PCDD/Fs in ambient air of Krakow – seasonal changes in congener distributions

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Introduction

In some new EU-Member States coal is still widely used for residential heating. In winter during the inversion conditions, emissions from solid fuel-fired residential appliances contribute to elevated concentrations of particles in ambient air. Moche and Thanner[1] have shown that these particles can contain high amounts of polychlorinated dibenzodioxins and -furans (PCDD/Fs), which results in a significant contribution to the overall PCDD/F emissions[2].

This study aims at identifying the influence of these PCDD/F emissions on ambient air in the region of Malopolska, Poland. PCDD/F concentrations and congener patterns in ambient air particulate matter were measured in *Zakopane*, a rural site predominated by residential heating and at two sites in Krakow, one of mainly industrial character and a site in the city center characterized by traffic, domestic heating and diffuse industrial sources. A summer/winter comparison was made in order to estimate the specific influence of domestic heating.

For comparison a soot sample was collected from the walls of a chimney of a domestic stove where a mix of brown coal and wood was used.

Methods and Materials

Ambient air particulate matter (PM10) was collected in 24 h intervals during summer and wintertime 2002 on glassfiber filters using an Anderson High Volume sampler. Sample volumes were between 800 and 1300 m^3. The vapour phase was not collected. Two sampling sites were in the city of Krakow: *Krakow Aleje* in the city-centre and *Krakow Nowa-Huta,* close to an industrial area dominated by the steel industry, approximately 8 km westnorthwest of the city-centre. In addition, PM10 was sampled in *Zakopane*, a mountain tourist resort with about 20,000 inhabitants and no industry, located circa 100 km south of Krakow.

Analysis of PCDD/Fs was based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry) for quantification. The applied methodology follows USEPA method 1613. A mixture of all ^{13}C-labelled WHO-TEQ relevant PCDD/F-congeners (400 pg each, except OCDD/OCDF with 800 pg each) was added to each sample prior to extraction. Extraction was done in 300 ml toluene using soxhlet extractors for 48 h. Extract purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA). The chromatographic principle is based on the method proposed by Smith et al.[3]. A detailed description of the Power-Prep method and its performance is given by Abad et al.[4]. The GC system was an HP-6890 (Hewlett Packard, Waldbronn, Germany), using a split/splitless-injector with borosilicate liner (4 mm i.d.) (Zwingen, Switzerland). The samples were analysed on a 60 m capillary column with 0.25 mm i.d. and 0.25 µm film (BP-DXN, SGE, Victoria, Australia). The GC was coupled with a VG Autospec Ultima mass spectrometer (Micromass, Manchester, UK) operating in EI-mode at 34 eV with a resolution of >10000. Two masses in the M+ isotope cluster were monitored for each analyte and each internal standard. Whenever interferences were encountered, more masses were monitored.

Results and Discussion

PCDD/F concentrations in atmospheric particulate matter PM10 (Table 1)

The highest PCDD/F concentrations of 3.2 pg/m^3 (WHO-TEQ[5]) were measured during wintertime in *Zakopane* air.

The summer/winter comparison of the particle-bound PCDD/F concentration in the ambient air of the three sites reveals the following:

Starting from summer levels of below 0.1 pg WHO-TEQ/m^3, in wintertime PCDD/F concentrations in ambient air of *Zakopane* and the centre of Krakow (*Krakow Aleje*) were higher by a factor of approximately 40 and 20, respectively. This increase may be attributed to emissions from the combustion of solid fuels used predominantly for domestic heating, supported by similar trends for benzo-a-pyrene (BaP) levels. The concentration of PM10 shows the same tendency but less expressed, which results in a higher PCDD/F concentration per mass unit of PM10 during wintertime.

The situation in the industrial area of Krakow (*Krakow Nowa-Huta*) is different. During summertime where only minor influence of domestic heating is assumed, PCDD/F levels in ambient air were at the level observed in *Krakow Aleje* in winter. Highly contaminated PM10 released from the industrial sources in the vicinity could be the source of these high levels,as indicated by the comparison of the PCDD/F-concentrations per unit mass PM10. During wintertime *Nowa-Huta* PCDD/F-levels did not show the increase observed in the other sites, although rising BaP- and PM10 concentrations indicate the possible influence of increased combustion activity and/or different dispersion characteristics of the atmosphere. In contrast to the non-industrial sites, the PCDD/F concentrations per unit mass PM10 decreased. The lack of influence of the heating period on PCDD/F levels in ambient air of *Krakow Nowa-Huta* leads us to the conclusion that the site is dominated by emissions from the adjacent agglomeration of industry during the whole year. Although during wintertime a contribution from emissions from domestic heating became visible (BaP, PM10), PCDD/F emissions from combustion do not seem to play an important role because of the high baseline of PCDD/F emissions at *Nowa-Huta*. For this reason a “dilution effect“ with comparably lower contaminated combustion particles can be observed when examining PCDD/F concentrations per unit mass PM10. The non-industrial sites showed an inverse tendency, where apparently high emissions from domestic combustion resulted in higher PCDD/F concentrations per unit mass PM10 during winter.

The TEQ-values of PM10 collected during summer months are likely understated due to the potential losses of the more volatile tetra- and penta-congeners during sampling. These isomers contribute significantly to the TEQ.

PCDD/F-Patterns

The comparison of the congener patterns of the three sites and the related summer/winter shifts reveals, that the air of the remote site in *Zakopane* and the industrial site in *Krakow Nowa-Huta* are under the influence of two very distinct emission sources (Figures 3-6). The fingerprints in the city-centre of Krakow, however, are influenced by a mix of both sources, domestic heating and industrial emissions (Figures 1-2).

Seasonal changes of the patterns are observed in the air of *Zakopane* (Figures 5-6) and the city center of Krakow (*Krakow Aleje;* Figures 1-2). In contrast the fingerprints in *Krakow Nowa-Huta* (Figures 3-4) remain nearly the same during summer and wintertime, again confirming the dominance of the emissions from the nearby industrial agglomeration.

The wintertime dominance of furans in *Zakopane* aerosol, with a large relative contribution of lower chlorinated PCDFs, is attributable to domestic heating with coal and wood, the prevalent source. This is confirmed by the results from a of soot sample taken from a stack of a domestic heating installation operated with a mix of brown coal and wood, showing a similar congener pattern (Figure 7). In summer, the pattern at *Zakopane* is dominated by Cl7 and Cl8-dioxins typical for atmospheric long range transport[6]. Due to the applied filter only sampling-technique for PM10, a temperature-dependent loss of low chlorinated congeners in summer months likely occurred, which influenced to some extent our findings for the tetra and penta-chlorinated compounds. However, this will not affect the findings about the differences in the ratio of the hepta- and octa dioxins compared to the high chlorinated furans.

The PCDD/F pattern in the air of *Krakow Nowa-Huta* is not changing from summer to winter. It is again dominated by furans, but in contrast to *Zakopane,* has a high abundance of OCDF and 1,2,3,4,6,7,8-HpCDF. Due to the high contamination level (Table 1) an influence of *Nowa-Huta* can be observed during summertime in the pattern of the city center of Krakow where low emissions from domestic sources can be assumed.

Consequently the summer pattern in *Krakow Aleje* (Figure 1) combines the signals from long-range transport (HpCDD, OCDD), as observed during summer in *Zakopane* (Figure 5) and the nearby industry (HpCDF and OCDF) in *Nowa-Huta* (Figure 3). In wintertime, the local emissions from domestic heating overrules other sources and results in a PCDD/F pattern almost identical to the one in *Zakopane* (Figure 6) and the soot sample from wood and coal combustion (Figure 7).

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Tab.1: Particle-bound concentrations in PM 10 samples from ambient air of Krakow

Sampling-Place & -Date	PCDD/F-WHO-TEQ (in air) [pg/m3]	B(a)P* [ng/m3]	PM10 [mg/m3]	PCDD/F-WHO-TEQ (per unit mass PM10) [ng/g]
Krakow Aleje				
03.06.2002	0.039	0.72	0.042	0.92
08.06.2002	0.078	1.7	0.037	2.1
20.12.2002	1.6	44	0.23	7.1
25.12.2002	0.71	21	0.15	6.1
Krakow Nowa-Huta				
03.06.2002	1.1	-	0.022	49
08.06.2002	1.1	0.53	0.022	49
10.12.2002	1.6	16	0.12	13
20.12.2002	2.2	44	0.18	12
25.12.2002	0.8	40	0.15	5.5
Zakopane				
08.06.2002	0.071	0.99	0.019	3.8
10.12.2002	3.2	49	0.16	20
25.12.2002	2.6	34	0.14	18

* B(a)P (Benzo-a-pyrene)- and PM10- concentrations were provided by Malopolski Voivodship, Inspectorate for Environmental Protection, Poland.

Figure 1: PCDD/F-concentration-patterns in PM10 filter of *Krakow Aleje* in summer

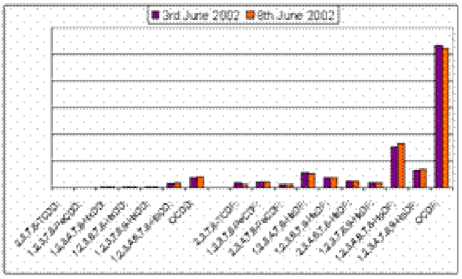

Figure 2:PCDD/F-concentration-patterns in PM10 filter of *Krakow Aleje* in winter

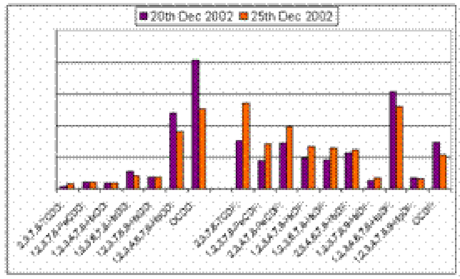

Figure 3: PCDD/F-concentration-patterns in PM10 filter of *Krakow Nowa-Huta* in summer

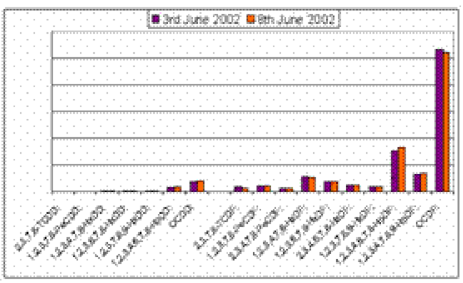

Figure 4: PCDD/F-concentration-patterns in PM10 filter of *Krakow Nowa-Huta* inwinter

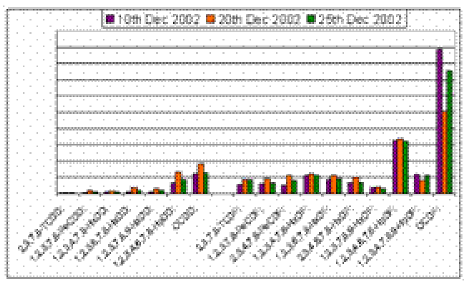

Figure 5: PCDD/F-concentration-patterns in PM10 filter of *Zakopane* in summer

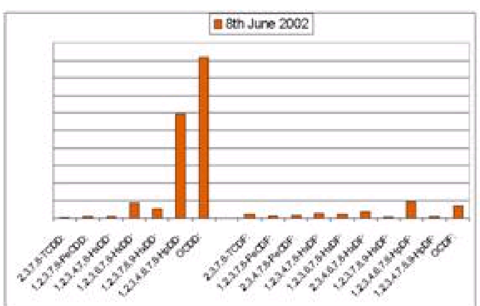

Figure 6: PCDD/F-concentration-patterns in PM10 filter of *Zakopane* in winter

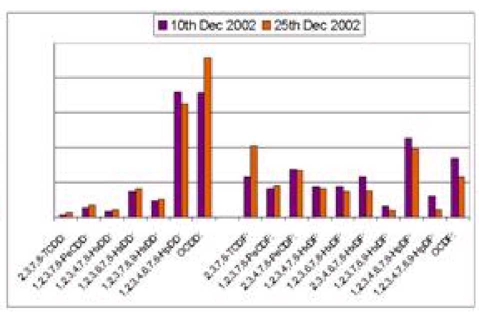

Figure 7: PCDD/F-concentrations [pg/g] in a chimney soot of a stove, fired with brown coal & wood (Czech Republic)