km SW from the sampling site.

TRANS

SAMPLING AND ANALYSIS.

The samples were taken simultaneously with two different sampling systems from April to October 1992. A commercial high volume sampler, Ströhlein HVS 150, collected the particles on a precleaned and conditioned glass fiber filter at a rate of 75 Nm^3/h during 24 hours. A second sampling system was built in our laboratory to collect the vapour phase as well as the particulates [3]. This system uses a 125 mm glass fiber filter and two polyurethane foam plugs with a diameter of 60 mm, a thickness of 50 mm each and 75 ppi. The intake was mounted at 1.0 m above ground level. The air samples with this apparatus were taken at a rate of about 24 m^3/hour .

After the sampling the filter and the filter and PUF were spiked with an internal standard of 10 ^{13}C-labeled congeners and soxhlet extracted with dichloromethane for at least 24 hours.

The separation and clean up procedures were based on liquid column chromatography on alumina with benzene, 2 % CH_2Cl_2/n-hexane and 50 % CH_2Cl_2/n-hexane. The last fraction contains PCDDs and PCDFs.

After addition of $^{13}C_{12}$-1,2,3,4-TCDD as recovery standard the analyses of the seventeen 2,3,7,8-chlorinated dioxins and dibenzofurans were performed on a HP 5890 Series II GC coupled with a HP 7673 auto-injector operating in the splitless mode and a VG Autospec Q high resolution mass spectrometer with selected ion mode detection.

PCDDs AND PCDFs IN AMBIENT AIR IN FLANDERS.

At each location at least three air samples were collected with a sampling period of 24 hours. When possible, periods with a dominating SW wind were selected to obtain samples that were typical of the locations. The SW wind direction is prevailing in Belgium. The results summarized in table 1 are expressed as fg 2,3,7,8-TCDD-equivalents/m^3 using the I-TEF NATO/CCMS scheme [4].

The levels found with the high volume sampler varied between 23,9 fg TEQ/m^3 in Mol and 587 fg TEQ/m^3 in Ham. With the sampling apparatus with PUF dioxin concentrations between 17,5 fg TEQ/m^3 and 379 fg TEQ/m^3 were analyzed. The concentrations are of the same magnitude as the 150 to 300 fg TEQ/m^3, measured in German industrial areas [5].

The total concentrations, expressed as fg TEQ/m^3 and averaged over all sampling periods, are highest at Ham, Vilvoorde and Zelzate. These locations also showed the highest TEQ levels in the soil [1]. Almost 80 to 98 % of the total mass of all 2,3,7,8 chlorosubstituted dioxins and dibenzofurans is made up by PCDDs, especially by hepta- and octa-CDD, except for Ham where the dioxin concentration amounts from 60 to 85 %. Also two samples from Vilvoorde are slightly different with only 74 % PCDD.

A typical contribution of the individual congeners as a percentage of the total TEQ is illustrated in figure 2. Especially 2,3,4,7,8 PeCDF is of interest while nearly no 2,3,7,8 TCDD, 1,2,3,7,8 PeCDF, 1,2,3,7,8,9 HxCDF or OCDF are analyzed. Averaged over all analyses the PCDDs account for 54 % ± 18 % of the total TEQ content.

With the exception of two measurements in Mol, the Ströhlein high volume sampler always collected more dioxins and dibenzofurans than the "two-phase" sampler. Since this two phase sampler is equipped with a PUF absorbent it is expected to collect the gas phase dioxins more efficiently. At higher temperatures and lower molecular weight an increasing part of PCDDs and PCDFs is present in the gas phase. However, when the data are plotted, no relationship between the ratio of the concentrations, analyzed with the two sampling systems and the temperature or molecular weight could be distinguished (fig.1). Therefore it is concluded that the PUF sampler had no enhanced collection efficiency for the more volatile dioxins. The Hi-Vol sampling always resulted in higher measured dust concentrations, and

in all but two cases in higher dioxin concentrations in the air. Consequently, the dioxin concentrations measured in ambient air are strongly influenced by the aerosol sampling procedure.

Table 1 : PCDD and PCDF concentrations as fg TEQ/m^3 in ambient air in Flanders.

Sampling location and date	High Volume 75 m^3/h	High Volume 24 m^3/h + gas phase	Wind direction; wind speed; temperature
Mol	149	140	209 °; 3.2 m/s; 10.5 °C
27/4/92-28/4/92	127	190	243 °; 2.7 m/s; 8.2 °C
28/4/92-29/4/92	23.9	46.3	268 °; 2.4 m/s; 7.7 °C
29/4/92-30/4/92	99.9 ± 66.7	125 ± 72.7	
Average conc.			
Berendrecht			
5/5/92-6/5/92	60.5	57.9	327 °; 3.2 m/s; 12.9 °C
6/5/92-7/5/92	151	97.8	271 °; 3.6 m/s; 14.9 °C
7/5/92-8/5/92	120	103	241 °; 4.4 m/s; 14.9 °C
Average conc.	111 ± 46.1	86.2 ± 24.7	
Zelzate			
11/5/92-12/5/92	161	70.2	216 °; 6.5 m/s; 10.0 °C
12/5/92-13/5/92	194	142	208 °; 6.5 m/s; 13.0 °c
13/5/92-14/5/92	164	143	118 °; 4.4 m/s; 19.1 °C
Average conc.	173 ± 18.2	118 ± 41.7	
Moerkerke			
19/5/92-20/5/92	107		86 °; 4.4 m/s; 20.2 °C
20/5/92-21/5/92	131	71.0	81 °; 4.0 m/s; 20.0 °C
1/7/92-2/7/92	122	79.8	S-SSW; 3.7 m/s; 17.7 °C
2/7/92-3/7/92	122	58.1	variable; 2.7 m/s; 17.4 °C
Average conc.	121 ± 9.8	69.6 ± 10.9	
Vilvoorde			
30/9/92-1/10/92	68.2	17.5	206 °; 3.1 m/s; 14.4 °C
1/10/92-2/10/92	337	194	321 °; 1.9 m/s; 12.5 °C
6/10/92-7/10/92	238	133	16 °; 4.9 m/s; 10.5 °C
Average conc.	214 ± 136	115 ± 89.5	
Ham			
13/10/92-14/10/92	587	379	347 °; 2.5 m/s; 4.4 °C
14/10/92-15/10/92	180	65.4	234 °; 4.2 m/s; 9.1 °C
15/10/92-16/10/92	170	50.7	239 °; 3.7 m/s; 5.6 °C
19/10/92-20/10/92	80.4	21.5	176 °; 3.5 m/s; 7.7 °C
Average conc.	254 ± 118	129 ± 167	

Figure 1: Relationship between the concentration ratio HiVol/Two-phase-sampler and the temperature (left) or molecular weight (right).

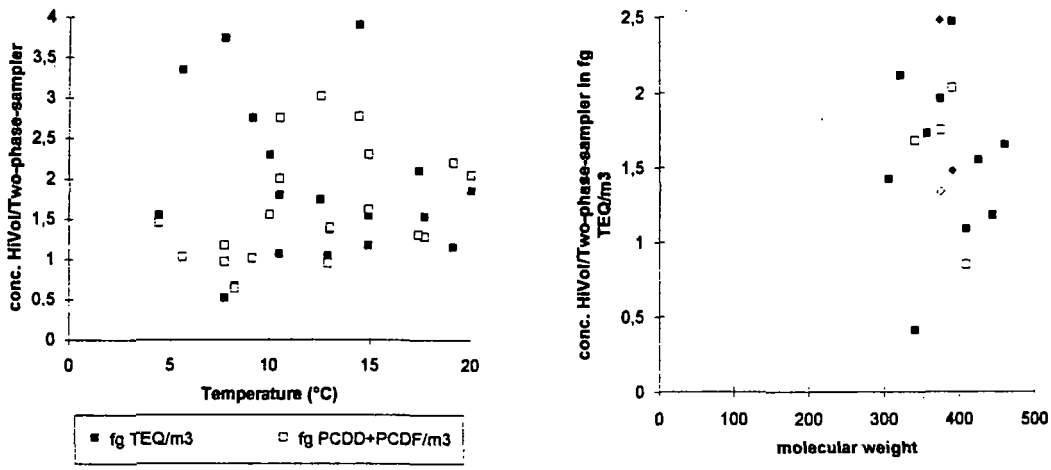
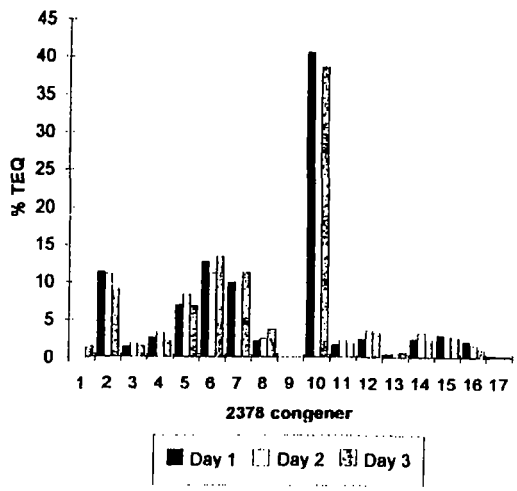


Figure 2 : Relative contribution of the individual congeners to the total TEQ content in Zelzate.



1= 2,3,7,8-TCDD
2= 1,2,3,7,8-PeCDD
3= 1,2,3,4,7,8-HxCDD
4= 1,2,3,6,7,8-HxCDD
5= 1,2,3,7,8,9-HxCDD
6= 1,2,3,4,6,7,8-HpCDD
7= OCDD
8= 2,3,7,8-TCDF
9= 1,2,3,7,8-PeCDF
10= 2,3,4,7,8-PeCDF
11= 1,2,3,4,7,8-HxCDF
12= 1,2,3,6,7,8-HxCDF
13= 1,2,3,7,8,9-HxCDF
14= 2,3,4,6,7,8-HxCDF
15= 1,2,3,4,6,7,8-HpCDF
16= 1,2,3,4,7,8,9-HpCDF
17= OCDF

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