Dioxins and dioxin-like pollutants in alpine forests

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Abstract

Norway spruce forests in the alpine region characteristically contain between 0.13 and 6.07 ng kg^{-1} WHO toxic equivalents of PCDD/F + PCBs, depending on the investigated compartment (humus, mineral soil or 6 month old needles). Of these compartments, humus has by far the highest PCDD/F and PCB concentrations. Needles show the lowest PCDD/F levels while their PCB content is similar to that of mineral soil. At a subset of Austrian sites, the PCDD/F content of needles decreased by an order of magnitude between 1993 and 2004, the reduction in humus PCDD/F levels was much smaller. Significant longitudinal and latitudinal concentration differences where found among alpine regions, and pollutant levels were always highest in one of the peripheral regions. This supports the assumption that the Alps bar the long-range transport of airborne pollutants.

Abbreviations / glossary: PCDD/F…polychlorinated dioxins and furans, PCBs…polychlorinated biphenyls, SOCs…semivolatile organic compounds, LOD…value below detection limit, sum indicator PCB…sum of PCB congeners 28, 52, 101, 138, 153, 180, TEQ_{WHO}…WHO toxic equivalents, d. m.…oven (105 °C) dry mass, n. d.…not detectable (value below analytical detection limit)

Introduction

Forest ecosystems are an important sink for semivolatile organic compounds (SOCs).[1] In the Alps, like in other mountainous regions, forests are a dominating type of ecosystem. With increasing altitude, higher precipitation and windspeed together with lower temperatures can be expected to enhance the deposition of airborne SOCs.[2] Aerodynamic roughness and chemical affinity (waxy needle surface) of the mostly coniferous canopy promote the aerial contamination of mountain forests. Slow litter decomposition and infrequent biomass harvest support SOCs accumulation in the ground. Estimated pools of various SOCs in Austrian forests exceeded the concurrent nationwide emissions by several orders of magnitude.[3,4] Large scale models investigate the role of the Alps as a sink for SOCs.[5] Stretching across Central Europe, the Alps are surrounded by regions of significant industrial or agricultural production with comparably dense population. Despite local industry, traffic and domestic activities, the jagged topology of the alpine range provides a sufficient number of sites that qualify as "remote", i. e. essentially affected by long-range SOCs transport only. Project "MONARPOP" investigates such remote forest sites to clarify the role of the Alps as a sink for SOCs.[6] Humus, mineral soil and needle samples from 40 sites, including seven height profiles, reveal spatial and altitudinal immission patterns. The present paper summarizes first results for PCDD/F and PCB.

Materials and Methods

Site selection: samples were taken from "remote" locations, i. e. by carefully excluding any predictable significant influence from local sources. Samples were taken from forest stands with at least 80% (stem count) Norway spruce (*Picea abies* [L.] Karst.) at a standard altitude of 1400 m a. s. l.

Sampling: (i) Needles: 3–5 branches were cut from the top 7th whirl of two dominant adult trees between late September and October 2004. Six months old twigs of the current year were collected, pooled, transferred to the

lab in airtight glass jars and stored at –20 °C until further processing. (ii) Humus: samples were taken at the 2 x 5 points of a rectangular sampling grid with 1 m spacing. At each point, the entire humus layer within a 0.09 m^2 square was collected in airtight glass jars, transferred to the lab and stored at –20 °C. (iii) Mineral soil: after removing all humus down to the mineral soil surface, 10 cm mineral soil cores were extracted from each pit, transported and stored like the humus samples (supplementary information about sites and sampling at http://www.monarpop.at).

Preprocessing: (i) Needles: twigs were defoliated mechanically after immersion into liquid nitrogen, needles were immediately filled into airtight and light-protected glassware and stored at –20 °C. All manipulations from the opening of the transport jars until transfer of the loose needles were done in inert atmosphere. Needles were transferred to the analysing lab at –50 °C (dry ice). (ii) Humus samples were lyophilised, pooled per site and ground (under cooling) to < 0.5 mm particle size. (iii) Mineral soil samples were lyophilised, pooled per site and sieved. The particle fraction < 2 mm was used for analysis.

Clean-up and detection of PCDD/F and PCB were conducted by the Umweltbundesamt (Austrian Environment Agency) as follows: All samples were spiked with ^{13}C-isotopes of the analysed compounds before Soxhlet (needles, humus) or ASE (mineral soil) extraction with toluene. The clean-up continued with sulphuric acid treatment on Celite, multilayer silica column and alumina column extraction, the latter also separating PCB from PCDD/F. ^{13}C-standards were then added for recovery calculation. **Detection**: PCDD/F and PCB were measured with a high resolution mass spectrometer coupled to a gas chromatograph with a cool injection system. PCDD/F were analysed with a J&W (Agilent Technologies) DB5 column and a DBDIOXIN column, PCBs with a DB5ms column. Mass spectrometry operated in single ion mode at a mass resolution of 8000–10000. Identification and quantification was done by isotope dilution according to EPA 1613. Table 1 lists the detection limits (LOD).

Table 1: Analytical detection limit (median, 95th percentile) for different compounds and matrices.

unit: ng kg $^{-1}$ d. m	PCDD	PCDF	dioxinlike PCB
needles	0.03 (0.06)	0.02 (0.05)	0.69 (2.5)
humus	0.08 (0.15)	0.08 (0.17)	0.70 (2.4)
mineral soil	0.05 (0.12)	0.05 (0.14)	0.28 (0.94)

Data analysis:
Statistics were calculated with any values below the analytical detection limit replaced with zero. Sites were grouped geographically (longitudinal: west, middle, east; latitudinal: north, centre, south: Figure 1). Differences among longitudinal or latitudinal groups were tested with Kruskal-Wallis' comparison of rank sums at a significance level of $\alpha \leq 0.05$. Spatial pollution patterns were visualised by colour-coding concentrations according to the five categories commonly depicted by boxplots (four quartiles, outliers; Figure 2).

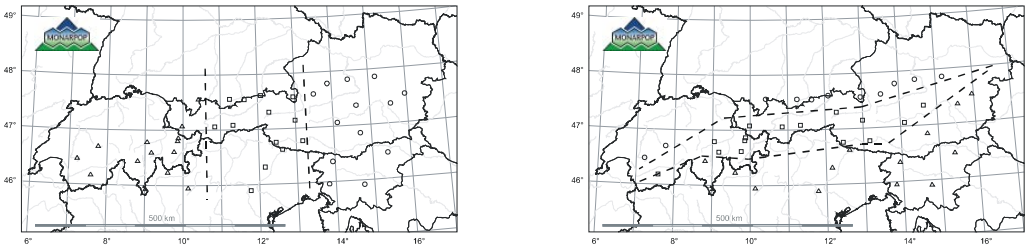

Figure 1: Longitudinal and latitudinal site grouping

Results and Discussion
The concentrations of PCDD/F and PCB increase from the needles to the humus layer and decrease from the humus layer to the mineral soil beneath (Table 2–Table 4). In needles, dioxinlike PCB constitute ten times as many toxic equivalents as PCDD/F (Table 2), whereas both pollutant classes contribute similarly to humus TEQ_{WHO} levels (Table 3), and PCDD/F clearly dominate total TEQ concentration in mineral soil (Table 4). At the investigated sites, humus and, after decomposition, the organic mineral soil fraction origin mainly from the same source, i. e. needle litter. Hence, the PCDD/F share of total TEQ in the forest ecosystem obviously increases with

the investigated compartment's age. For herbivors (insects, game), PCB represent the more important TEQ source in conifer needles.

Table 2: PCDD/F and PCB content of Norway spruce needles.

unit: ng kg^{-1} d. m.	**Min**	**P_{25}**	**Median**	**Mean**	**P_{75}**	**Max**
PCDD/F	n. d.	1.25	2.14	3.36	4.64	10.72
sum PCDD/F in TEQ_{WHO}	n. d.	n. d.	0.01	0.03	0.04	0.17
sum indicator PCB	394	652	815	910	1062	2370
sum dioxinlike PCB	56.1	92.3	111.6	127.8	134.7	362.0
sum dioxinlike PCB in TEQ_{WHO}	0.01	0.03	0.11	0.13	0.16	0.87
sum PCDD/F and PCB in TEQ_{WHO}	0.01	0.07	0.13	0.16	0.21	0.98

sample size n=40; Min…minimum, $P_{25\,/\,75}$…25^{th} / 75^{th} percentile, Max…maximum, n. d.…not detectable

Table 3: PCDD/F and PCB content of forest humus.

unit: ng kg^{-1} d. m.	**Min**	**P_{25}**	**Median**	**Mean**	**P_{75}**	**Max**
PCDD/F	115.7	155.8	262.3	313.8	404.6	758
sum PCDD/F in TEQ_{WHO}	1.37	2.55	3.70	4.44	5.21	10.81
sum indicator PCB	3160	5005	7670	8301	11040	17220
sum dioxinlike PCB	439	1067	1482	1591	1985	3266
sum dioxinlike PCB in TEQ_{WHO}	0.70	1.51	2.06	2.32	3.01	4.92
sum PCDD/F and PCB in TEQ_{WHO}	2.12	4.09	6.07	6.76	8.11	14.16

sample size n=31; Min…minimum, $P_{25\,/\,75}$…25^{th} / 75^{th} percentile, Max…maximum

Table 4: PCDD/F and PCB content of 0–10 cm forest mineral soil.

unit: ng kg^{-1} d. m.	**Min**	**P_{25}**	**Median**	**Mean**	**P_{75}**	**Max**
PCDD/F	17.6	74.8	131.2	207.6	252.8	625.9
sum PCDD/F in TEQ_{WHO}	0.14	0.84	2.01	3.20	3.96	10.15
sum indicator PCB	109	496	747	1135	1447	4012
sum dioxinlike PCB	21.25	97.98	122.05	218.56	297.98	831.4
sum dioxinlike PCB in TEQ_{WHO}	0.01	0.14	0.23	0.41	0.57	1.55
sum PCDD/F and PCB in TEQ_{WHO}	0.15	0.98	2.24	3.61	4.52	11.70

sample size n=20; Min…minimum, $P_{25\,/\,75}$…25^{th} / 75^{th} percentile, Max…maximum

Several needle and humus PCDD/F and PCB concentrations differ significantly between site clusters. The northern fringe (Figure 1) of the Alps shows significantly higher concentrations in the humus layer than the central and/or southern sections. Particularly needle concentrations of the central sites were often lower than in the North or South (Figure 2 gives an example). In addition, the western and eastern section of the study area tended to have more polluted needles than the middle region (Figure 2). Single PCBs, however, showed a west-eastern decrease of needle and humus concentrations. The peripheral regions of the Alps with their higher precipitation thus seem to receive notably more pollutants than the more shielded regions in the centre. Apart from the quantitative differences, PCDD/F and PCB composition varies in a way that seems to be affected by the physico-chemical properties of the single homologues/congeners (not shown). The results indicate that the Alps are a barrier for long-range pollutant transport.

Needle PCDD/F concentrations at six Austrian sites were significantly lower in 2004 than in 1993 [7] (Figure 3). The corresponding differences of humus concentrations were not so pronounced, probably due to a slower response of this compartment to abating atmospheric concentrations.

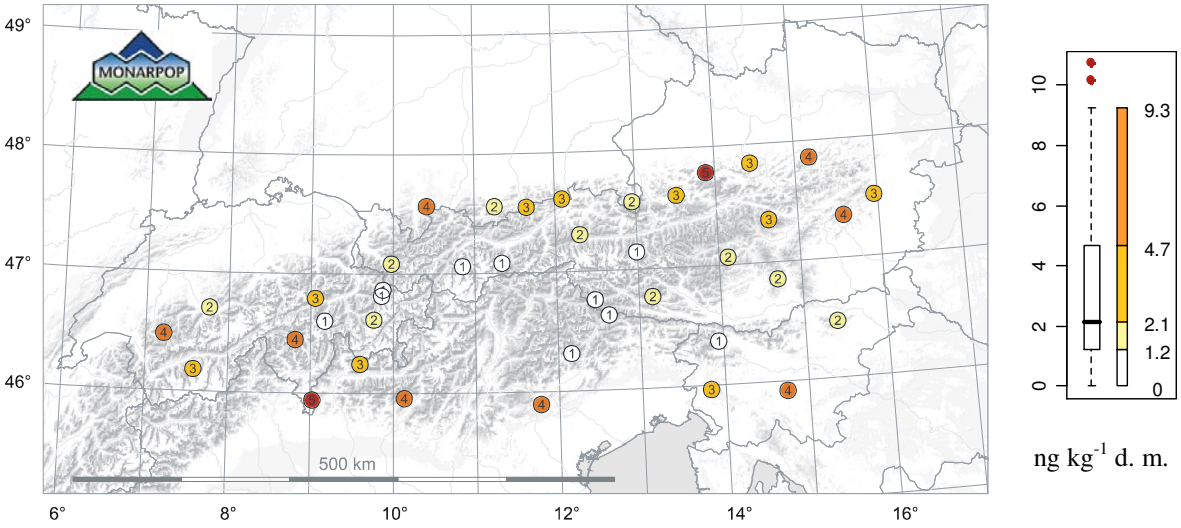

Figure 2: Total PCDD/F content (ng kg^{-1} d. m.) of six month old Norway spruce needles from alpine forest sites. Classes 1–5 correspond to quartiles and outliers in the boxplot (1: lowest quartile, 5: outliers).

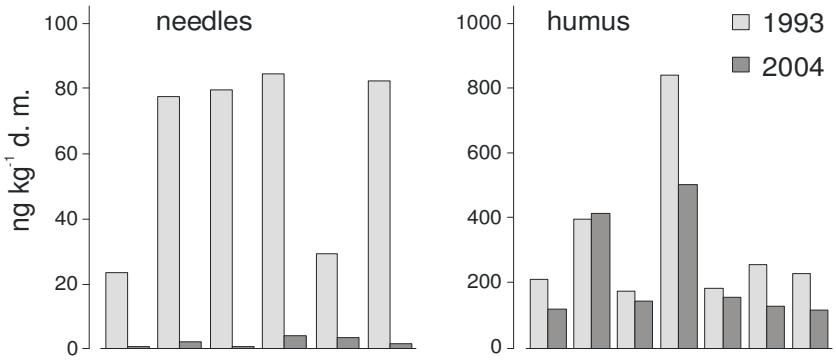

Figure 3: PCDD/F concentrations in compartments of alpine spruce forests (needle age: six months; 1993 data given in [7]).

Acknowledgements

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