PCDDs, PCDFs AND DIOXIN-LIKE PCBs IN AMBIENT AIR IN SLOVAKIA

Kočan Anton, Dömötörová Milena, Čonka Kamil, Chovancová Jana, Sejáková Zuzana

Department of Toxic Organic Pollutants, Research Base of SMU, Slovak Medical University, Limbová 12, 833 03 Bratislava, Slovakia

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs) belong to persistent organic pollutants (POPs) that are lipophilic, stable, toxic compounds with known adverse effects on human health such as cancer, neurological defects, reproductive anomalies, birth defects. PCDDs and PCDFs are released into the atmosphere predominantly during various anthropogenic processes. Besides industrial activities, non-industrial diffuse sources such as traffic and residential combustion are important sources of emission. The major source of PCBs released in to the atmosphere is an environmental cycling process of PCBs previously introduced into the environment. Monitoring of PCDDs, PCDFs and PCBs which are on the list of current 12 substances in the Stockholm Convention (SC) on POPs is recommended to evaluate the effectiveness of the SC. Two core media have been identified by the Conference of the Parties to the SC for the first evaluation: ambient air and mother's milk (or maternal blood). In Slovakia, the initial measurements of PCDDs, PCDFs and PCBs in ambient air were realised in October 1996 – July 1997 within the Phare Project EU/93/AIR/22[1]. This presentation shows which situation was in the Slovakia's ambient air concentration of PCDDs, PCDFs and dioxin-like PCBs (dl-PCBs) in 2007 and compares it to that of 10 years ago.

Materials and Methods

Sampling areas and sites

In total, 20 ambient air samples were collected during two campaigns in March (mild winter) and June (summer) 2007 at five selected areas in Slovakia:

- Košice area – SW rural vicinity of Košice city (iron ore sintering in a metallurgical plant; municipal waste incinerator); Sampling sites: Haniska village (N 48º 37´ 22.7˝ E 21º 15´ 19.4˝) and Veľká Ida village (Gomboš settlement) (N 48º 34´ 08.8˝ E 21º 10´ 35.4˝)
- Krompachy area (metallurgical plant processing copper scrap); Sampling sites: Krompachy town (N 48º 54´ 38.5˝ E 20º 53´ 00.1˝) and Kluknava village (N 48º 56´ 13.7˝ E 20º 56´ 25.2˝)
- Nemecká area (hazardous waste incinerator in a petrochemical plant); Sampling sites: Predajná village (N 48º 48´ 40.0˝ E 19º 27´ 45.6˝) and Nemecká village (N 48º 48´ 45.6˝ E 19º 25´ 17.0˝)
- Šaľa area (hazardous waste incinerator in a chemical plant); Sampling sites: Diakovce village (N 48º 08´ 14.3˝ E 17º 50´ 39.0˝) and Močenok village (N 48º 12´ 50.6˝ E 17º 55´59.9˝)
- Starina area (eastern Slovakia's background area around the Starina lake serving for drinking water production); Sampling sites: Jalová village (N 49º 02´ 24.2˝ E 22º 13´ 58.1˝) and Stakčín village (N 49º 00´ 07.4˝ E 22º 14´ 03.1˝)

Air samplers were deployed in the back gardens of family houses.

Sampling

Two air samples were simultaneously collected in March and 2 ones in June at each area according to USEPA Method TO-9 using high-volume samplers GPS-1 (Graseby Andersen, USA). During simultaneous sampling, the distance between the two samplers was several kilometres as well as several kilometres from a potential pollution source. Airborne air particles were trapped on a glass fibre filter (GFF). Organics present in the vapour-phase were adsorbed in a polyurethane foam (PUF) plug. The GFFs and PUF plugs were pre-cleaned with toluene ultrasonically and by PLE extraction respectively. Approximately 400 m^3 of ambient air could be drawn through the GFF and PUF plug during 24-h sampling. One field blank was taken on each campaign at one of the sites. During the sampling, atmospheric pressure and ambient air temperature were regularly measured to adjust sampled volumes to reference

conditions of 298.15 ºK and 101.325 kPa. Data on wind speed and direction were obtained from the nearest meteorological station. The sampling media placed in clean and sealed glass containers were transported to the dioxin laboratory of the Research Base of SMU and stored in the dark until analysis.

Chemical analysis

The GFFs (air-dried and weighed[A]) and PUF plugs were stuffed into a 34-mL ASE®300 extractor (Dionex, USA) cell and after adding $^{13}C_{12}$-labelled PCDD, PCDF and dl-PCB extraction standards the sampling media were extracted with toluene at 100 ºC, 10 MPa, 5-min static time, 2 cycles. Extracts were cleaned-up and fractioned by a semi-automated PowerPrep™ apparatus (Fluid Management Systems, USA) equipped with pre-packed disposable multi-layer silica (H_2SO_4, KOH, $AgNO_3$), basic alumina and PX21 carbon columns. Eluates were analysed by an HRGC/HRMS MAT 95 XP instrument (Thermo Finnigan, USA) using a 60-m DB-5ms column for the separation of a mono*ortho*-PCB fraction and a 60-m Rtx-2330 column for a PCDD/PCDF/non*ortho*-PCB fraction using the isotope dilution method. The laboratory analysing the samples has been accredited for PCDD/PCDF and PCB analysis in environmental samples according to ISO 17025 since 2002 and participates regularly in intercalibration studies aimed at environmental samples organised by the International Intercal, Sweden.

Results and Discussion

An overall view of concentrations of PCDDs, PCDFs and dl-PCBs expressed as WHO_{98}TEQs and summed 2,3,7,8-substituted PCDD and PCDF congeners determined in 10 air samples collected in March and 10 ones in June 2007 can be seen in Fig. 1 and Fig. 2. The arithmetic mean, geometric mean and minimum and maximum values for TEQs and sums are given in Table 1. Some of these parameters are also reported for air concentrations measured in 1997; 11 samples collected in winter and summer at sites similar to those in 2007 were selected. Although the 1997 samples were collected identically and analysed also by HRGC/HRMS analytical sensitivity and selectivity was lower and much more individual PCDD/PCDF congeners findings were below the limit of detection. Nevertheless, after 10 years a certain drop in both TEQ and summed levels can be seen.

Table 1: Basic statistical data on TEQ and summed congener concentrations measured in ambient air samples in Slovakia

	WHO_{98}TEQ (fg/m^3)				Sum (pg/m^3)			
					2,3,7,8-substituted congeners			dl-PCBs
2007	PCDDs	PCDFs	PCDDs+Fs	dl-PCBs	PCDDs	PCDFs	PCDDs+Fs	
Arith. mean	11.7	39.6	51.3	7.8	0.27	0.51	0.78	8.2
Geom. mean	6.9	19.9	27.0	6.2	0.14	0.22	0.37	6.4
Minimum	1.3	3.2	4.7	2.4	0.010	0.029	0.038	2.1
Maximum	72.0	257.5	329.4	26.5	1.06	4.48	5.54	25.3
1997								
Arith. mean			78.8				0.99	
Geom. mean			56.9				0.67	

It is known that combustion of fossil fuels such as coal and wood or other biomass increases PCDD/PCDF emissions into the air[2,3]. One of the important dioxin sources is residential heating because of its large scale, no or limited combustion control and no house chimney gas cleaning. It is anticipated that in many countries the residential heating based on fossil fuels particularly in rural areas may be the dominant source of PCDD/PCDF emissions. Because residential heating with natural gas has become the most expensive heating in Slovakia the vast majority of family houses in rural areas have again begun to use dioxin-generating fossil fuels. Although open burning and combustion of garden and household waste, which is another important dioxin source[4], has recently been banned in Slovakia this regulation is often being broken.

[A] Glass fibre filters were weighed before and after air sampling to determine TSP (total suspended particles) concentration

Figure 1: $WHO_{98}TEQs_{PCDDs}$, $WHO_{98}TEQs_{PCDFs}$ and $WHO_{98}TEQs_{dl\text{-}PCBs}$ in ambient air in Slovakia

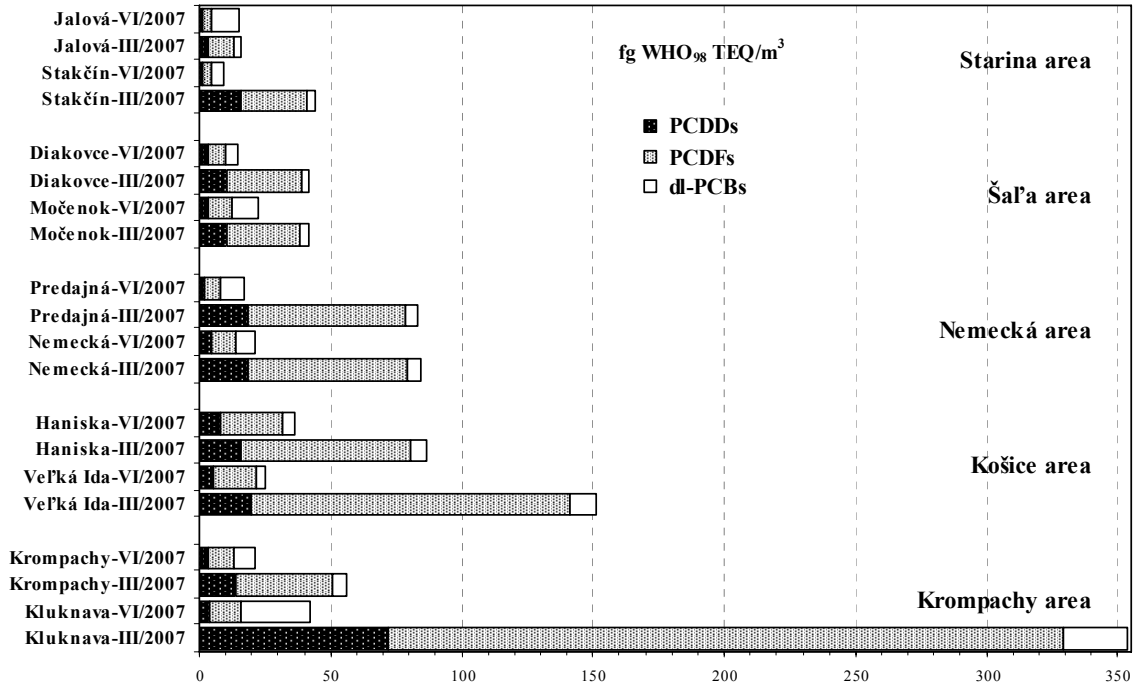
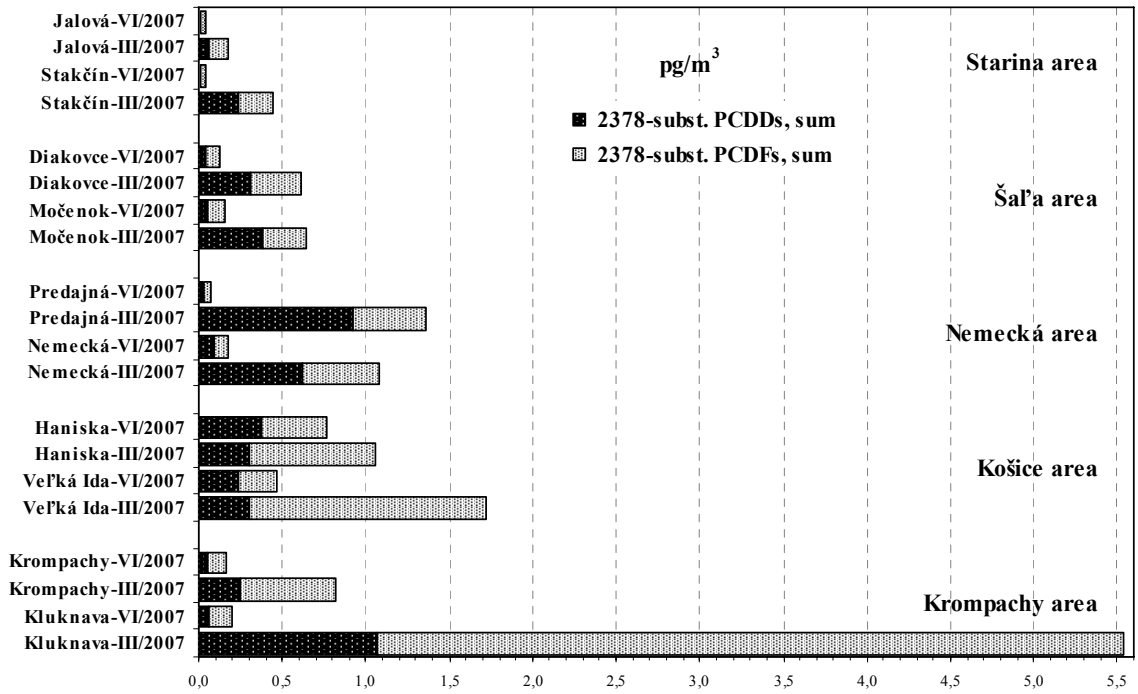


Figure 2: Summed 2,3,7,8-substituted PCDD and PCDF congeners in ambient air in Slovakia



The differences between $TEQ_{PCDDs/PCDFs}$ levels in the Slovak air samples taken in winter and summer are evident and confirm published findings[5]. In spite of atypically mild winter 2006/2007 an influence of emissions from household heating systems is unambiguous. On average, winter $TEQ_{PCDDs/PCDFs}$ concentrations were 3- to 21-times than summer ones. Unlike PCDDs/Fs, summer summed dl-PCBs levels were 2- to 6-times higher (except one site) than winter ones. That corresponds with the fact that air-borne PCBs come from the environment rather than emissions. With several exceptions, the contribution of dl-PCBs to the total TEQs was lower than that of PCDDs/Fs. PCDF contribution to $TEQ_{PCDDs/PCDFs}$ was 2- to 6-times higher than that of PCDDs. TSP concentrations (geom. mean: 33 $\mu g/m^3$; range: 14 – 86 $\mu g/m^3$) were higher in the air samples collected in winter at 8 sites out of all 10 sampling sites. TSP concentrations measured at the 11 sampling sites in 1997 were 50 $\mu g/m^3$ (geom. mean), i.e. higher than those in 2007 likewise PCDDs/Fs (see Table 1). However, there is a low correlation (~ 0.4) between TSP concentrations and summed PCDDs/PCDFs or $TEQs_{PCDDs/PCDFs}$.

Mean $WHO_{98}TEQ_{PCDDs/Fs}$ and $WHO_{98}TEQ_{dl\text{-}PCBs}$ measured in 2002/2003 at 10 sample collection sites across Australia[5] ranged from 1.05 to 17.17 fg/m^3 (min 0.11 fg/m^3 – max 121.6 fg/m^3) and from 0.11 to 7.04 fg/m^3 (0.02 fg/m^3 – 12.34 fg/m^3) respectively which is substantially less than found in Slovakia (see Table 1). Dioxin-like PCBs were determined in 11 air samples collected in 2002/2003 in Japan (Yokohama city)[6]. Arithmetic mean, geometric mean, and min – max range were 4.6, 3.9, and 1.4 – 9.7 fg WHO_{98} $TEQ_{dl\text{-}PCBs}/m^3$ respectively. These values are about half of those measured in Slovakia. PCDD, PCDF and dl-PCB monitoring in California[7] in 2002 – 2005 provided this range of mean annual values: 23 – 26 fg $WHO_{98}TEQ_{PCDDs/Fs}$ and 3.7 – 6.2 fg $WHO_{98}TEQ_{dl\text{-}PCBs}$ which are concentrations slightly lower than Slovak values. Mean I-TEQ concentration calculated from monthly values within four-year monitoring (2004-2007) of PCDDs/PCDFs in Hong Kong[8] ambient air was 65 fg/m^3.

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References
1. Stenhouse I., Moncur J., Kocan A., Violova A. *Organohalogen Compounds* 1998; 39: 77.
2. Quaß U., Fermann M., Bröker G. *Chemosphere* 2004; 54: 1319.
3. UNEP. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases. 2nd edition, February 2005.
4. Wevers M., De Fré R., Desmedt M. *Chemosphere* 2004, 54: 1351.
5. Grass J., Müller J. Dioxins in Ambient Air in Australia. National Dioxins Program [Technical Report No. 4]. Commonwealth of Australia, May 2004.
6. Kim K-S., Masunaga S. *Environmental Pollution* 2005, 138: 290.
7. California Ambient Dioxin Air Monitoring Program. California Environmental Protection Agency (http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm).
8. Environmental Protection Department, The Government of the Hong Kong. Ambient air monitoring (Dioxins) from 2004 to 2007 (http://www.epd.gov.hk/epd/english/environmentinhk/waste/data/dioxin.html).