

DIOXIN IN AMBIENT AIR IN THE NETHERLANDS
A pilot study

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1. Introduction

In The Netherlands, combustion has become an important means of waste management. At present, about 15% (3×10^6 tons) of the total household waste (20×10^6 tons) is combusted by 12 incinerators.

The largest incinerator (AVR) is situated in a major industrial area near Rotterdam (see figure 1). This incinerator has a capacity of 1 million tons waste a year. The capacity of the other incinerator varies between 20 and 400 ktons a year. In recent years, the majority has been equipped with additional gas cleaners. Present total emissions into the air of polychlorinated dibenzodioxins (PCDDs) and furans (PCDFs) are estimated at about 0.5 kg/yr.

Depositions in particular in the vicinity of incinerators, has caused in the recent past to severe contamination of the vegetation and in some places also in soil, which has caused contamination of cow's milk¹. These findings were reason to the closure of four incinerators and to start a comprehensive study on levels biological and environmental samples, modelling of the kinetic behaviour in the cow² and distribution and transport from sources into the dairy food chain.

Results were used for principal component analysis (PCA) to identify dioxin sources on the basis of the pattern of 2,3,7,8-PCDD/Fs in milk¹.

Estimations based on a model of air transport and distribution³ indicate an average ambient air level of about 25 fg TEQ/m³ and associated deposition rate of 8.1 ng TEQ/m²/yr (see figure 1) for a total emission of 870 g TEQ/yr.

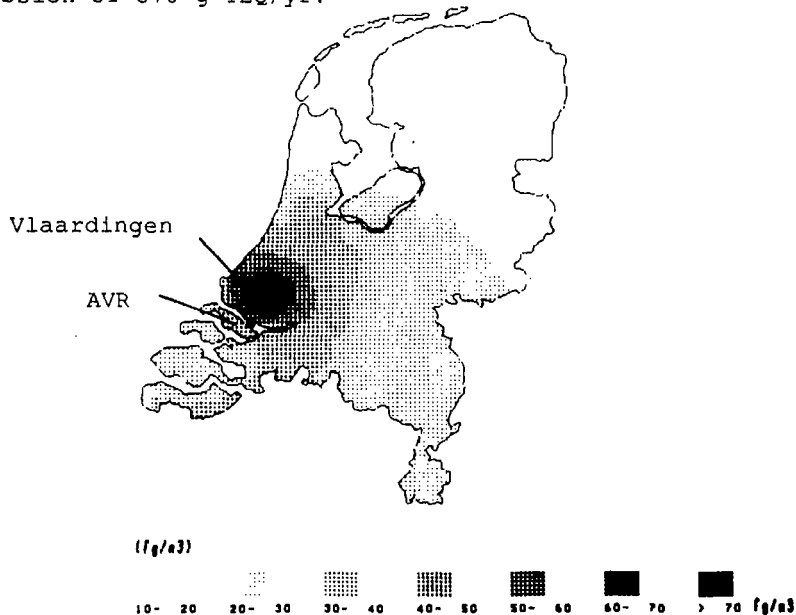


Figure 1. Calculated concentration of PCDD/Fs for the year 1990

The aim of this research program is to measure ambient air levels at different sites over the country, including an incinerator deposition area, a rural area and two urbanised areas. The data will be used for a further evaluation and validation of the modelling of short range distribution and to estimate PCDD/F fluxes crossing the country.

In addition differences in congener profiles and the isomer pattern were used to distinguish between the contribution of local sources, like traffic and others to the background, which is most likely dominated by incinerators releases.

In this contribution, the methodology of sampling and measurement of low fg levels in air will be discussed as well as first results of current measurement program at the deposition area and a rural area.

2. Materials and methods

Instruments and materials

- High Volume Sampler (HVS, LIB/P-Sampler, type III, Stranovsky GmbH, Essen, GER).
- Gas chromatograph (HP 5890A, Hewlett Packard, Nederland B.V.).
- Mass spectrometer (VG Autospec, VG Analytical, Manchester, UK).
- Glassfiber filters (GFF, No. 8 Schleicher & Schuell, Den Bosch, NL, 0.75-1.5 μm and GFF type A/E, Gelman Sciences, Inc., Ann Arbor, MI, USA, 1 μm), precleaned at 450 °C in a muffle furnace.
- Polyurethane foam plugs (PUF, GA 3035, Klaus Ziemer GmbH, Mannheim, BRD, density 25 kg/m³ and PUF: D.P. Sunde & Co., 1903 Gan, Norge, Soesilfabrikk for Skumplastartikler, same density) extracted for 24 h with acetone and 24 h with toluene before use.

Sampling and clean-up

Samples were taken with a High Volume Sampler between April and October 1991. Precleaned filters were placed in the sampling train which was connected to a vacuum pump. Prior to sampling the system was checked for leaking by sealing the sampling entry and measuring the vacuum and flow. The sucked air first passes the GFF and secondly the PUF backup filter. A second PUF filter was placed in series to control eventual break through. Air samples were approximately 1000 m³ sucked with a sampling speed of 16 m³/h.

PCDD/Fs were isolated by Soxhlet-extraction with toluene of the GFF filter and PUF filter for 72 and 24 h, resp. In the initial stage of the study, carbon-13 labelled internal standards were applied to the filter after the sampling. Currently, these standards are added to the GFF filter before the sampling.

Isolation and clean-up was performed in a two step column chromatography procedure using activated carbon (Carbosphere) and alumina. The method is similar to the procedure for analysis of fly-ash samples, except that air samples are not treated with concentrated hydrochloric acid. The details of the procedure are reported previously¹.

GCMS-analysis

Gas chromatographic separations were carried out on a RTX 2330 column (Restec, Baltimore, USA, 30m x 0.25mm I.D., 0.1 μm filmthickness). The gas chromatographic conditions were: injector temperature, 275 °C; carrier gas He, linear velocity 30 cm/s; injection 2 μl splitless; GC-oven temperature programming 100 °C (1 min), 15 °C/min to 200 °C (1 min), 4 °C/min to 275 °C (1 min).

Mass spectrometry: quantification was carried out in EI (31 eV) multigroup selected ion monitoring mode on two isotope peaks of analytes and internal standards. The mass resolution was 5000:1.

3. Results and Discussion

Initially, glassfiber filters as well as PUF filters contained considerable amounts of mainly hepta and octa CDD, which could in our hands not fully been removed. The remaining caused a procedural background level corresponding with 0.13 ± 0.05 and 0.08 ± 0.03 fg TCDD toxic equivalents (TEQ)/m³ for the GFF and PUF filter, respectively. Although this background contributed only a few percent to typical TEQ values in air samples, their absolute values and the quite large variation caused a considerable disturbance of the congener profile in real samples. In addition, in this stage of the study samples were spiked with carbon-13 internal standards after sampling and prior to extraction. Tashiro and Clement⁵ have shown that spiking on the GFF filter prior to sampling is possible with reasonable recoveries. The background problem has been solved by the use of much cleaner filters (GFF: Gelman type A/E and PUF: Sunde & Co.), of which the background after cleaning was almost neglectable (see figure 2). The recovery of filter spikes was over 75% on average, and no significant difference were observed for the lower and higher chlorinated congeners (table 1). The mean extraction recovery of the added internal standards was $70 \pm 10\%$. The detection limit of the method was at the sub fg/m³ range for sample sizes of approximately 1000 m³ of air.

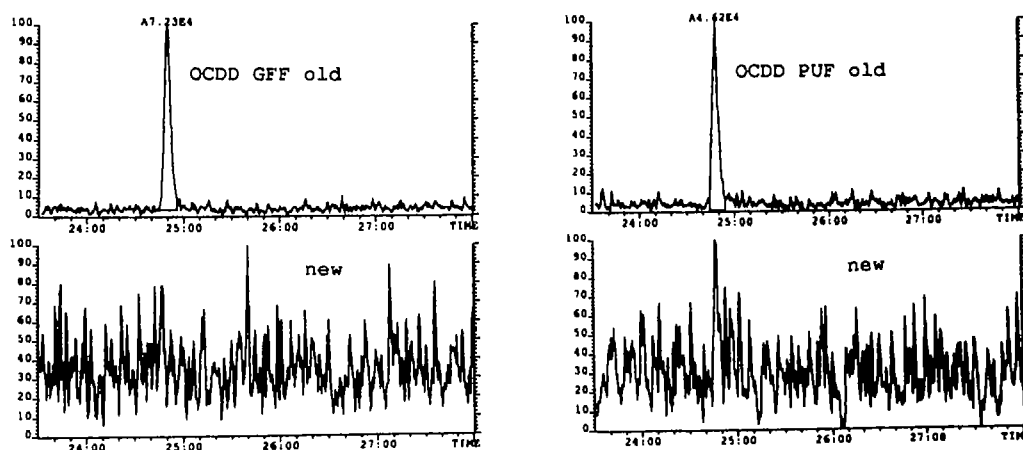


Figure 2. Background levels of OCDD in filter materials

Table 1. Average recovery of ¹³C-congeners spiked on GFF filter

¹³ C-Congener	recovery %
13C-2,3,7,8-TCDD	71
13C-1,2,3,7,8-PeCDD	76
13C-1,2,3,4,7,8-HxCDD	79
13C-1,2,3,6,7,8-HxCDD	79
13C-1,2,3,7,8,9-HxCDD	80
13C-1,2,3,4,6,7,8-HpCDD	83
13C-OCDD	76
13C-2,3,7,8-TCDF	69
13C-1,2,3,7,8-PeCDF	73
13C-2,3,4,7,8-PeCDF	71
13C-1,2,3,4,7,8-HxCDF	76
13C-1,2,3,6,7,8-HxCDF	74
13C-1,2,3,7,8,9-HxCDF	76
13C-2,3,4,6,7,8-HxCDF	75
13C-1,2,3,4,6,7,8-HpCDF	77
13C-1,2,3,4,7,8,9-HpCDF	81

Samples were collected at various wind directions at a distance of about 10 km North East from the incinerator AVR. In each sample, air mass directions are integrated during three days. The results of seven samples are shown in figure 3 together with the wind direction. Results are the values captured by the glass fiber filter. Losses due to migration from the GFF filter to the first PUF filter was on average between 10 and 20% on TEQ basis, and showed a gradually decrease for individual congeners from tetra to hexa chlorinated⁶.

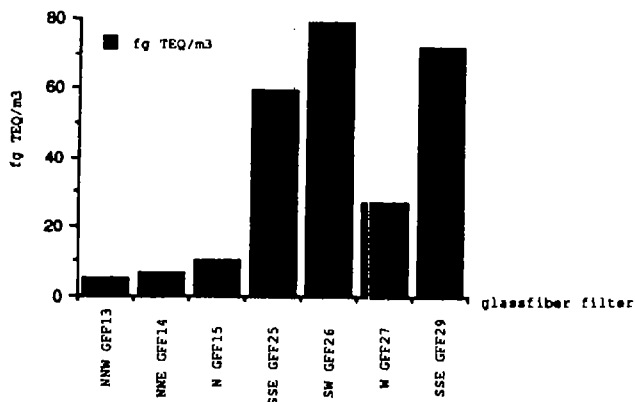


Figure 3. PCDD/Fs levels at 10 km N E of a waste incinerator

Levels found varied between 5 and 80 fg TEQ/m³. Highest levels were found when the wind came from the direction of the incinerator. In air masses coming from the North Sea (distance about 30 km) levels were about 5 fg TEQ/m³. The local background level is estimated when the wind came from the North, which is an urbanized, agricultural area with a few industries. This background level was between 10 and 15 fg/m³, which means that incinerator emissions caused additional ambient air levels of about 60 fg/m³. The temperature was quite constant during the sampling period and no correlation was found between temperature and levels measured. Congener profiles found were uniform for all directions and were close to that found in fly ash.

References

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