Underestimation in dioxin emission inventories

R. De Fré, M. Wevers

VITO, Vlaamse Instelling voor Technologisch Onderzoek, Boeretang 200, 2400 Mol, Belgium

Introduction

More dioxins are present in the environment than can be accounted for by known sources. This phenomenon was reported on a national scale and on a world wide scale (1), generally as a difference in the balance between levels in atmospheric depositions or soil samples, and the emissions inventory of known sources. Often "missing sources" of dioxins are suspected with an emission that amounts to a multiple of the known sources. This paper describes cases of underestimation of dioxin emissions by point measurements in existing municipal waste incinerators in Belgium. The size of this underestimation is of the same magnitude as the emissions sometimes attributed to the missing sources.

Estimation of long-term average emissions by concentrations in soil samples

In 1993 VITO measured emissions and soil concentrations of dioxins in the surroundings of the MIWA municipal waste incinerator in Sint-Niklaas, Belgium. In a grid of approximately 4 by 2 km a total of 50 soil samples were taken and analysed for groups PCDDs and PCDFs. Twelve samples were analysed for 2,3,7,8 congeners. The area of maximum impact of the plume was clearly marked by the soil concentrations, but in the areas of lower concentrations some deviations occurred, indicating the presence of other local sources, like fires or pesticide use. The highest values of all groups were found between 1 and 1.5 km in the northeast direction.

The incinerator with a capacity of 60 000 tons/y had been in operation for a period of 12 years, until 1991 with no other gas cleaning equipment than an electrostatic precipitator. In 1990 the dioxin emissions without wet scrubber were determined at 23.9 ng TEQ/Nm³ (6.7 - 66.8 ng TEQ/Nm³) as an average of 8 measurements in autumn and winter. After the 2-step wet scrubber had come into service in 1991 the dioxin emission concentrations were measured as 10.1 ng TEQ/Nm³, as an average of 9 measurements, with a range of 3.1 - 37 ng TEQ/Nm³.

The emission data were used to calculate the deposition of dioxins in the environment with the IFDM dispersion model. This is a bigaussian model with experimentally determined dispersion parameters. An emissions scenario with the operating times, the number of starts and stops, and the measured dust emissions for each year were used. The model was allowed to calculate deposition maps and subsequently different types of regression were applied in order to fit the calculated and the observed patterns of dioxin concentrations in the soil for all groups. The best fit was obtained from a logarithmic regression (meaning that the data are more or less log-normally distributed) and values for the following unknown parameters could be estimated:

- the dry deposition velocity in the neighbourhood of the plant (v_d = 1 cm/s)
- wash out coefficient for wet deposition ($\Lambda_p = 0.00018\ s^{-1}$)
- the most probable emission flows of PCDDs and PCDFs, corresponding to the following average emission concentrations over 12 years:

Table 1: Most probable 12 year average emission concentrations of MIWA incinerator from regression analysis on concentrations in soil

PCDDs	ng/Nm³, 11 %O_2	PCDFs	ng/Nm³, 11 %O_2
T4CDD	59	T4CDF	95
P5CDD	95	P5CDF	125
H6CDD	180	H6CDF	243
H7CDD	403	H7CDF	220
O8CDD	1754	O8CDF	175
Total PCDDs	2490	Total PCDFs	858

With the profiles of 2,3,7,8-congeners in the emissions, the corresponding average dioxin emission concentration in TEQ was estimated at 50 ng TEQ/Nm³. If the same profile as in the soil was assumed the result would be 25 ng TEQ/Nm³. This difference in profiles is caused by the higher OCDD concentration in the soil, probably due to its persistence over the years. It is worthwile to mention that 2 soil samples at the point of highest impact needed to be rejected as outliers from the regression for their extremely high OCDD content. For the dry deposition velocity and the average emission concentrations the regression results were two times or more higher than the values assumed previously.
The results of the MIWA regression have led us to assume that higher emission factors need to be used for municipal waste incinerators of the most common types in Belgium, constructed between 1970 and 1980. Two more deposition studies by VITO, around incinerators in Menen and Antwerp have later confirmed the conclusions of the first study concerning deposition and emission. In the latter cases however other sources were obviously present. As emission factors for different types of gas cleaning systems the values as in table 2 are applied for MWI's.

Table 2: Dioxin emission factors used for top-down emission inventory calculation

MWI gas cleaning equipment	Emission factor µg TEQ/ton	Emission concentration ng TEQ/Nm³
Electrostatic precipitator only	240	40
Dry removal of acidic compounds	50	10
Wet gas scrubber	22	4
Active carbon injection	1.8	0.3

Table 3 shows the two approaches for calculating the dioxin emission inventory for MWI's in Flanders. In the bottom-up approach (Table 3 last column) the measurement data are multiplied by the total annual stack gas flow. The example shows that plants where no measurements are available are not accounted for. In the top-down system an emission factor is applied according to the technology as in table 2. It is clear that this system does not take into account particularities of individual plants. The total dioxin emission for the 13 incinerators is estimated 4 times higher than the result based on individual measurements. It should be noted that the

dioxin emission measurements are required annually to prove compliance with the emission limit and that plants are operated with more care during these sessions. Sometimes unfavorable results are not reported officially and will lead to repetitions. Therefore we believe that the top-down method gives more reliable estimations for the total emission.

Table 3: Dioxin emission inventory 1996 for MWI's in Flanders, calculated with top-down (E-factor) and bottom-up (measurements) approaches

Site and name of MWI	Waste burned	Emission factor	Estimated dioxin emission g TEQ/year	
	tons/y	µg TEQ/ton	top-down	bottom-up
Oostende IVOO	62 948	22	1.38	-
Menen IVMO	46 198	1.8	0.083	0.091
Roeselare IVRO	54 701	50	2.74	0.17
Brugge IVBO	194 844	22	4.29	0.75
Harelbeke IMOG	73 489	22	1.62	0.28
Knokke Montenay	27 283	1.8	0.049	0.018
Eeklo IVM	74 737	1.8	0.13	0.33
Gent IVAGO	35 827	22	0.79	-
Lokeren IDM	25 645	50	1.28	0.005
St. Niklaas MIWA	55 774	22	1.23	0.041
Wilrijk ISVAG	115 062	22	2.53	2.55
Edegem IHK	28 901	24	0.69	0.77
Houthalen ReMi	66 474	50	3.32	-
Total	**861 883**		**20.1**	**5.0**

The following illustrates that even with the recent technological improvements for dioxin abatement the standard measurement technique underestimates the long-term emissions.

Representativity of point sampling of dioxin emissions

It is known that the start-up and shut-down periods in the operation of a MWI give particular risks for high dioxin emissions (3). This is especially the case for plants where by-passing of filters is possible. By-passing of fabric filters is often related to abnormal gas temperatures, where too low temperatures may cause condensation or collation of lime, and too high temperatures may damage the fabric filter material. In plants that are not using support burners to assure combustion gas temperatures above 850 °C for a residence time of 2 seconds or so, these transient phases are more likely to produce high dioxin emissions.

From January 1997 there is an emission limit of 0.1 ng TEQ/Nm³ for all MWI's in Flanders. In November 1997 the Minister of the Environment ordered the immediate shutdown of 5 MWI's that did not comply with the 0.1 ng TEQ/Nm³ emission limit. A special commission on incineration was created to investigate the technical problems of all MWI's to comply with this emission limit. After improvements 3 plants were allowed to start up again with the condition that a permanent dioxin sampling system would be installed, in order to demonstrate compliance with the 0.1 ng TEQ/Nm³ limit at all times. The results from one plant are given in table 3. The Amesa system (GfA, Münster) was used for continuous sampling during periods of 15 days. The analysis was carried out in double by 2 laboratories, VITO and GfA. They show that a standard

emission measurement according to the European standard method EN 1948 during a period of 6 hours resulted in an emission concentration of 0.25 ng TEQ/Nm³, while the average over 2 weeks in the same period was 8.2 to 12.9 ng TEQ/Nm³. This illustrates that the standard measurement underestimated the average emission by a factor 30 to 50. As a result of these findings doubts have risen over the real emission of the incinerators, and the special commission on incineration has asked from all incinerators in the Flemish region to use the continuous sampling system in order to demonstrate their compliance with the emission limit.

Table 4: Results from continuous and 6-hour dioxin samples at IVOO incinerator

Period of measurement	Measured dioxin concentration as ng TEQ/Nm³ at 11 % O_2	
(day-month-year)	Continuous sampling	6-hour sample
29-12-97 - 12-01-97	13.4 (14.3)	
12-01-98 - 26-01-98	8.2 (12.9)	0.25
26-01-98 - 30-01-98	12.6 (10.1)	
09-02-98 - 23-02-98	2.11 (2.12)	
23-02-98 - 09-03-98	0.44	
09-03-98 - 23-3-98	0.33	0.12
23-03-98 - 06-04-98	0.8	

Memory effects as an indicator of short time high emissions

Memory effects have been reported as a particular difficulty in systems where a wet scrubber is used as the final gas cleaning step, after dioxin removal by adsorption. The large surfaces of polymer material in linings and packings can accumulate dioxins, causing difficulties to obtain emissions below the limit value of 0.1 ng TEQ/Nm³. The data in table 4 are from a system with a wet scrubber at the end. Memory effects in the IVAGO MWI in Gent are reported elsewhere (4). This plant is equiped with lime and active carbon injection, fabric filters and a wet scrubber. After 6 months of operation the wet scrubbers produced 6.2 ng TEQ/Nm³ in the flue gas on line 1, and 21.9 ng TEQ/Nm³ on line 2. The following month the scrubbers caused a net increase in the flue gases of 1.58 and 1.18 ng TEQ/Nm³ respectively. The extent of the memory effects can only be explained by relatively high concentrations during shorter periods of accumulation. Assuming that the results were representative for a month of operation would imply an unlikely dioxin release of 0.7 g TEQ in one month by the wet scrubbers. Peak emissions e.g. due to blockage of the activated carbon injection are the more probable explanation of the observed memory effects. Gas cleaning systems with memory effects behave as a dioxin capacity, and produce emission concentrations that are a better approximation of the time averaged emission. The time constant of this memory is rather short as can be seen from the drop in the measurements after one month.

References

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