Dioxin in Danish Air

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Introduction

To gain more knowledge about dioxin levels, sources and emissions in Denmark [1], the Danish government year 2001 initiated the Danish Dioxin Monitoring Program. The program is a series of investigations, comprising soil, compost, percolate, bio-ash, incineration of municipal and hazardous waste, deposition, air, lake and fjord sediment as well as cows milk and human milk. The present paper describes the preliminary results for the continued investigation of air [2,3]. Deposition of dioxin over land or sea is of major importance for the human exposure, which takes place mainly from food intake. The dioxin are emitted mainly to the atmosphere, therefore air measurements are well suited for tracking the transport and fate of dioxin from sources to exposure. Whereas measurements from chimneys has been frequently used to estimate the industrial emission from point sources such as incinerators, air measurements also include emission from diffuse sources such as larger urban or industrial regions, residential quarters, and from evaporation. Furthermore, emission measurements must be done on known sources, whereas air measurements include contribution from unknown source. The major drawbacks of air measurements are the long duration required (years), and the results depends on meteorological conditions, such as temperature, rainfall, wind speed and direction.

The purpose of the present study has been to measure dioxins in Danish air, emphasizing

- background concentrations and annual variation
- difference between urban, rural and residential zones
- influence from local sources and long range transport
- connection between dioxin in air and deposition.

Methods and Materials

Stations. 3 stations are used all located in North Zealand. Rural: Fredensborg (main station), a rural but densely populated region 30 km North of Copenhagen (samped from Feb. 02). Urban: The Botanical Garden in central Copenhagen, the largest Danish urban and industrialized region (sampled from Mar. 03). Village: Gundsømagle, a residential village in rural settings 30 km East of Copenhagen (sampled Nov 02, Aug. to Dec.03).
Sampling. US EPAs method for the American Dioxin Air Monitoring Program is employed [4]. The sampling train operates at a flow of 130 m^3/day and contains a quarts fiber filter (QFF) and 2 polyurethane foam plugs (PUF). Monthly samples are collected having air volumes of about 4000 m^3. In some cases, samples from consecutive months are pooled. The samplers are shielded from direct or reflected sunlight to reduce photo-degradation.
Analytical. Performed according to European flue gas standard [5], modified to air as previously described [3]. Repeatability 6 %. Recovery (mean all data ± sd): Extraction 79% ± 14 %, sampling 69% ± 23%. DL (mean all data): Ranging from 0.1 fg/m^3 (TCDD) to 0.4 fg/m^3 (PeCDD).

Results and Discussion

Figure 1 shows results from the main station Fredensborg separately for PCDD and PCDF in fg/m^3 I-TEQ. Pooled samples are shown by the beginning month.

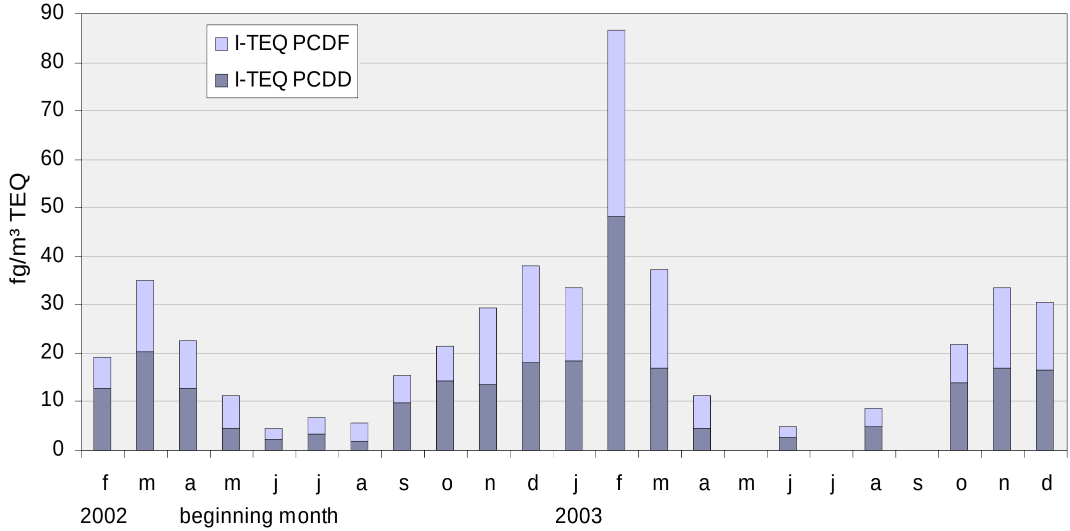

Figure 1. Two years of dioxin in air at rural main station Fredensborg 30 km North of Copenhagen.

As seen, in both years the minimum is in June and the maximum in February or March. The maximum in Feb. 03 is record high and must be caused by an unusual air pollution episode, but otherwise the two year are alike. The variation spans a factor of 19. An almost equal distribution between PCDD and PCDF is found for most of the measurements.
Figure 2 shows results from all stations on a common time axis. It is noteworthy that the at dioxin concentration in Copenhagen and Fredensborg follow each other almost synchronously in spite of the distance and the location in rural and urban zone, respectively. This indicates that a substantial contribution is due to long range transport, because it is highly improbable that zones so different in type could have synchronous emissions from local sources. A weak tendency to higher levels is seen in Copenhagen, this is undoubtedly caused by local sources. This tendency is lesser pronounced than expected from the soil concentrations [2,6,7]. The minor difference and the low level in Copenhagen air is surprising. It is an important conclusion that other sources than air must be (or have been) responsible for dioxin found in central Copenhagen soil.

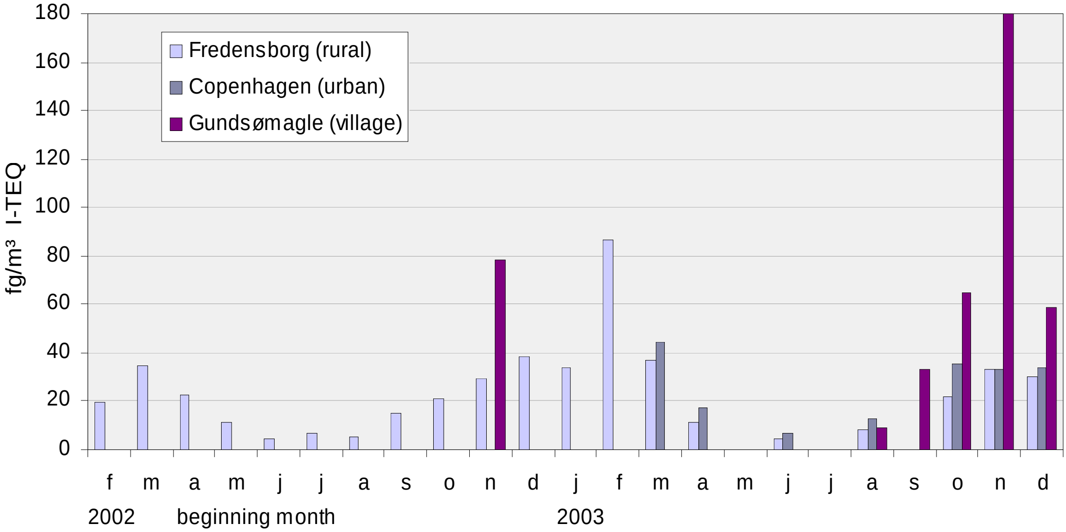

Figure 2. Results from all stations on a common time axis. Gundsømagle is a rural residential village 30 km West of Copenhagen having many wood stoves.

In contrast, the results from the rural village deviates much from the above pattern. The village is residential, having many wood stoves. During the NERI monitoring program for PAH in air [8], a sample for dioxin was taken Nov. 02, displaying a considerably higher level than that in Fredensborg. The wood stoves were suspected, and this initiated the present follow-up investigation, which also comprised an investigation emission from the wood stoves in the village still in progress. It is remarkable that the August result is on level with Fredensborg; but as the heating season begins in October an increase sets in, followed by the record high level in November. The much higher levels compared to Fredensborg (which as mentioned mainly reflect long range transport) indicates that the causation is local sources. It will further enhance the concentrations if the emission are confined to an air layer in low altitude, as is the case for local emissions. The observed increase during the heating season points to domestic heating as the cause. This is supported by the PAH results, which also increased during the heating season [8].

Other studies. The present rural and urban results are within range of the American air network results for rural and suburban sites [9], annual means ranging from 2.0-58.3. The Americans found no signs of long range transport, however. The present results also agree with results from urban sites in Florence, Italy, annual means ranging from 11,2 – 19,6 fg/m^3 I-TEQ [10].
The present village results, however, are higher. In Austria, higher results were reported, winter ranging from 4.4-353 fg/m^3 I-TEQ and summer from 2.7-132 fg/m^3 I-TEQ. The Austrians also found domestic heating was the major source in the winter [11]. In Catalonia, Spain, a comprehensive study reported rural air concentrations of 21-51 fg/m^3 I-TEQ and urban of 25-300 fg/m^3 I-TEQ [12].

Table 1.	Dioxin in Air, Statistics		
Location	Rural	Urban	Village
Name	Fredensborg	Copenhagen	Gundsømagle
Start	feb-02	mar-03	Aug-03
Duration, d	668	275	152
n	20	7	6
Unit	I-TEQ fg/m³	I-TEQ fg/m³	I-TEQ fg/m³
Mean	23.1	24.6	70.6
Minimum	4.5	6.8	8.9
Maximum	86.7	44.2	179.9

Conclusions. The air concentrations at an urban (Copenhagen) and a rural site are almost equal and synchronous, pointing to long range transport as a significant contribution. The urban air level is lower than expected from soil measurements. The level in a rural residential village increases substantially during the heating season, pointing to local heating sources, probably wood stoves.

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