PCDD/F in air and spruce needles in Bavarian and Bohemian Forest Mountains (Sumava)

Karl-Werner Schramm[1], Bernhard Henkelmann[1], Gert Jakobi[1], Jarmila Kotalik[1], Norbert Fischer[1], Manfred Kirchner[1]

[1]GSF-IEC

Introduction

Airborne contaminants can pose serious health threats to wildlife and humans. The contaminants of concern are compounds that are frequently called semi-volatile organic compounds or SOCs. This group contains a variety of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and the pesticide DDT. These chemicals are direct or indirect products of human activities and can be transported thousands of kilometres in the atmosphere. They can be deposited to aquatic or terrestrial ecosystems and then be re-emitted into the atmosphere. Because of their physical properties, some of these pollutants tend to accumulate, preferentially in colder areas of the globe. Investigations in the Alps (Weiss, 2000) and in the Rocky Mountains (Blais et al., 1998) showed higher concentrations of accumulating organic compounds at higher-altitude sites. This phenomenon has been termed “cold fractionation” and has been observed for PCB, HCH (hexachlorocyclohexanes), and PCDD/F (polychlorinated dibenzo-dioxins and –furans). Therefore, we assume that high-latitude and high-elevation ecosystems with their lower temperature regimes may have a greater risk of accumulation. The notable difference between cold trapping in high latitudes and high altitudes in the mid-latitude zone may be due to different amounts in precipitation (Daly & Wania, 2005).

The purpose of the current study is to clarify the load of organic compounds in the Bavarian and Bohemian Forest, which is located remote from Central and Northern Bohemian and Bavarian emission sources and scarcely influenced by local sources. By selecting sites at both sides of the German-Czech (Bavarian Forest and Sumava Mts.) trans-boundary perspectives are considered and barrier effects on both sides of the mountain crest should be detectable. We suppose that the extreme climate and the high surface roughness conspire to make the forested mountain crest become convergence zone for selected persistent organic chemicals (Daly & Wania, 2005). The monitoring programme, which lasts from 2004 to 2006, is performed by using active and abiotic and biotic passive sampling. In the present article the first results which are restricted to active measurements and the content of dioxins and furans (PCDD/F) in plant tissues, will be presented.

Materials and Methods

Sampling Locations: The four sampling sites are situated along the German-Czech border inside or near the two National Parks, which are on the Bavarian side the German National Park of Bavarian Forest and on the Bohemian side the Czech National Park of Sumava. The region is characterized by cold climate with a yearly temperature mean between 3 and 5 °C, high precipitation amounts (frequently up to 2000 mm per year along the mountain ridge) and long lasting snow covers of depths up to 300 cm; but, as reported for whole Central Europe, the summer of 2003 was characterized by extremely dry conditions. Compared to the lowlands there is a strong vertical gradient of precipitation combined with a sharp lee side effect in Sumava (Kirchner et al., 2001). Similarly to the precipitation rate there is a strong deposition increase of inorganic contaminants, like nitrate, ammonia and sulphate with height (Kirchner et al., 2001).

Abiotic and biotic passive sampling is performed at Mitterfels/Ödwies (1030 m a.s.l.), Rukowitzschachten (1130 m a.s.l.), Haidel (1160 m a.s.l.) and Boubin (1300 m a.s.l.); all sites are situated in more or less closed spruce stands. Additionally we conduct active measurements at Haidel site, where electricity power is available.

Active air sampling: Active air sampling encompassing particulate and gas phase as total is conducted by a DIGITEL blower DPA96; this low volume sampler has an operation range between 5 to 60 litres per minute and is able to separate several wind directions by switching over from one to another filter. For the sectors (N-W, N-E, S-E, S-W) and the calm situation (wind velocity < 0.5 m/s) we use correspondingly five XAD glass cartridges in combination with five back-up cartridges in order to avoid and check breakthrough of substances. Additionally to

wind direction and velocity other meteorological parameters like temperature, humidity and air pressure are monitored. All measurements are performed at a height of 3.5 m above ground in a forest spruce stand.

Passive sampling by spruce needles: Passive sampling is conducted by using ½, 1 ½ and 2 ½ years old needles collected from the 7th branch whorl of three well-exposed dominant spruce trees of 80-100 years. Conifers are well suited for investigations about pollutant levels because of their evergreen character and often long-lasting foliage. They make up a large hydrophobic surface in contact with air and may act as sink for airborne POPs. In ambient conditions re-volatilisation may be of minor extent.

Chemicals and Sample Preparation: For the active sampling Supelpak-2B (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), a purified form of Amberlite XAD-2, was used as adsorbent and 50 g of it was filled in each glass cartridge. All solvents used were of trace analysis quality and purchased from LGC Promochem (Wesel, Germany) as well as the silica, alumina and florisil adsorbents. All ^{13}C-labelled PCDD/F standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) or Wellington Laboratories (Guelph, Ontario, Canada).Before extraction the ^{13}C-labelled PCDD/F standards were added to the samples. The XAD glass cartridges were extracted in a Soxhlet apparatus for 24h with a mixture of acetone:n-hexane 3:1 as extraction solvent. The extraction procedure and cleanup of the spruce needles is described elsewhere (Niu et. al., 2003).The PCDD/F analysis was performed with a high resolution mass spectrometer Finnigan MAT 95S (Thermo Electron GmbH, Bremen, Germany) coupled with an Agilent GC 6890 (Agilent Technologies, Palo Alto, CA, USA).

Results

PCDD/F content in needles show concentration ranges of 10.5 – 15.5, 13.5 – 17.4 and 15.9 – 21.6 ng/kg d.w. for ½, 1 ½ and 2 ½ years old needles, respectively. For all singular homologues the highest concentrations could be found at Haidel and Boubin. In terms of toxic equivalents TEQ, the concentrations show the highest values for Haidel and the lowest at Mitterfels (Fig. 1); the relative portion of highly chlorinated PCDD/F is greater at Haidel than at the other sites.

PCDD/F concentrations in ambient air measured by low volume sampler for 4 periods are attributable to four wind direction sectors and to the situation with wind velocity lower than 0.5 m/s ('calm'); we observed great differences during the year with a marked concentration peak in late winter. The highest concentrations of more than 700 fg/m^3 PCDD/F could be measured during calm situations and with wind blowing from the sector N-W. Expressed by I-TEQ, which has been developed as an administrative tool and allows to convert quantitative analytical data for individual PCDD/F congeners into a single toxic equivalent (NATO/CCMS, 1988), the mean concentrations over the total monitoring period are higher during 2 of 4 periods. No evidence could be found that main emission centres are situated north of the monitoring site in the CR, although statistical proof is not reasonable on the basis of the data present.Taking in consideration the frequency range of the four wind direction sectors in the four periods (N-E: 1-10 %, S-E: 2-17 %, S-W: 23-33 %, N-W: 2-14 %, calm: 40-65%) we obtained overall mean concentrations of 2.0-9.0 fg-NATO-I-TEQ/m^3 (2.2-9.3 fg WHO-I-TEQ/m^3).

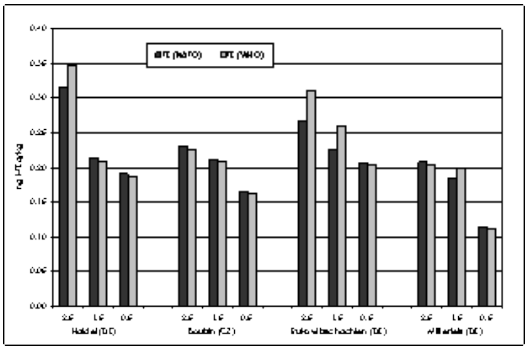

Fig. 1. Concentrations of PCDD/F in 0.5, 1.5 and 2.5 years old spruce needles (d.w.) in fg NATO/WHO-I-TEQ/m^3 at Haidel, Boubin, Rukowitzschachten and Mitterfels

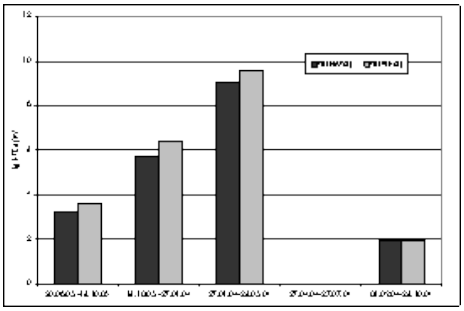

Fig. 2. Ambient air concentrations of PCDD/F in fg NATO/WHO-I-TEQ/m^3 at Haidel during 4 measuring intervals

Discussion

Toxic equivalents of the total amount of PCDD/F have been calculated in order to estimate the toxicity of a mixture of chlorinated dioxins and furans. Whereas the TEQ system is imperfect, it is a basically reasonable way to describe the total contamination; furthermore it facilitates comparisons to other results from literature.

The concentrations, which we found in the ½ year old needles are in the range of 0.11-0.19 ng/I-TEQ/kg d.w., are lower than the results from Köhler et al. (1994) for other sites in Bavaria situated closer to emission sources (0.53-1.12 ng/ I-TEQ/kg d.w.). Weiss (1998, 2002) found concentrations of 0.3 and 1.9 ng/I-TEQ/kg d.w. in Slovenia and Carinthia for the early 1990ies. Needle contents of spruces in more polluted sites of Sumava Mts. and Beskydy Mts. were about 2.75 and 14.3 ng/kg d.w., respectively (Holoubek et al., 1998). However, this may reflect the decrease of concentrations of PCDD/F in needles in the last decade.

As expected, the concentration levels of dioxins do not show great differences from site to site because all stands are subjected to the same climate zone and situated far from major sources. Nevertheless smaller effects due to local climate and additional nearby emissions, e.g. from by local combustion of wood, cannot be totally excluded. Different relative shares of highly chlorinated PCDD/F can give an indication of origin of the load. Comparing the four sites which are situated at similar elevations vertical gradients - as they have been measured in Tyrol and Carinthia (Austrian Alps) by Weiss (1998, 2002) - could not be expected. The results from the sites far from the central mountain ridge near the German-Czech border, particularly at Mitterfels, show lower concentrations. No explicit indication is given to higher overall contamination in Southern Bohemian region; however the ratio between furans and dioxins seems to be higher at Boubin (0.77-0.93) than at the three Bavarian sites (0.51-0.77). Such differences may be associated with different contaminations of PCB and their accompanying PCDF in both countries.

Former measurements performed by BGA/UBA (1993) in other rural areas of Germany show air concentrations of 25-70 fg I-TEQ/m^3. The lower concentration range at Haidel reflects on the one hand the negative trend in Central Europe and indicates on the other that the site is far remote from possible emission centres of Southern Bavaria, Northern Bohemia and Upper Austria, where mean air concentrations greater than 40 fg I-TEQ/m^3 have been found (Fiedler et al., 1997). Air concentrations of PCDD/F show a clear winter peak and thus appear to be related to residential wood and coal combustion in the local and regional surroundings. A similar concentration raise in winter months by a factor of 2 to 20 has been found in other rural sites of Eastern Bavaria (Franke & Knapp, 1996).

Acknowlegments

The authors wish to thank the Bavarian State Ministry for Environment, Health and Consumer Care (Project-No. 76a-8731.2 – 2000/1) for supporting the study, the Bavarian State Institute for Forestry for the valuable input to the work and the Deutsche Telekom for electrical power support at Haidel .

References

BGA/UBA, 1993. Dioxine und Furane – ihr Einfluss auf Umwelt und Gesundheit. Bundesgesundheitsblatt Sonderheft/93, 36. Jahrgang, Mai 1993.

Blais, J.M., Schindler D.W., Muir D.C.G., Kimpe L.W., Donald D.B., Rosenberg B., 1998. Accumulation of persistent organochlorine compounds in mountains in Western Canada. Nature 395, 585-588

Daly, G. L., Wania, F., 2005: Organic contaminants in mountains. Environmental Science and Technology 39,2, 385-398.

Fiedler, H., Sverev, M., Nordsieck, H., Dörr, G., Hutzinger, O., 1997. Long-term ambient air measurements of PCDD/F in Southern Germany (1993-1996). OrganohalogenCompd. 33, 93-98.

Franke, B., Knappe, F., 1996. Umweltvertäglichkeitsuntersuchung zur geplanten Thermischen Restmüllbehandlungsanlage (TRA) im ERZ Außenzell, ifeu.institut für Energie und Umweltforschung Heidelberg GmbH, im Auftrag der Abfallwirtschaftsgesellschaft Donau-Wald mbH.

Holoubek, I., Tříska, J., Cudlín, P., Čáslavský, J., Schramm, K.-W., Kettrup, A., Kohoutek, J., Čupr, P., Schneiderová, E., 1998.Project TOCOEN. The fate of selected organic pollutants in the environment. Part XXXI. The occurrence of POPs in high mountain ecosystems of the Czech Republic. Toxicol. Environ. Chem. 66, 17-25.

Kirchner, M., Leuchner, M., Braeutigam, S., Peichl, L., Hoppe, A., Kettrup, A., 2001. Depositionsmessungen im ostbayerischen Grenzgebirge. Materialien 160. Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen München.

Köhler J., Peichl L., Dumler R., Thoma H., Vierle O., 1994. Der PCDD/F -Gehalt in Fichtennadeln vor und nach der winterlichen Heizperiode. Ber. des LfU, München. Schriftenreihe Heft 126, 171-173

Kylin, H. and Sjödin, A., 2003. Accumulation of airborne hexachlorocyclohexanes and DDT in pine needles. Environ SciTechnol in press.

NATO/CCMS, 1988: International toxicity equivalence factor method of risk assessment for complex mixtures of dioxins and related compounds. Report Number 176, August 1988, NATO, Committee on Chalanges of Modern Socity.

Niu, J., Chen, J., Henkelmann, B., Quan, X., Yang, F., Kettrup, A., Schramm, K. -W., 2003. Photodegradation of PCDD/Fs adsorbed on spruce (Piceaabies (L.) Karst.) needlesundersunlightirradiation. Chemosphere 50, 1217 -1225.

Weiss, P., 1998. Persistente organische Schadstoffe in Hintergrund -Waldgebieten Österreichs. Monographien Band 97, Bundesministerium für Umwelt, Jugend und Familie.

Weiss P., 2000: Pflanzentoxische organische Schadstoffe und enzymatische Reaktionen in Fichten emittentenferner Waldstandorte Österreichs. Monographien Band 123, Bundesministerium für Umwelt, Jugend und Familie

Weiss, P., 2002. Organic pollutants at remote forest sites of Slovenia and Carinthia. Umweltbundesamt BE -195 Wien.