LEVELS AND PATTERNS OF PCDD/FS IN AIR, SOIL AND BIOTA FROM KRAKOW AND THE MALOPOLSKA REGION (POLAND)

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Introduction

In the new EU Member States domestic combustion of coal and wood in small heating appliances has been discussed as a potential source of PCDD/Fs into the atmosphere[1,2]. The existing Dioxin emission inventories from the old Member States-EU 15[3] are lacking quantitative information about their actual contribution to total PCDD/F emissions, since these type of heating appliances do not play a big role in the EU 15. However, high PCDD/F levels in ambient air measured during winter time in Poland[1,2] indicated an important contribution from domestic heating. The widespread use of hard coal in Krakow for domestic heating makes this area appropriate for studying the influence on ambient PCDD/Fs levels.

In a first study[2] during summer and winter 2002 particulate matter in air from the city-centre (Aleje) and an industrial area (Nova Huta) in Krakow were compared to a mountain resort without industry (Zakopane approximately 100 km south of Krakow), in order to visualize urban and industrial impacts. The air samples of summer and winter 2002 showed differences in the levels of Dioxin concentrations and also in Dioxin congener patterns. At Zakopane the Dioxin concentrations were low during summer with a Dioxin congener pattern typical for long range transport and remote areas[4]. During winter, the congener-pattern changed drastically and also the Dioxin-concentration rose about 40 times to the highest levels found at this study. Since there is no industry present at Zakopane, the use of hard-coal for domestic heating was assigned as the main source for the Dioxins in Zakopane air. The city centre of Krakow showed the same summer winter change: A rise of 20 times in concentrations and also similar fingerprints as Zakopane in winter, indicating that domestic heating with hard coal is the dominant emission source also in Krakow. Dioxin emissions from traffic and industry, which should be visible during summer as well, had only minor impact on the investigated sites in the center of Krakow. In contrast, Nova Huta showed no change between summer and winter. High concentrations were measured in summer and in winter and the fingerprint, which was different compared to Krakow and Zakopane, did not change. This indicated that Dioxins in Nova Huta air resulted from continuous industrial emissions close to the surface level from nearby located coke production and metal industries.

In the study reported here, additional air samples (this time particulate matter *and* gas phase) were collected during 2 weeks in winter 2005 from two sites in Krakow. To extend the study on the impact of emissions on environmental pollution in the region, a transect of soil samples (the sink of atmospheric bulk deposition) and biota (spruce needles as an indicator for the bio-availability of airborne PCDD/Fs) were taken between Krakow and Zakopane and from Krakow to the east.

Materials and Methods

In January/February 2005 air samples of about 200 m^3 per day were taken over a period of two weeks at two locations at Krakow. One at the northwest of Krakow under agricultural use (AGRI) and one near the city-centre with a high abundance of hard coal for domestic heating (POLI). Particle matter was collected on glass fiber filters, gas phase on polyurethane foam (PUF). In addition soil from grasslands (0-30 cm) and one year old spruce needles (picea abies) were collected at 17 locations from Krakow to Zakopane and from the city centre of Krakow to the east. The samples were stored at –18°C until sample preparation.

Samples were Soxhlet-extracted for 24h using n-hexane/acetone (220/30) except for the glass fiber filters where toluene was used. The applied methodology follows USEPA method 1613. Prior the extraction 16 carbon-13 isotope labeled internal standards were added (400 pg each, except OCDD with 800 pg). Extracts were evaporated to nearly dryness, refilled to 10 mL with n-hexane, and purified with an automated clean-up system (Fluid Management Systems, USA) operating with a silica/sulfuric acid-, a basic aluminia-, and a carbon-column[5]. The purification principle is described by Smith et al. (1984)[6]. Purified extracts were evaporated to nearly dryness using nitrogen (Turbovap, Zymark, USA) and filled up with 30 µL of toluene. Prior the injection, two C^{13}-labeled recovery standards were added.

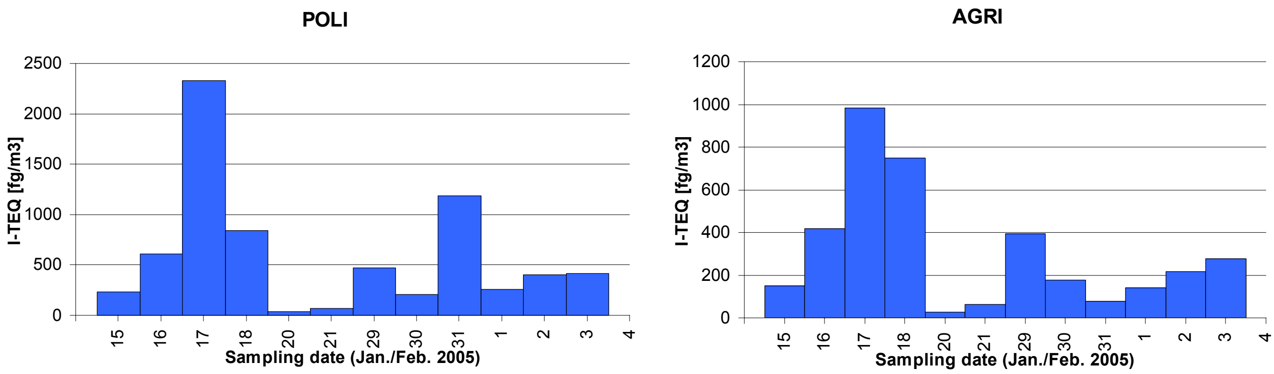
Quantification was done with a high resolution gas chromatograph (HRGC) (Hewlett-Packard/Agilent, Germany) with split/split less injection. Chromatographic column was a 60 m BPX-DXN (SGE, Australia) with 0.25 mm inner diameter and 25µm film thickness. The HRGC was coupled with a high resolution mass spectrometer (HRMS) (Autospec, Micromass/Waters, USA), working in the electron impact mode at 34 eV and with an average resolution of 10 000. For parent congener and corresponding labeled standards two ions each were registered. Quality assurance and quality control were done by determining laboratory blanks together with each batch of 15 samples, running reference samples in parallel[7] and calibrating the HRGC/HRMS with certified PCDD/F standard mixtures (CS from Welligton Laboratories, USA). All solvents (Sigma-Aldrich, Switzerland) and gas (Alphagaz, Italy) used were ultrapure grade suitable for PCDD/F analysis.

Results and Discussion

Ambient air samples (figure 1): Less then 1% of the PCDD/F-concentrations in air were detected in the gas phase, therefore the following discussion refers only to PCDD/F-concentrations in particulate matter.

The two weeks average PCDD/F levels in the city centre of Krakow (AGRI & POLI, figure 2) were of 307 and 589 fg/ I-TEQ m^3, respectively. Concentrations were in the range of those measured in Aleje during winter 2002/03 and the PCDD/F patterns were similar to the previous study. The daily concentrations varied considerably. In general, the PCDD/F levels near the center of Krakow (POLI) were about two times higher than those at the more western located AGRI.

Figure 1: Air sampling at POLI & AGRI during 2 weeks

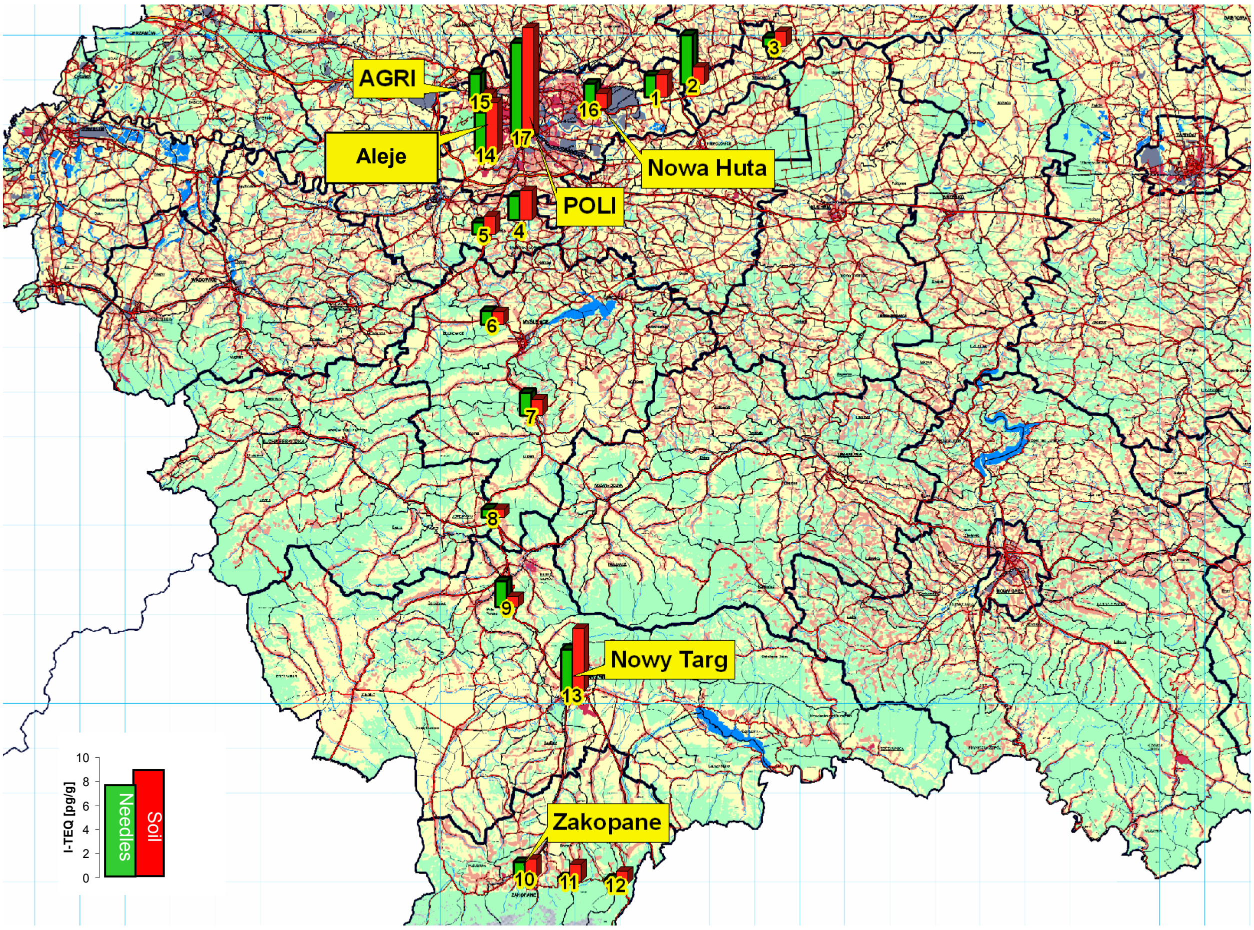


PCDD/F concentrations in soil from grasslands and spruce needles (figure 2): The highest concentrations were determined in the centre of Krakow at POLI (soil 9.0 and spruce-needles 7.8 pg I-TEQ / g dryweight). Along the transect east of the center, comparably low concentrations were measured although the locations are in the west wind zone of Krakow. Apparently the emissions from Krakow city (and Nova Huta) have only local impacts on the contamination of soil and biota.

Following the transect in the direction to Zakopane, concentrations in soil and spruce needles decreased first and rose again in Nowy Targ (soil 5.2 and spruce-needles 3.4 pg I-TEQ / g dryweight).

Nowy Targ is geographically located in a valley between Krakow and Zakopane, causing a kind of trap for atmospherically transported particles, which seems to lead to elevated deposition into soil and biota. Finally, the sampling locations around Zakopane showed relatively low levels in soil and biota, typical for rural areas in Europe[8].

Figure 2: PCDD/F-concentrations in soil and spruce needles



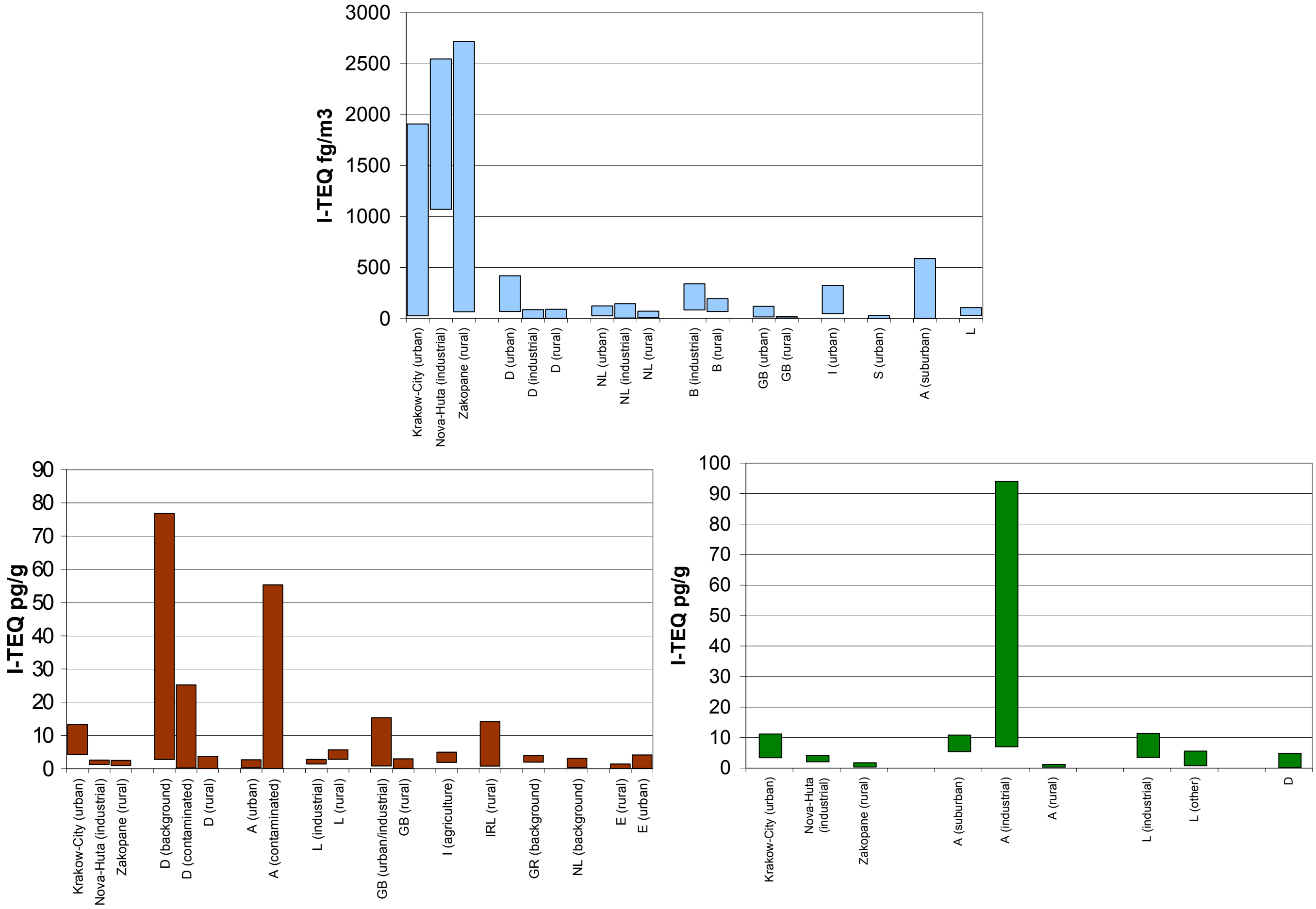
PCDD/Fs in air, soil and spruce needles in comparison to EU 15 (data from Fiedler 1999[8]) (figure 3): The range of PCDD/F concentrations measured in 2002 and 2005 in the air of Krakow/Malopolska region significantly exceeds the ranges reported for countries in Western Europe. In contrast, the PCDD/F-concentrations in soils from grassland and spruce-needles, showed similar or even lower values compared to other European countries.

Apparently and in slight contradiction, the high PCDD/F levels in ambient air in Krakow, Nova Huta and Zakopane did not result in equivalently high deposition rates into soil and biota of these sites.

A possible explanation is the existence of different emission characteristics when compared to Western Europe: Waste incinerators for example, one of the main sources of PCDD/F emissions in EU 15[3], have high chimneys, like most of the combustion facilities in Western Europe. Thus, PCDD/F emissions occur into a higher section of the air column (→ better mixing, dilution) when compared to the emissions from domestic heating, the main source in the case studied here, where PCDD/Fs are released near the ground due to the shorter chimneys.

This can result in a situation where the total PCDD/F amount present in the atmosphere of Krakow is similar to Western EU sites, although near ground levels are much higher. In such a situation, the wet and dry deposition of contaminated particulate matter (which affects the whole troposphere) into soil and biota, would be in the same range

Figure 3: Comparison of Dioxin Data (Air=blue; Soil=brown; Spruce-needles=green) from Krakow/Malopolska region with other European Countries.



Conclusions

The 2002 campaign on ambient air demonstrated a major role of domestic heating on the PCDD/F levels present in the ambient air of urban and especially rural areas where coal is used, but also diffuse release from industrial processes at Nova Huta may have an impact on a local scale.

Thus, the comparably high PCDD/F concentrations found in ambient air of Krakow/Malopolska region do not seem to result in enhanced PCDD/F deposition into the Malopolska ecosystem (the concentrations of PCDD/Fs in soil and spruce were comparable to data available from Western Europe).

The comparison of human breast milk data supports the hypothesis that the overall PCDD/F exposure in Poland does not exceed the EU average: A recent breast milk study from Poland[9] reports Dioxin levels of 12-13 pg TEQ /g fat, which is in the range found in other European countries with median TEQ-values between 6 and 18 pg/g fat[10].

These observations are in line with the findings of a study entitled "Environmental Levels and Human Exposure to Dioxins and PCBs in Candidate countries" released in 2004 as a joint initiative of the JRC and DG Environment which gave no indications of enhanced PCDD/F levels in the new MS[11].

Obviously, this does not mean that there is no problem with PCDD/Fs in ambient air at the sites investigated in this study. However, reduction measures targeted towards particulate matter will reduce at the same time the levels of PCDD/Fs originating from combustion, which have been shown to be predominantly particle bound.

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