Dioxin Levels in the Ambient Air in Slovakia

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Introduction

A comprehensive ambient air quality project in Slovakia, funded by the European Union under the Phare Programme, has recently been completed. The project was undertaken under the technical supervision of the Slovak Ministry of Environment and was the first aimed at monitoring the ambient air quality with respect to a range of Volatile Organic Compounds (VOCs), Persistent Organic Pollutants (POPs) and Heavy Metals (HMs), evaluating the resultant health risk, identifying and evaluating the main potential pollution sources and defining general strategies to reduce impacts so comprehensively. Monitoring was undertaken at 20 locations throughout Slovakia, including urban, industrial, agricultural and rural background sites, in 8 separate sampling campaigns (two per season) over a period of a year from October 1996 to August 1997.

At 15 of the sampling locations, samples for the measurement of dioxins/furans were taken. Thirteen of the locations were urban/industrial. The remaining two locations were representative of agricultural and rural background situations. The twenty locations were given numbers for ease of reference, and those where dioxin/furan monitoring took place are listed below with a brief indication of the type of location:

Number	Location	Description
1 to 5	Bratislava	Urban/Industrial, incl. city centre and residential
6	Topolniky	Agricultural (but 40km SE of Bratislava)
12	Ruzomberok	Urban/industrial (pulp and paper)
13	Krompachy	Industrial (copper)
14	Strazske	Industrial (chemical, former PCB manufacture)
15	Starina	Rural background
16 to 19	Kosice	Urban/industrial, incl. city centre and residential
20	Velka Ida	Industrial (iron and steel)

Locations 1 to 5, 12, 13, 14 and 16 to 20 had samples taken in all eight campaigns; locations 6 and 15 had samples taken in four campaigns, one in each season. (In fact a fifth sample was taken at location 6 because of contamination problem) This gave a total of 113 samples.

Methodology

Sampling for dioxins/furans was carried out according to USEPA Method TO-9 using GPS1 Samplers. 24hr samples were taken at each location giving sampling volumes of approximately $400m^3$. During each sampling period, meteorological data, for temperature, pressure, relative humidity, wind speed and wind direction, were also monitored and recorded as 5 minute averages. This was required for three different reasons. The first was to correct the sampling volumes to standard conditions of 101.3 kPa and 298 K. The second reason was to be able to establish, from the wind speed and wind direction, which possible industrial sources were likely to contribute to the measured pollutants. The final reason was to provide meteorological data which would be relevant for short term dispersion modelling.

Analysis of the samples was by HRGC/HRMS based on USEPA Methods TO-9 and 8290. Detection limits were usually $\leq 0.01 pg/m^3$ for most congeners. Field blanks were taken on four of the eight campaigns and were all below detection limits. Additionally parallel sampling was done on two occasions and gave results within 10% on each occasion.

Results and Discussion

The results of the 113 measurements of dioxins/furans in the Slovakian ambient air made during this project are given in Table 1. They are quoted as I-TEQ (max) values where the value of any congeners below the detection limit are included in the I-TEQ calculation at their detection limit. Because each sample was obtained sequentially over a 24hr period, excluding Sundays, it took 4 weeks to complete each sampling campaign. Therefore, the values are given for each sampling location and the month during which the major part of the sampling campaign occurred.

The table also includes a mean value for each sampling location. The mean values are geometric means, since it is assumed that the pollutant levels follow a log normal distribution in which case the geometric mean of a sparse data set more closely corresponds to a median value than does an arithmetic mean. Because the means are derived from maximum I-TEQ values, they may be slightly elevated. However they are in line with a WHO indication that urban ambient air concentrations in Europe are about $0.1 pg/m^3$ and certainly do not indicate problems different or more severe than the rest of Europe.

The results are also displayed graphically. This shows more clearly the seasonal variation which would be expected if the major source is combustion, particularly associated with energy requirements. This is further confirmed by a strong negative correlation between the measured I-TEQs and the mean temperature recorded during sampling at most of the sampling locations. The variation and the correlation with temperature is less marked where there is expected to be a significant contribution from industrial processes and traffic which does not vary as significantly with the seasons. An analysis of the identifiable stationary sources and traffic densities may enable the contribution from the three sources to be determined.

The I-TEQ levels also have quite a strong positive correlation with the PAH and total particulate levels measured at the same time, tending to indicate a common source.

Almost all the congener and total homologue patterns observed were very similar and typical of the pattern associated with general fossil fuel combustion. However, one very distinctly different pattern was observed from the sample taken at sampling location 4 (Bratislava - Starohajska) in the November '96 campaign. This was dominated by the dioxins, and with a very distinct congener pattern. Its source is not clear, but probably results from the combustion of specific chemical material.

A final observation on the results relates to the ratio of dioxins to furans, either as I-TEQ or total. Excluding the one sample mentioned above, the dioxin/furan ratios vary from about 0.2 to 1.8. However the values for the samples at each sampling location appear to show quite a good negative correlation with the corresponding I-TEQ values. An examination of the separate dioxin and furan totals shows that the furan values exhibit a similar variation as the total I-TEQ values in Table 1, whereas the dioxin values show much less variation with samping campaign. This would suggest that the seasonal variation is mainly due to increased furan emissions associated with energy production, whereas the dioxin levels may be more indicative of the seasonally invariant emissions from traffic and industrial processes. The dioxin/furan ratio may therefore be useful in indicating the contribution of different types of sources to the overall ambient air levels.

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Table 1: Ambient Air I-TEQ (max) Values (pg/m³)

Sampling Location	1	2	3	4	5	6	12	13	14	15	16	17	18	19	20
Oct 96	0.11	0.06	0.09	0.10	0.11	0.08	0.06	0.18	0.06	0.05	0.09	0.20	0.09	0.06	0.31
Nov 96	0.10	0.09	0.03	0.44	0.08		0.10	0.10	0.07		0.23	0.17	0.19	0.06	0.17
Jan 97	0.20	0.15	0.16	0.13	0.30	0.22	0.37	0.34	0.08	0.07	0.69	0.24	0.44	0.19	0.11
Feb 97	0.11	0.23	0.20	0.09	0.13	0.15	0.06	0.11	0.05		0.09	0.13	0.08	0.04	0.18
April 97	0.04	0.04	0.15	0.04	0.03	0.03	0.11	0.13	0.06	0.03	0.15	0.13	0.05	0.06	0.09
May 97	0.07	0.03	0.03	0.04	0.05		0.06	0.08	0.03		0.03	0.16	0.04	0.03	0.06
June 97	0.05	0.04	0.05	0.04	0.05	0.03	0.03	0.15	0.04	0.03	0.06	0.11	0.05	0.04	0.05
July 97	0.03	0.03	0.12	0.04	0.04		0.05	0.08	0.04		0.05	0.05	0.03	0.03	0.15
Mean (Geom)	0.08	0.06	0.08	0.08	0.07	0.07	0.08	0.13	0.05	0.04	0.11	0.13	0.08	0.05	0.12