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PCDD/F in Spruce Needles and Soils of Background Forest Sites in Austria

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Abstract

One year old spruce needles of 25 investigated Austrian background forest sites showed PCDD/F-concentrations between 14.3 and 167.9 ng/kg (median 39.5 ng/kg) and between 0.3 and 1.9 ng ITEQ/kg (median 0.7 ng ITEQ/kg) respectively. The range of PCDD/F in the raw humus of these sites was 106 to 2,676 ng/kg (median 319 ng/kg) and 1.6 to 31.0 ng ITEQ/kg (median 4.0 ng ITEQ/kg). These values cover the expectable range and correspond to the ones of comparable investigations in other Central European countries. The more polluted sites of this investigation show concentrations that reach magnitudes which are known from sites close to conurbations and PCDD/F sources. It could be proved that the group of sites north of the Central Alps showed significantly higher concentrations in the humus layer than the group of the southern sites. This indicates that the total PCDD/F input in this region over the last years was comparably higher.

Introduction

Needles of Norway spruce are good indicators of atmospheric pollution with lipophilic organic pollutants and are therefore often used for such investigations (1-6). Comparison of PCDD/F concentrations and PCDD/F content per hectare in forest soils and in adjacent agricultural or grassland soils reveal higher values for the forest soils (7, 8). The reasons for this are - as with other pollutants - the filtering of pollutants by the forest canopy, no annual harvesting of biomass in the forests and the preferential sorption of organic pollutants to the organic substance in the soil, which is comparably higher in forest soils (9, 10). In comparison to agricultural soils forest soils are nearly undisturbed. This is why spruce needles, the raw humus and the underlying mineral soil of 25 Austrian background forest sites were investigated for their concentrations of PCDD/F, namely to get an idea of the ubiquitous pollution with these substances in Austria.

Methods

In October 1993 one, two and three year old needles of Norway spruce were taken at 25 background forest sites. In August of the same year at the same sites samples of raw humus and the mineral soil layers 0-5 cm and 5-10 cm were taken. All sites were in big distance to settlements, factories and public roads. All forests were stocked to one hundred per cent with Norway spruce. We chose such sites to guarantee that the raw humus of all sites has the same source material.

The spruce needles were taken in the range of the seventh branch whorl from the top and from all wind directions of two predominant or dominant trees (within the light crown). By separating the twigs according to their needle ages mixed samples were made. All the sampled trees were within the forest to

LEVELS IN THE ENVIRONMENT

avoid possible edge-effects. By standardizing the sampling method in that way we tried to reach the best possible comparability of the individual concentrations (11).

10 samples of each, raw humus and the underlying mineral soil layers 0-5 cm and 5-10 cm were taken at random along a rectangle of 25 x 5 m and according to the individual layers mixed to samples. All samples were taken with defined volume (30x30 cm raw humus, Ø 7 cm mineral soil layers).

During transport samples were kept cool and in the dark and were stored at -20 °C until analysis. The needles were separated of the twigs in liquid nitrogen and as the humus and soil samples freeze-dried. The needle concentrations represent the whole needles and the raw humus concentrations represent the whole homogenized raw humus without living roots and stones. The mineral soil was sieved to the fraction < 2mm. During these steps of work the needed masses for calculations of mass balances were defined. For calculating the concentrations on a dry weight basis a portion of each sample was dried at 105 °C. All concentrations given in this paper are on a dry weight basis of 105 °C.

The chemical analysis was done by the isotope-delution-method with ¹³C-marked surrogates for all 17 congeners with toxic equivalents. Freeze-dried samples - soxhlet-extraction - two to three steps of liquid column-chromatographic cleaning, measuring with HRGC/HRMS (MID) using two different GC-columns, quantification by isotope-delution-method. The detection limits were 0,08 ng/kg for the tetra- to hexachlorinated congeners, 0,10 ng/kg for the heptachlorinated isomers and 0,25 ng/kg for the OCDD/F. In this paper the results for the needles representing one growing period and for the raw humus are presented.

PCDD/F concentrations in the spruce needles

The concentrations between 14.3 and 167.9 ng/kg (median 39.5 ng/kg) and between 0.3 and 1.9 ng ITEQ/kg (median 0.7 ng ITEQ/kg) are within the expected range and are similar to those found by comparable investigations in background areas (Table 1). The PCDD/F concentrations in the needles of

Table 1) PCDD/F in one year old spruce needles of Austrian background-forests and values of comparable investigations

PCDD/F	median n=24	range n=24	mean n=24	background (literature)	(ind.) conurbation (literature)	close to sources (literature)
ng/kg	39.5	14.3-167.9	52.2	58.3 ⁵	196.3 ⁶ 82.6 ⁷	4180 ³ 250 ⁴
ng ITEQ/kg	0.6	0.3-1.9	0.7	0.44 ¹ 0.18-1.21 ¹ 0.44 ² 0.14-1.10 ²		
ng TE(BGA) /kg	0.9	0.4-1.8	0.8	1.2 ⁵	4.5 ⁶ 1.8 ⁷	75 ³ 8.8 ⁸

¹ Bavaria/Germany (n=26), October 1992, median and range, (4, 5)

² Bavaria/Germany (n=15), October 1993, median and range, (4)

³ close to a copper reclamation plant, Brixlegg/A (n=1), (6)

⁴ close to Brenner highway/A (n=1), (6)

⁵ background area near Passau/Germany, mean (sampling period December!, n=10), (2)

⁶ ind. conurbation Nürnberg/Germany, mean (sampling period December!, n=10), (2)

⁷ small conurbation Schwandorf/Germany with waste incineration plant and coal-fired power station, mean (sampling period December!, n=10), (2)

⁸ Nürnberg centre, maximum value of ⁵ (sampling period December!), (2)

Dioxin '97, Indianapolis, Indiana, USA

the more polluted background sites reach magnitudes which are known to be typical for conurbations. This is accurate for the concentrations in ng/kg. The concentrations in toxic equivalents are clearly higher in conurbations. The reason for this is that spruce needles close to conurbations have higher contents of low chlorinated PCDD/F with higher toxic equivalent factors than the ones of background areas. Needles which were taken close to known PCDD/F sources show much higher concentrations (Table 1).

In general the measured PCDD/F values in background areas confirm the long-range transport of PCDD/F in background areas and the ubiquitous pollution with these substances. The needle concentrations representing the PCDD/F pollution during the growing period of 1993 do not indicate a more polluted region in Austria during this period of time. Sites showing concentrations above the median can be found in all of Austria (Figure 1). No statistically significant differences were found between the concentrations of the groups of northern and southern sites, eastern and western sites and the groups representing several regions.

The results for the sites 11, 12 and 13 of an altitude gradient revealed higher PCDD/F concentrations in the needles of the highest site 13 (Figure 1). The homologue profiles of this site indicated that the source for the higher concentration was very far away as compared to the ones of the low-lying sites 11 and 12 (12).

PCDD/F concentrations in the raw humus

The concentrations of the raw humus represent the whole PCDD/F input of several years by dry and wet deposition and litterfall. This is one of the reasons why the mean concentrations are about ten times higher compared to the ones of the needles.

Again the ranges between 106 and 2,676 ng/kg (median 319 ng/kg) and 1.6 and 31.0 ng ITEQ/kg (median 4.0 ng ITEQ/kg) respectively represent magnitudes which are comparable to the ones of other Central European investigations. In background areas of this region PCDD/F pollution of raw humus is much higher than for example in background areas of the Amazonas basin (Table 2). The more polluted background sites in Austria showed concentrations which are comparable to the ones found close to conurbations and even close to known PCDD/F sources (Table 2). The total PCDD/F concentration of the highest polluted background site 1 (Figure 2) has about the same magnitude as the raw humus of a site on an exposed slope to a conurbation and a sintering plant. Even in terms of toxic equivalents this background site has a concentration which is still half of the one close to the sintering plant. This is a clear indication of the general impact of long-range transport for the pollution with PCDD/F.

The comparison of Figure 1 and Figure 2 reveals that the sites with higher concentrations in the needles rarely have higher concentrations in the raw humus, too. This result is confirmed by correlation analyses. There are no significant correlations between any PCDD/F in the needles and in the raw humus. There are many possible reasons for this result. Both compartments have different indications. The concentration of raw humus represents total PCDD/F input for several years, while the PCDD/F concentration in the needles represents the atmospheric PCDD/F concentration during the growing period of 1993. Maybe the PCDD/F pollution during this year was different to the one in the years before. The fact that the winter period and associated PCDD/F emissions from domestic heating or different input conditions during this time are not considered in the needle concentrations could be reasons for this discrepancy, too.

The PCDD/F concentrations of the raw humus were different in several regions. The group of the sites 1-5 in the Mühl- and Waldviertel in the north of Austria were significantly higher polluted than the group of sites 21-25 representing the region in the south-east of Austria. The group of sites north of the Central Alps (sites 1-16, 18) had significantly higher concentrations than the group of the southern ones (Figures 2, 3). This result indicates that the PCDD/F-input into the north of Austria was significantly higher during the last years. Investigations of the input and the pollution with other pollutants (sulfur- and

LEVELS IN THE ENVIRONMENT

Figure 1) PCDD/F in one year old spruce needles of Austrian background forests

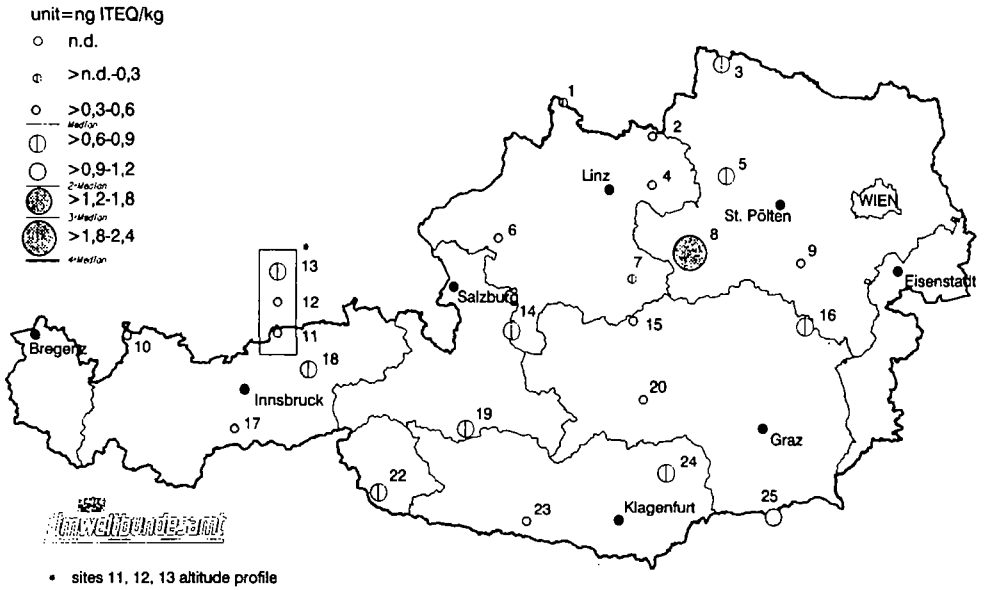
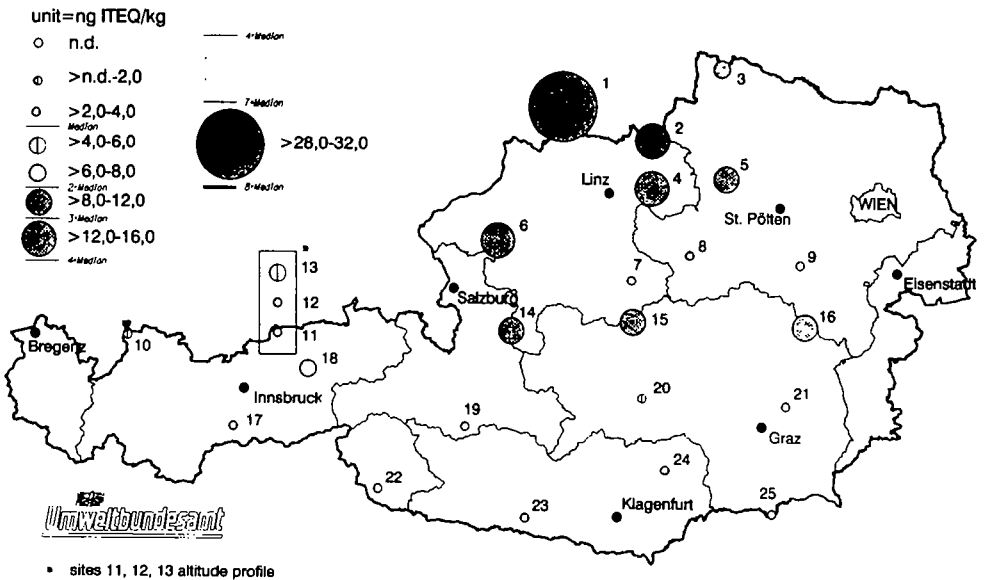


Figure 2) PCDD/F in the raw humus of Austrian background forests



Dioxin '97, Indianapolis, Indiana, USA

nitrogen-compounds) revealed similar results and show that long-range transboundary air pollution is an important reason for the higher pollution of Austrian regions north of the Alps (13, 14). We assume that this holds true for the PCDD/F, too. This is confirmed by the high PCDD/F concentrations of sites 1-3 in the north of Austria, a region which has very little industry and only small settlements. The main wind direction in this region is from the north-west (Figure 2).

Between the groups of eastern sites and western sites and the groups of sites at more than 1,000 m and those at less than 1,000 m above sea-level there were no significant differences in the concentration of the raw humus. But again the highest site 13 of the investigated altitude gradient showed higher PCDD/F concentrations in the raw humus than the sites 11 and 12 at lower altitudes (Figure 2), (12).

Table 2) PCDD/F in the raw humus of Austrian background forest sites and values of comparable investigations

PCDD/F	median n=25	range n=25	mean n=25	background (literature)	(ind.) conurbation (literature)	close to sources (literature)
ng/kg	319	106-2,676	525	792 ¹		2,363 ⁶
ng ITEQ/kg	4.0	1.6-31.0	6.9	16 ¹ 12-27 ¹ (8.8) ² (n.d.-38) ² 23 ⁹ 1-54 ⁹ 12.0 ⁷ 0.02-0.1 ⁸	(10) ³ (n.d.-50) ³	(37) ⁴ (21-139) ⁴ (3.7) ⁵ (3.9) ⁵ 63.5 ⁶

¹ Baden-Württemberg/Germany, median and range 25-percentile to 75-percentile (n=18), (8)

² Bavaria/Germany, median and range (n=20), raw humus without litter!, (15)

³ Bavaria/Germany, median and range (n=32), raw humus without litter!, (15)

⁴ Bavaria/Germany, close to possible PCDD/F sources, median and range (n=7), raw humus without litter!, (15)

⁵ Bavaria/Germany, close to waste incineration plants (n=1), raw humus without litter!, (15)

⁶ industrial conurbation Linz/A, slope exposed to steelworks and sintering plant (n=1), (16)

⁷ 10 km north of Linz/A (n=1), (16)

⁸ Amazonas basin, range (n=15), (17)

⁹ Brandenburg/Germany, median and range (n=16), (18)

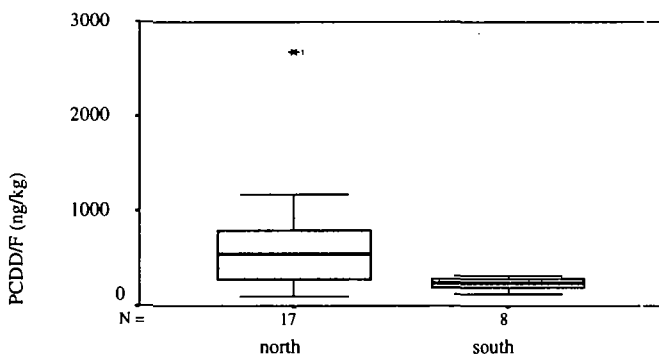


Figure 3) PCDD/F in the raw humus of sites north of the Central Alps and sites in the south of Austria

LEVELS IN THE ENVIRONMENT

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