ENVIRONMENTAL TRANSPORT AND FATE

METHODOLOGICAL SURVEY OF THE DIOXIN DEPOSITION MEASUREMENT WITH BERGERHOFF GAUGES

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Introduction

Since 1995 the Flemish Environment Agency has been measuring dioxin deposition in Flanders (Belgium). The number of measurement sites increased from 10 to over 70 sites in 2001. The measurement results have been described previously[1].

In this study we want to focus on additional research regarding the variation of mean monthly depositions, the stability of dioxins in the deposition sample and acid treatment during processing of the deposition samples.

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 limits of the congeners are below 1 pg.m^{-2}.d^{-1}, fulfilling the VDI 2090/1E standard requirements.

Results and discussion

Variation of the mean monthly deposition

The deposition measurement campaigns are carried out at 70 sites in Flanders during spring and fall. Mean monthly depositions are determined during these measurement campaigns, while the proposed environmental standards rather involve annual averages. The purpose of this survey is to determine the variation of mean monthly depositions. In addition, the possibility of combining various monthly depositions into a single sample is examined. Annual averages can thus be calculated with a reduced number of analyses. For this purpose two sets of Bergerhoff jars are installed. The first set of jars was analysed monthly and the average deposition was calculated on the basis of three monthly samples (M+M+M). The second set was processed into an extract and combined with the extracts of two successive monthly deposition samples and were then analysed as one mean three-monthly sample (3M). Prior to analysis, the extracts of the monthly samples were stored in a cool, dark place. Since the congeners are characterised by a different toxicity factor (TEF), a comparison was made for the results, expressed in pg/sample, in pgTEQ/sample and in pgTEQ/(m².day). In 14 of the 18 samples the ratio in

ENVIRONMENTAL TRANSPORT AND FATE

pg TEQ/sample between the 3M and M+M+M samples lies between 0.9 and 1.3. In 2 of the 18 samples much higher dioxin concentrations were found in the sum of the mean monthly samples (factor ³ 1.7). In both instances this was due to a significantly increased dioxin concentration in one monthly sample. In 2 of the 18 samples much lower dioxin concentrations were found in the sum of the mean monthly samples (factor £ 0.7). In both cases the depositions of the three monthly samples varied only minimally. One of the main reasons for the difference between the M+M+M sample and the 3M sample is that, by combining various monthly samples, virtually no "non-detects" occur, thus reducing measurement uncertainty. Still, we want to point out that both a 'positive' and 'negative' difference is found between the M+M+M sample and 3M sample. For this reason, the Flemish Environment Agency decides for a continuation of the monthly samplings and has decided not to combine the monthly samples.

The evolution of the monthly dioxin depositions per measurement site during one year is summarised in the table 1 below.

Table 1. Monthly deposition measurements at a number of measurement sites in Flanders (expressed in pg TEQ/m².day – values < detection limit not included)

	Mol	Antwerp	Wilrijk	Ghent	Zelzate	Olen
2-3/00		14			13	56
3-4/00		8.7			7.8	4.5
4-5/00	6.4	7.8	2.5	4.9	10	
5-6/00		6.1	9.5	5.7	14	27
6-7/00	36	4.1	16	13	6.0	30
7-8/00	14	2.9	20	0.6	0.04	51
8-9/00	0.96	4.9	1.5	3.9	5.1	11
9-10/00	2.3	7.2	4.8	4.9	9.6	15
10-11/00	3.8	8.6	3.2	6.6		14
11-12/00	8.0	9.8	4.8	6.3	28	20
12-1/01	5.1	7.8	4.0	5.4	7.2	6.3
1-2/01	6.8	16	7.3	10	21	14
2-3/01	7.5		5.7	9.2		
3-4/01	6.5		9.2	38		
average	**8.9**	**8.2**	**7.4**	**9.0**	**11.1**	**22.6**

The results of the monthly measurements show a large variation in the monthly depositions. In a rural area (Mol) and in an urban area (Antwerp), both without an apparent source except a coal based power plant in Mol, once-only increased values were recorded. In Wilrijk the average deposition was somewhat lower: 7.4 TEQ/m².day. Ten of the twelve samples show depositions below 10 pg TEQ/m².day. In the samples collected from mid-June to mid-August dioxin depositions of 16 and 20 pg TEQ/m².day were measured, respectively. This concerns a clearly increased deposition, the cause of which cannot be ascertained. Monthly measurements in Ghent showed low values, with the exception of the value recorded in March/April 2001. The average was 9 pg TEQ/m².day. In Zelzate the average deposition amounted to 11 pg TEQ/m².day. Two of the eleven samples were above 20 pg TEQ/m².day.

Finally, the highest average deposition was recorded in Olen: 22.6 pg TEQ/m².day. In the February-August 2000 period four out of five measurements were above 25 pg TEQ/m².day with a maximum value of 56 pg TEQ/m² .day. From August 2000 onwards a maximum deposition of 20 pg TEQ/m².day was recorded.

From these monthly samplings we can conclude that the dioxin deposition strongly fluctuates. In Mol, Antwerp, Wilrijk, Ghent and Zelzate the average deposition was on an acceptable and comparable level. However, once-only increased values were recorded at all measurement sites, for which no immediate explanation can be given.

Stability of dioxins

Stability tests by means of spike addition

Regarding research on the influence of meteorological circumstances on the open-air stability of dioxins, a set of jars was set up, doped in advance with a known quantity of each of the 2,3,7,8-chlorinated congeners, in addition to the ordinary set of jars. The intention is to examine the degradation of this spike during the one-month sampling period. The spike recovery was determined from the difference between the doped set of jars and the non-doped set.

The added spike largely degraded for all congeners during the sampling period. The highest temperatures and highest amount of sunshine in the summer resulted in average recovery percentages between 6 and 23 % for PCDDs+PCDFs. In the winter period from December 14, 2000 to January 16, 2001 the highest average recovery percentages for PCDDs and PCDFs lie between 49 and 66 %. For all measurement sites and measurement periods higher average recovery percentages are found for PCDDs than for PCDFs.

However, these findings are based on the degradation rate of a spike. This spike largely differs from an atmospheric sample. For instance, dioxins in a real sample are attached to dust particles, while the spike is administered in an apolar solvent. Consequently, only a part of the spike will mix with the water phase added at the start of the sampling. This limited solubility and possible surfacing of the spike results in a higher evaporation probability. The recovery percentage can also be influenced by the attachment of a part of the spike to the wall. That is why additional measurements will be carried out to find the degradation of dioxins in a real sample.

Stability of real samples

For three samples a comparison was made between the mass quantities of the various congeners in immediately processed en analysed jars en in jars that were stored at ambient temperature for one month (away from light). In the stored samples 75, 77 and 90 % of the original total mass of PCDDs+PCDFs, respectively, were recovered. Considering this limited variance, degradation of dioxins, but also uncertainties of analysis + sampling, may be the cause of these reduced percentages.

This result shows that the degradation detected through the spike addition approach may give an incorrect idea. In a real sample the variance is much less outspoken. Presumably then, the spike degradation might be subject to other factors. However, this hypothesis has to be confirmed by additional experiments.

Acid Treatment

A number of deposition samples were used to examine the influence of acid treatment during processing of the samples. After filtration of the precipitation jars the filters are air-dried for 72 h and then sprinkled with one ml of HCl 37 %. The filters are then dried again, followed by extraction and purification of the extract. Ten comparative measurements between acid-treated and non-acid-treated deposition samples were done at various measurement sites. With five comparative measurements

ENVIRONMENTAL TRANSPORT AND FATE

hardly any difference is found between the total sum of PCDDs+PCDFs in the acid-treated and non-acid-treated samples (ratios between 0.8 and 1). For four measurements the sum of PCDDs and PCDFs is higher in acid-treated samples. In three of these samples the ratio exceeds 1.5. In one set of samples, a much lower total mass of PCDDs+PCDFs is recorded in the acid-treated sample (ratio = 0.3).

The ratios differing from "1" between acid-treated and non-acid-treated samples may be explained by the measurement uncertainty for both samples.

This survey thus does not show that an acid treatment systematically releases more dioxins.

References

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