Ambient Air Concentrations of Dioxins in Austrian Conurbations

Wolfgang Moche, Gerhard Thanner

Federal Environment Agency, Spittelauer Laende 5, 1090-Vienna, Austria

1. Introduction

In November 1992 the Federal Environment Agency Austria started a one year monitoring programme for ambient air concentrations of dioxins (polychlorinated dibenzo-p-dioxins and dibenzofurans) at industrial and population centres of Linz, Graz and Vienna. This programme was the first systematically approach to record the situation of ambient air concentrations of dioxins in Austria.

2. Sampling and Analysis

Air samples were collected at six measuring sites, three of them located in Vienna, two in Linz and one in Graz. Vienna, the capital of Austria, is a city with approximatly 1.7 million inhabitants and has a high degree of urbanization. There are only few inustrial plants within the municipal area. Graz, with a lower degree of urbanization, has an approximate population of 200,000. Its industry consists mainly of service industries and adminstration facilities. Linz, the second largest city of Austria with approximatly 250,000 inhabitants, has a large industrial area along the River Danube, east of the city-centre. The industrial zone is dominated by steel- and chemical plants. The position of the sampling sites and a brief description of the immediate surroundings are given in Table 1.

Air has been sampled with a two-stage high volume air sampler, as described elsewhere [1,2]). The particle-bound PCDD/F were collected on a glasfibre-filter, while the gaseous PCDD/F were adsorbed on a polyurethan foam plug. The sampler flow rates were adjusted to 14m³/h. Samples were taken over 72-hour periods resulting in air volumes in the order of 1000m³.

Air samples taken by two samplers operating side by side were used to determine the precision of the method. From these duplicate samples the precision of the entire method , in average 25%, could be calculated. Samples with concentrations near the detection limits showed worse precision than samples with concentrations significantly higher than the detection limits.

The analysis of the air samples were carried out seperately for gaseous and particle-bound PCDD/F. The methods for cleanup and detection (HRGC/HRMS) are described previously [2]).

The total measuring programme comprises 100 samples, including 15 duplicate samples.

Table 1

Measuring Sites for Ambient Air Samples

Nov. 1992 - Oct. 1993

Measuring Site	Topography	Nature of the Site
Graz South	south of city centre on the grounds of a garden nursery	suburb of residential conurbation
Linz ORF Centre	between city centre and the site of the Chemie-Linz AG	urban residential area
Steyregg, Weih	on slope east of Linz	agricultural and residential area opposite the industrial site on the Danube (VOEST, Chemie-Linz)
Vienna, 9th District	on the grounds of the General Hospital of Vienna	urban residential area
Vienna 14th District	on the grounds of the Psychiatric Hospital at Baumgartner Höhe	urban residential and recreational area
Vienna 22nd District	on eastern fringe of Vienna	farmland

3. Results

The main objectives of this measuring programm were the calculations of annual average values of ambient PCDD/F levels. The evaluation of the data obtained from the measurements taken between November 1992 and October 1993, as shown in Figure 2, showed a high variation of the ambient air concentration of PCDD/F during the winter period, thus a separate calculation of winter and summer average values, as shown in Table 2, seemed to be more meaningful.

Table 2

	GRAZ South	LINZ ORF-Centre	STEYREGG Weih	VIENNA 9th District	VIENNA 14th District	VIENNA 22nd District
Winter period: October - March						
n	7	7	8	8	8	3
$\bar{x}$ [fg TEQ/Nm³]	221.6	120.9	119.0	125.6	50.1	64.4
$s_{rel.}$ [%]	73	77	88	101	68	48
Summer period: April - September						
n	10	8	8	8	7	2
$\bar{x}$ [fg TEQ/Nm³]	28.4	33.7	32.3	32.2	22.1	40.8
$s_{rel.}$ [%]	61	31	33	65	79	103

At the measuring sites in Vienna and Linz during the winter months, the ambient dioxin concentrations lay mostly below 200 fg TEQ/Nm^3. The winter dioxin values at Graz South, at approximately 300 fg TEQ/Nm^3, lay clearly above the levels recorded at Vienna and Linz.

It could be observed that periods of extremely stable meteorological conditions (inversion) can lead in the short term to major increases in ambient dioxin levels. During the measuring period 1-4 February 1993 this phenomenon led to the the highest ambient dioxin concentrations recorded during this measuring programme. Such weather conditions are to be expected more frequently in the basin area of Graz than, for example, in Vienna.

It could be found that in winter the temporal variations in ambient dioxin concentrations were analogous to those demonstrated for the „classical" air pollutants sulphur dioxide and nitrogen dioxide. This observation, together with the increased proportion of the higher chlorinated PCDD/F compounds, points to domestic heating as the major cause for the marked rise in ambient dioxin levels in the winter months along with the usually poorer dispersion conditions and the correspondingly weaker dillution of aerial pollutants.

During the summer months, ambient dioxin levels at all measuring sites were similarly high, lying in the region of 10 to 70 fg TEQ/Nm^3. This qualitatively and quantitatively similar ambient dioxin situation suggests, for the summer months at least, a similar emission pattern at the sites in question.

Common to all measuring sites is the diminishing proportion of furans from tetrachloro- to octachloro-congeners whereas the proportion of dioxins from tetrachloro-congeners to octachloro-congeners increases. This distribution is in accordance with results described in the literature for measuring sites which do not lie in the immediate area of influence of a potent emitting source. An average homologue profile from the sampling site GRAZ-South is shown in Figure 1.

However, within this regular distribution of the homologues, it is possible to detect differences which are specific to the individual measuring sites. For example, there is a higher proportion of octa- and heptachloro-dibenzo-p-dioxins at the Graz South measuring site. This contrasts with the situation at the Linz ORF-Centre, Steyregg-Weih and the General Hospital in Vienna where tetrachlorofurans predominate.

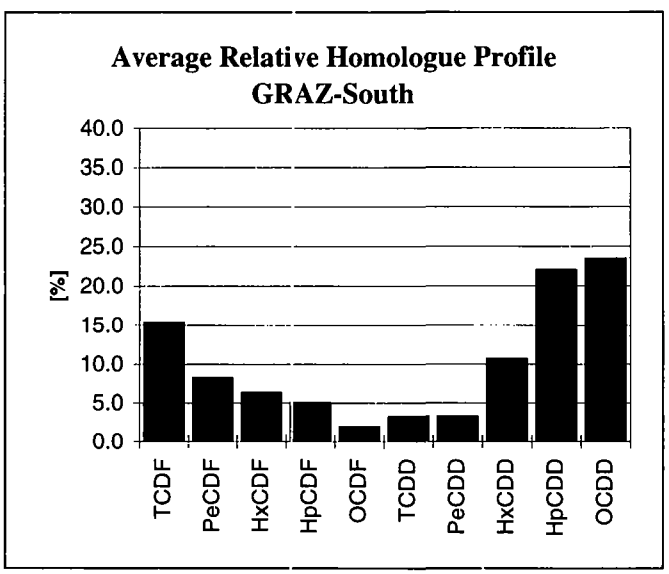

Figure 1

Further evaluation of the obtained data showed that partitioning of PCDD/F between vapour and particle-bound phases is mainly controlled by the vapour pressure of the individual congenere and the ambient temperature. The physical properties of PCDD/F favor the enrichement of the more chlorinated congeners in the particle-bound phase. At ambient temperatures lower than approximately 10°C, the PCDD/F are mainly particle bound. This corresponds with results published elsewhere [3,4,5,6,7]).

4. References

1) Oehme, M.; Manø, S.; Mikalsen, A.; Kirschmer P. (1986): Quantitative Method for the Determination of Amounts of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Outdoor Air. *Chemosphere* 15: 607-617.

2) Thanner, G.; Moche W. (1994): Dioxine in der Luft von Ballungsräumen; Meßergebnisse aus Graz, Linz, Steyregg und Wien; Teil I. Monographie Bd. 50, Umweltbundesamt (Austria), Vienna.

3) Hites, R. A. (1991): Atmospheric Transport and Deposition of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. *EPA/600/3-91/002.*

4) Junge, C.E. (1977): Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. *Fate of Pollutants in the Air and Water Environments*: 7-25, Wiley, New York.

5) Rappe, C.; Marklund, S.; Kjeller, L.O. (1989): Long-Range Transport of PCDDs and PCDFs on Airborne Particles. *Chemosphere* 18 (1-6): 1283-1290.

6) Rordorf, B. F.(1989): Prediction of Vapor Pressures, Boiling Points and Enthalpies of Fusion for Twenty-Nine Halogenated Dibenzo-p-dioxins and Fifty-Five Dibenzofurans by a Vapor Pressure Correlation Method. *Chemosphere* 18: 783-788.

7) Yamasaaki, H.; Kuwata, K. and Miyamoto H. (1982): Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons. *Envir. Sci. Technol.* 16: 189-194.

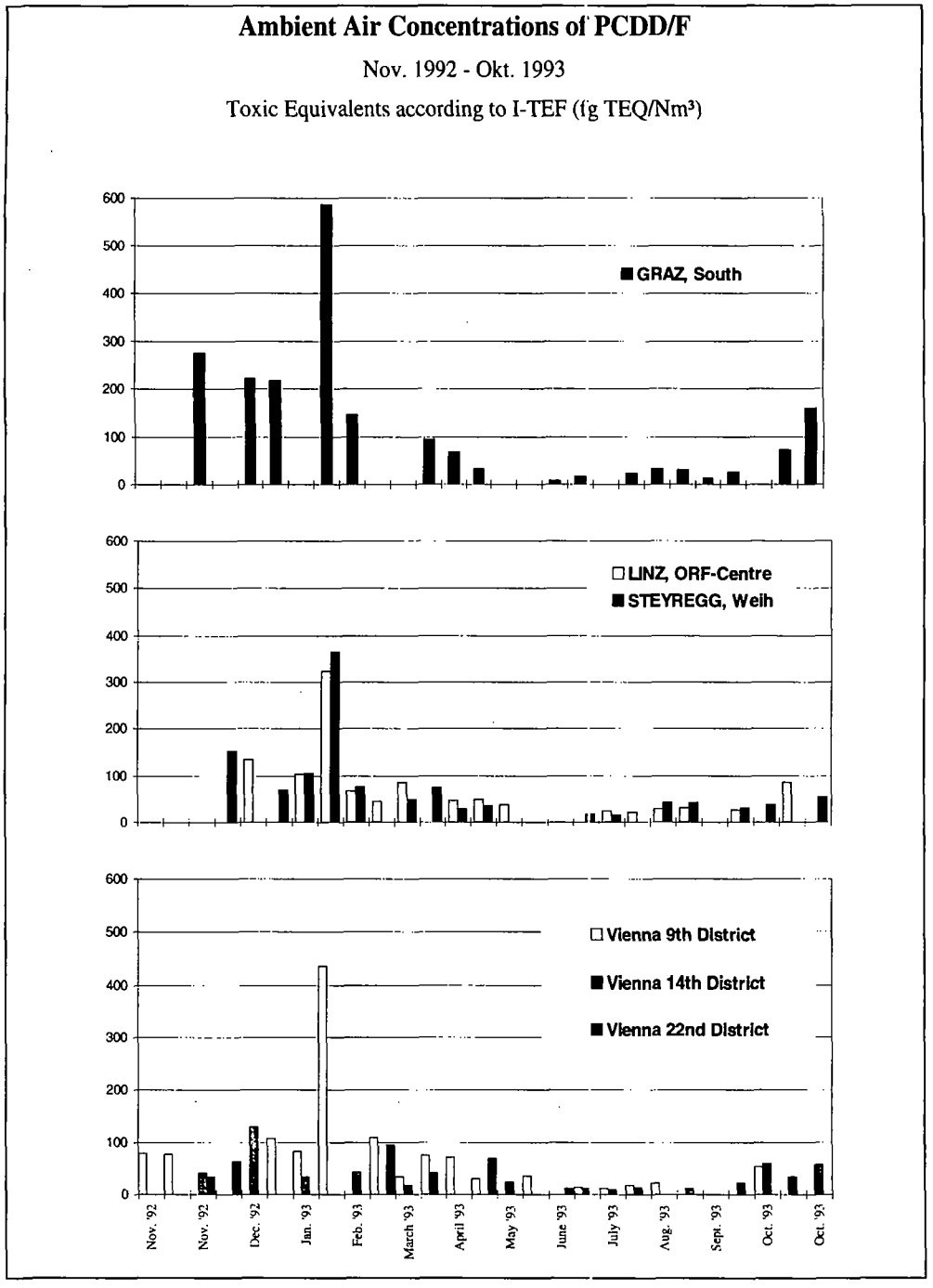
Ambient Air Concentrations of PCDD/F
Nov. 1992 - Okt. 1993
Toxic Equivalents according to I-TEF (fg TEQ/Nm³)
GRAZ, South
LINZ, ORF-Centre
STEYREGG, Weih
Vienna 9th District
Vienna 14th District
Vienna 22nd District
0
100
200
300
400
500
600
Nov. '92
Nov. '92
Dec. '92
Jan. '93
Feb. '93
March '93
April '93
May '93
June '93
July '93
Aug. '93
Sept. '93
Oct. '93
Oct. '93

Figure 2