DEPOSITION OF DIOXINS IN FLANDERS (BELGIUM) AND A PROPOSITION FOR GUIDE VALUES

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Introduction

Investigations of deposition samples are able to indicate the pollution of the environment with PCDDs and PCDFs. Our goal was to examine if a decline of PCDD/F levels in air was noted in Flanders (Belgium). Therefore, the emission and deposition ranges of dioxin during the nineties were analysed. Since there are no legal guide values for the deposition of PCDD/F, a guide value for this parameter is proposed.

Methods and Materials

For a period of 30 ± 3 days samples were collected in Bergerhoff deposition gauges, as described in the German VDI 2090/1 Entwurf-standard of December 1999. The content of the 3 gauges is put together and analysed as one sample after removal of coarse objects, the solid fraction is filtered in a pre-extracted glass fibre thimble, dried in air for 48 hours, spiked with internal ^{13}C standards, and extracted with toluene by soxhlet for 24 hours. The water fraction is extracted 3 times with dichloromethane. The extracts from both fractions are combined, dried with anhydrous Na_2SO_4 and cleaned by column chromatography on Alumina B Super I. ^{13}C-1,2,3,4-TCDD is used as the syringe spike. The 17 congeners with 2,3,7,8-Cl-substitution are analysed by HRGC-HRMS. Gas chromatography is done on a DB-Dioxin column of 60 m x 0.25 mm x 0.25 µm. The instruments used are a HP5890II GC with VG Autospec Q mass spectrometer[1] and a HP6890GC with a Micromass Autospec Ultima mass spectrometer[2]. The detection limit of the congeners are below 1 $pg.m^{-2}.d^{-1}$, fulfilling the VDI 2090 standard.

Results and Discussion

1. Emission inventory

From 1985 to 1998, the dioxin emission in Flanders was reduced by 58 % mainly due to a decrease by 99 % in municipal waste incinerators, which are subjected to an emission limit of 0.1 ng $TEQ.Nm^{-3}$ since January 1997. Emission reduction programs and closing-down of medical waste incinerators resulted in a 99 % decline relative to 1985. In 1998 the emission of the iron and steel sector was reduced by 44 %. No improvement was seen in the other sectors.

2. Dioxin deposition measurements

The levels of dioxin deposition were measured in several surroundings: near waste incinerators, in industrial areas, in cities and in background areas.

2.1. Measurements in the vicinity of waste incinerators

The results of the PCDD/F deposition in the vicinity of waste incinerators are presented in Figure 1. The number of measurements increased from 4 in 1993 to 29 in 2000. During the observed time span the average dioxin deposition fell from 298 to 7.9 pg TEQ.m^{-2}.day^{-1}. This significant decrease can be related to the closure of several incinerators and to the installation of dioxin removal units to comply with the Flemish emission limit of 0.1 ng TEQ.Nm^{-3}. Moreover, the drop is in agreement with the decline in emissions. Also seasonal fluctuations can be noticed; the mean as well as the maximum deposition level is higher in fall than in spring.

When the maximum deposition values are taken in account, two "hot spots" strike the attention. During the first measurements in 1993, an extremely high deposition value occurred in Menen. Although a significant decrease was noticed from 1995 onwards, the measured depositions remain high. Well known sources are municipal waste incinerators in Menen and in the North of France. Less known are open fires, reported at the French border and smaller industrial installations. Since several municipal waste incinerators were closed in the North of France in 1998 and the municipal waste incinerator of Menen complies the 0.1 ng TEQ.Nm^{-3} emission standard in 1999, the high deposition values in 2000 have to be attributed to unidentified sources.

High depositions measured in Ghent resulted in the closure of a hospital waste incinerator in 1998 and the sanitation of the local municipal waste incinerator. In 1999, samples were taken on an additional location oriented upwind the municipal waste incinerator. The measurement of 168 pg TEQ.m^{-2}.day^{-1} led to the discovery of an unknown industrial waste incinerator. Very probably, the incineration of waste packaging material in a nearby plant causes this high deposition (personal communication with the Flemish Environmental Inspection AMINAL, AMI).

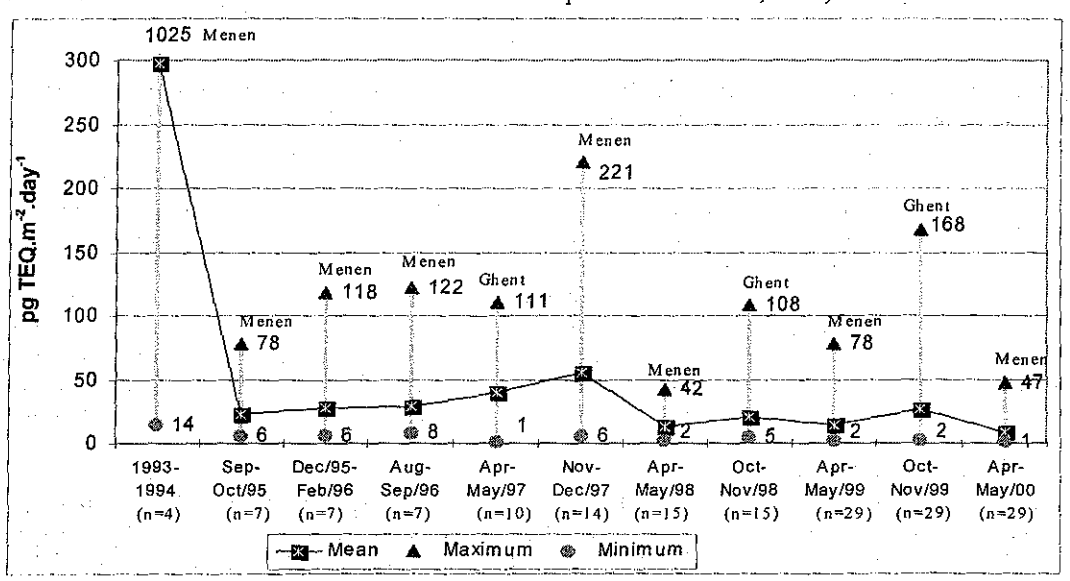

Fig. 1. Deposition of dioxins (pg TEQ.m^{-2}.day^{-1}) in the vicinity of waste incinerators. For every sampling period, minimum and maximum values are indicated. Average values are connected by a line. The location with the highest dioxin deposition is marked. n=number of measurements

2.2. Measurements in industrial areas

Figure 2 shows the results of the measurements between 1993 and 2000. During this period, their number increased from 3 to 29. With the exception of the first, the mean deposition value does not

exceed 22 pg TEQ.m^{-2}.day^{-1}. The source of the high value measured in Berendrecht could not be identified as this sampling point is located downwind a large port, harbouring various industrial plants.

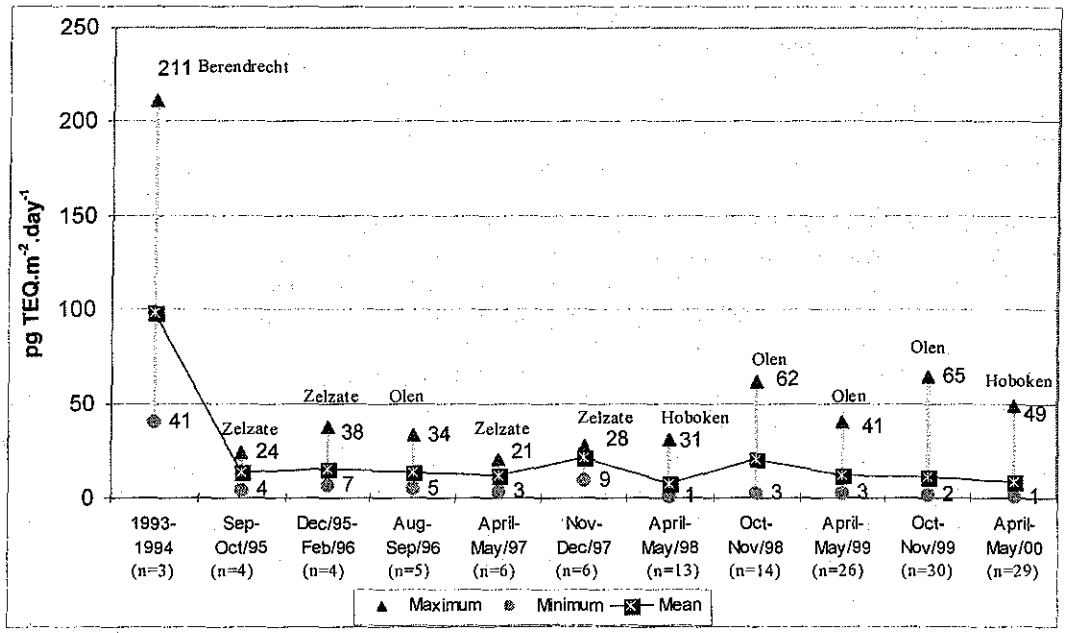

Fig. 2. Deposition of dioxins (pg TEQ.m^{-2}.day^{-1}) in industrial areas. For every sampling period, minimum and maximum values are indicated. Average values are connected by a line. The location with the highest dioxin deposition is marked. n=number of measurements

High deposition levels are repeatedly found in the surroundings of metallurgical processes. The sinter plant at steel works may cause the high PCDD/F burden at the sampling location in Zelzate while non-ferrous metal plants may contribute to the PCDD/F contamination in Hoboken and Olen. Although the influence of unknown sources on the deposition of dioxins can not be excluded, high emission fluxes measured at the plant in Olen implies its role as potential source. On the contrary, the emission measured at the plant in Hoboken is low. Transport and/or storage of dioxin-contaminated products may cause the observed elevation. Since these industries have taken actions to improve the PCDD/F release, a reduction in dioxin deposition is expected in the nearby future.

2.3. Urban and rural sites

The deposition levels measured in urban and rural areas are significantly lower than near incinerators or at industrial sites. In urban sites, the values varied between 3.4 and 25 pg TEQ.m^{-2}.day^{-1} with an average of 11 pg TEQ.m^{-2}.day^{-1}. The reason for two peak values of 25 pg TEQ.m^{-2}.day^{-1}, measured on a total of 20 samples is unknown. In rural areas 0.7-11 pg TEQ.m^{-2}.day^{-1} with an average of 6 pg TEQ.m^{-2}.day^{-1} is found.

3. Proposition for guide values

A chain model was used to establish the relationship between the Tolerable Daily Intake (TDI) and guide values for deposition[3]. Taking into account all pathways of human exposure, the model was applied to derive total human intake by highly exposed population subgroups near sources[2]. The

resulting reference values for dioxin deposition are summarised in Table 1. The TDI values proposed by the WHO of 1 to 4 pg TEQ.kg^{-1}.d^{-1} corresponds to deposition limits of 3.4 to 14 pg TEQ.m^{-2}.day^{-1} as a yearly average. A commission on air quality standards in Flanders decided to allow a 2 fold higher value for the monthly measurements, in order to account for the shorter measurement period and the observed seasonal fluctuations.

TDI	Allowed deposition of dioxins on a yearly basis	Allowed deposition of dioxins on a monthly basis
4 pg TEQ.kg bw^{-1}.day^{-1}	14 pg TEQ.m^{-2}.d^{-1}	27 pg TEQ.m^{-2}.d^{-1}
3 pg TEQ.kg bw^{-1}.day^{-1}	10 pg TEQ.m^{-2}.d^{-1}	20 pg TEQ.m^{-2}.d^{-1}
1 pg TEQ.kg bw^{-1}.day^{-1}	3.4 pg TEQ.m^{-2}.d^{-1}	6.8 pg TEQ.m^{-2}.d^{-1}

Table 1: Proposal of guide values for the deposition of dioxins

4. Exceedance of the proposed guide values

Fluctuations in the exceedances of the proposed guide values between the different measurement campaigns can be noticed. In the first campaign, 70 % of the deposition samples surpass the deposition guide value of 27 pg TEQ.m^{-2}.day^{-1}, while in 2000 this percentage drops to less than 10 %. On the contrary, only 10 % of the samples of the first campaign score below the value of 6.8 pg TEQ.m^{-2}.day^{-1} while in 2000 this number reaches a percentage of more than 40 %. Although it has to be taken in account that measurements are often performed in places where high deposition can be found, it can be concluded that improvements in time can be noticed.

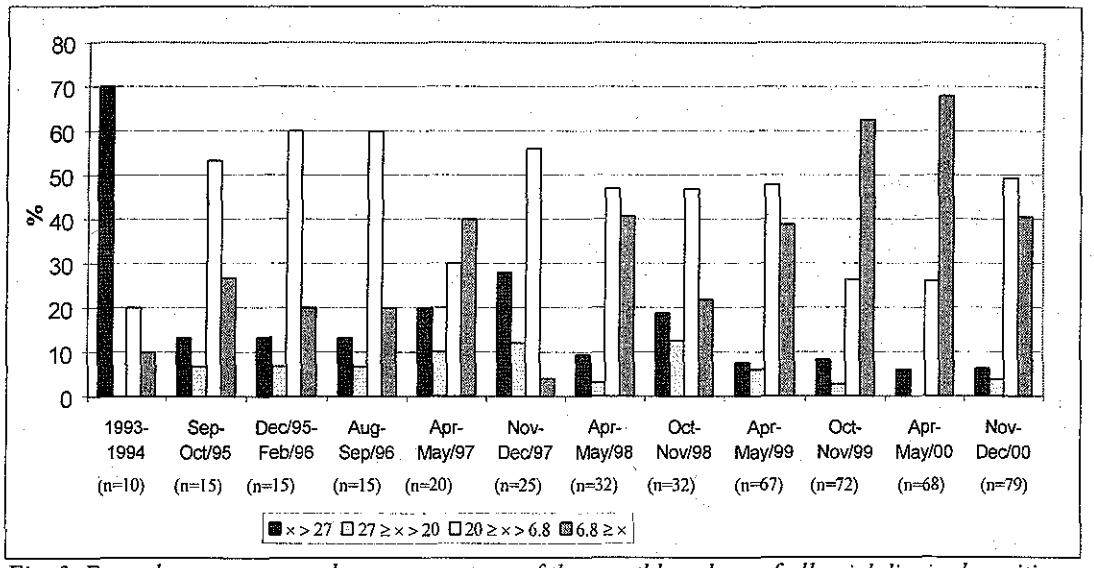

Fig. 3. Exceedances expressed as a percentage of the monthly values of allowed dioxin deposition. The bars represent the percentage of samples which comply the guide values presented in table 1. The guide values are expressed in pg TEQ.m^{-2}.day^{-1}. n=number of measurements

References

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2. De Fré R, Cornelis C, Mensink C, Nouwen J and Schoeters G (2000) Organohal. Comp. 45, 324
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