DIOXINS AND DIBENZOFURANS IN TUNNEL AIR.

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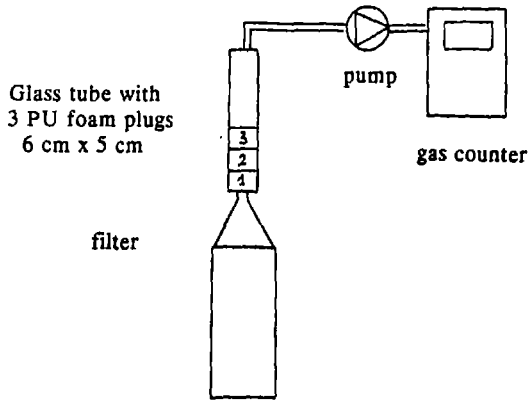
Motor vehicle emissions are known as a significant source of environmental dioxin but only few measuring data are available [1]. Therefore during the last months of 1991 air samples were taken inside the Craeybeckx tunnel in Antwerp (Belgium). Sampling in a tunnel provides the opportunity of analyzing emissions from automobiles under more concentrated conditions and with less interferences from other sources. The Craeybeckx tunnel is a two tube tunnel with a length of 1.6 km. Each tube has 4 lanes in the same direction. The sampling site was located in the tube toward Antwerp at about 1/4 of the exit. In the same period background concentrations were determined outside the tunnel in the vicinity.

Because of the very low concentrations of PCDDs and PCDFs in ambient air, large samples have to be collected for a successful measurement. Two different sampling systems were used and compared with each other. A standard high volume sampler, type Ströhlein HVS 150, collected the particles on a glass fiber filter (ø = 25.5 cm) at a rate of 75 Nm^3/h during 24 hours. Simultaneously, a modified high volume sampler equiped with a glass fiber filter (ø = 12.5 cm) and a polyurethane foam plug (ø = 6 cm, thickness = 3 x 5 cm, 75ppi) collected PCDDs/PCDFs at a sampling rate of 25 Nm^3/h (fig. 1). The intake was mounted at 1.0 m above the ground level.

Figure 1 : Scheme of the gas and particle phase high volume sampler.



After the sampling the filters were reconditioned, weighthed, spiked with a C-13 labeled internal standard of 10 pure isomers and soxhlet extracted

with n-hexane for about 24 hours. In the case of the filter/PUF equipment, filter and foam plugs were extracted together. To evaluate the vapour/particulate partitioning for PCDDs and PCDFs one of these samples was splitted in different parts which were analyzed separately.

The separation and clean up procedure were based on alumina liquid column chromatography with benzene, 2% CH_2Cl_2 /n-hexane and 50% CH_2Cl_2 /n-hexane. The last fraction contains all dioxins and furans [2].

The analyses of the seventeen 2,3,7,8-chlorinated dibenzo-dioxins and -furans were performed on a HP 3980 GC coupled with a VG AUTOSPEC Q high resolution mass-spectrometer. Quantitation of the PCDDs and PCDFs was based on calibration with the pure isomers.

In this paper results are reported of the chemical analyses of air samples on the occurrence of the seventeen toxic isomers of PCDDs and PCDFs. The levels of dioxins are expressed as fg (10E-15 g) 2,3,7,8-TCDD-equivalents, calculated on the basis of international toxicity equivalence factors (I-TEF NATO/CCMS).

Table 1 shows the partition of dioxins between particles and vapour phase.

Table 1 : Partition of dioxins between particles and vapour phase.

Congener	Filter	PUF 1	PUF 2	PUF 3
	fgTEQ/Nm^3	fgTEQ/Nm^3	fgTEQ/Nm^3	fgTEQ/Nm^3
2,3,7,8 - TCDD	1.71	<0.12	<0.27	<0.35
1,2,3,7,8 - PCDD	12.55	<0.06	<0.06	<0.10
1,2,3,4,7,8 -H_xCDD	2.49	<0.04	<0.06	<0.08
1,2,3,6,7,8 -H_xCDD	4.18	<0.04	<0.04	<0.06
1,2,3,7,8,9 -H_xCDD	3.00	<0.04	<0.04	<0.06
1,2,3,4,7,8,9 -H_pCDD	4.36	0.16	<0.02	0.16
1,2,3,4,6,7,8,9- OCDD	1.93	0.12	<0.00	0.14
2,3,7,8 - TCDF	1.17	0.16	<0.02	<0.02
1,2,3,7,8 - PCDF	6.73	0.21	<0.00	0.23
2,3,4,7,8 - PCDF	19.27	<0.06	<0.06	<0.06
1,2,3,4,7,8 -H_xCDF	7.28	<0.04	<0.06	<0.06
1,2,3,6,7,8 -H_xCDF	9.32	<0.02	<0.04	<0.06
1,2,3,7,8,9 -H_xCDF	14.25	<0.04	<0.06	<0.06
2,3,4,6,7,8 -H_xCDF	0.35	<0.04	<0.06	<0.06
1,2,3,4,6,7,8 -H_pCDF	4.81	0.18	<0.00	0.06
1,2,3,4,7,8,9 -H_pCDF	0.74	<0.02	<0.02	<0.02
1,2,3,4,6,7,8,9- OCDF	0.25	<0.00	<0.00	<0.00
Total	94.4	0.83	<0.81	0.59

This table indicates that the use of a standard high volume sampler with a filter only for the collection of particulates leads to the same result for dioxin concentration in the air, in TEQ, within analytical precision : at least twelve isomers of the "dirty seventeen" are found on the filter for 100%. The remaining five congeners are collected for almost 90% on the filter and for only 5 to 10% on the polyurethane foam.

The results of the dioxin analyses in the tunnel and the background air are presented in table 2. The PCDD and PCDF concentrations are expressed as fg TEQ/Nm^3. The dust concentrations on both locations are summarized in table 3.

Table 2 : PCDD and PCDF concentrations in the tunnel and background air.

Sample	filter + PUF fg TEQ/Nm^3	filter fg TEQ/Nm^3
tunnel air	96	130
tunnel air	116	44
tunnel air	29.5	39
tunnel air	/	186
mean value	80.3±45.1	100±71
background air	21	/
background air	55	71
background air	24	/
background air	35	45
mean value	35±18	58±19

Table 3 : Dust concentrations in the tunnel and background air.

Sample	filter + PUF mg dust/Nm^3	filter mg dust/Nm^3
tunnel air	0.18	0.82
tunnel air	0.29	1.05
tunnel air	0.26	0.67
tunnel air	/	1.41
mean value	0.24±0.06	0.99±0.32
background air	0.08	0.12
background air	0.03	0.05
background air	0.02	0.03
background air	0.07	0.10
mean value	0.05±0.03	0.08±0.04

The results indicate a difference in measured dioxin and dust concentration depending on the sampling system used : the standard high volume sampler collects more dust and dioxins than the two phase sampler. This can be attributed to the size distribution of the dust and the difference in cut-off diameter of the sampling systems.

The dioxin concentration in air sampled with a filter and PUF at a rate of 25 Nm^3/h is 74% to 78% of the value obtained after simultaneous sampling with a filter at a rate of 75 Nm^3/h.

Table 3 demonstrates that the dust concentration inside the tunnel determined by sampling with the filter/PUF equipment is only 22% to 39% of the concentration with the standard high volume sampler while in background air 60% to 70% is obtained.

Independently of the sampling equipment used, these measurements indicate that the mean dioxin concentration inside the tunnel is about twice as high as outside due to the motor vehicle exhaust.

From simultaneous CO_2 measurements in the tunnel and background air it can be calculated that the sampled air contains 0.1 vol % of exhaust gases. The average dioxin emission concentration of the vehicles passing through the tunnel, as a 24 hours average, can therefore be estimated to a 1000 fold of the tunnel air concentration, after substraction of the background level, i.e. 42 to 45 pg TEQ/Nm^3.

Therefore motor traffic can be indicated as an important source of dioxins in the environment.

1 Marklund S, Rappe C, Tysklind M and Egebäck K-E. Chemosphere 16, 1987 : 29-36
2 Hagenmaier H, Brunner H, Haag R, Kunzendorf H-J, Kraft K, Tichaczek K and Weberruss U. 1987 : VDI Berichte 634, VDI-Kommission Reinhaltung der Luft, 67