Semivolatile organic compounds in spruce needles and forest soil of Austrian background forest sites

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Introduction

Known to accumulate lipophilic organic compounds, tree foliage has been widely used as a bioindicator [1-11]. To achieve results which allow a comparison of the detected concentrations in the sense of identification of different environmental loads, careful planning of applied methodologies and sampling is necessary [12,13]. Forest soil represents a main sink for semivolatile organic compounds and has therefore been included in soil monitoring programmes for semivolatile organic compounds [14-16]. Both spruce needles and forest soil have therefore been investigated at background forest sites for their concentrations of various semivolatile organic pollutants to get an idea of the load with such compounds in remote areas of Austria.

Methods

25 background forest sites from all over Austria and located far away from settlements, factories and public roads were investigated. Since velocities of litter decomposition and different humus properties varying with the tree composition of forests influence detectable concentrations, only sites that were stocked to 100 % by Norway spruce (*Picea abies* Karst.) were chosen. Spruce needles (1st needle age class taken in October) and the whole humus layer (L-, O_f-, O_h-layers) were investigated. Detailed information on site characteristics, sampling and sample preparation is given in [17].

Chemical analysis:
PCB, HCH, HCB, DDX: Extraction with n-hexane, cleaning with florisil-column, measuring with GC-ECD using two capillar-columns with different polarity. The results were confirmed by mass-spectrometry, detection limit: 0.2 µg/kg per isomer.
PCP: Soxhlet-extraction with acetone/hexane under acidic conditions, cleaning by liquid-liquid extraction, derivation with acetanhydride, cleaning with silicagel, measuring with GC/MS, detection limit: 1 µg/kg.
PAH: Soxhlet-Extraction with n-hexane and cleaning with PAH-SOIL-solid phase and sephadex, measuring with HPLC with fluorescence- and photodiode array-detection, detection limits: 0.25-10.5 µg/kg (depending on the substance).

Results and Discussion

The magnitudes of concentrations detected in spruce needles and humus layer are similar to those reported from other European remote areas (table 1, overview in [17]). Similar findings have been shown for PCDD/F in a previous paper [18]. Differences in the overall pollution with all investigated semivolatile organic compounds due to location of the sites have been revealed by cluster analysis. Especially the group of sites in the region north of the Danube (north-east of Austria) showed a pollutant pattern ("fingerprint") indicating a higher load if all semivolatile organic compounds together were taken into consideration. For individual compounds this was not always the case. The results of an altitude profile as well as homologue-specific calculations for the PCDD/F in the needles showed higher concentrations in high alpine areas compared to sites below [17,19]. As the sites north of the Danube do not belong to the Alps the clearly higher pollution of this area is further confirmed.

Some results for the individual compounds:

PCB: In addition to the PCBs listed in table 1 the coplanar congeners PCB 77, PCB 81, PCB 126 and PCB 169 were analysed. Due to the analytical procedure these congeners were below detection limit at nearly all sites. However, a calculation of the toxic equivalents for the detected concentrations of coplanar PCBs according to the new WHO TE-factors [20] and a comparison to the PCDD/F TE-concentrations of the same samples [18] indicates that a several times higher toxic equivalent load in soil of background areas is attributable to PCB, as compared to PCDD/F. These results clearly show that the current PCB load plays probably a more important role than the current PCDD/F load.

HCH: The HCH concentration in the needles is at nearly all sites higher than the corresponding HCH concentration in the humus layer (table 1). This result has been obtained for the more volatile PCB- and PAH-congeners and HCB, too, and is discussed in [21]. The sites north of the Central Alps and in the eastern half of Austria showed significantly higher needle concentrations than the corresponding other parts of Austria (figure 1). The group of sites with a lower α-HCH/γ-HCH ratio in the needles indicating less distant or more recent lindane uses [8,22-25] had significantly higher HCH concentrations in the needles. The results for the humus layer are the other way round (figure 2). The reasons for this difference remain unknown, but we assume that differences in indication between needles and humus layer might play a role [26].

HCB: The HCB concentrations are clearly lower than those of lindane (table 1). Especially the sites in the north-eastern part as well as in the eastern half of Austria showed a significantly higher HCB load (figure 1). On account of the location of the more polluted sites and main wind directions it is assumed that higher HCB concentrations are partly attributable to transboundary air pollution [26].

PCP: Most samples were below the detection limit of 1.0 µg/kg. However, the few results above detection limit and results in literature [6,10,15] might indicate that current PCP concentrations in the investigated compartments of Austrian background areas are similar to those of HCB. It is noteworthy that the use of HCB, PCP and DDT as pesticides was banned in Austria several years ago.

DDX: The DDX concentration in the humus layer was dominated by p,p'-DDT (about 50% of DDX), o,p'-DDT (20 %) and p,p'-DDE (25%). However, regional differences were identified. The sites of the regions north of the Danube and in the far south of Austria with higher DDX concentrations in the humus layer had significantly lower p,p'-DDT/p,p'-DDE ratios than the sites in the Central Alps. A lower p,p'-DDT/p,p'-DDE ratio is seen as an indication of more distant or less recent DDT uses [24,25,27].

PAH: All sites with above-average concentrations in the humus layer are north of the Central Alps. Besides, the eastern half of Austria showed significantly higher concentrations in the humus layer than the western half (figure 3). This indicates a comparably higher PAH input in these regions. The relative PAH patterns in the humus layer were very similar for all sites and showed – compared to the needles – higher shares of more lipophilic and less volatile PAH [21]. Higher PAH concentrations in the needles were associated with higher shares of chrysene and benzo(b)fluoranthene, which might be attributed to influences of combustion and pyrolysis of coal [28].

Table 1: Semivolatile organic compounds in spruce needles (1^{st} needle age class taken in October) and humus layer of Austrian background forest sites in µg/kg dw

	Spruce needles (n=24)		humus layer (n=25)	
	Median	range	median	range
PCB (Σ of PCB 28, 52, 101, 138, 153, 180)	0.2	n.d.-0.4	3.3	0.2-7.5
HCH (Σ of α, β, γ, δ, ε)	6.4	2.7-9.7	3.3	0.6-6.6
lindane	5.1	2.0-7.9	2.2	0.6-3.4
HCB	0.6	0.3-1.1	0.5	n.d.-1.9
PCP	n.d.	<2.0	n.d.	n.d.-2.1
DDX (Σ of p,p'- and o,p'-DDT, -DDD, -DDE)	0.2	n.d.-2.4	7.8	n.d.-22.0
PAH (Σ of 16 EPA-PAH without naphthalene)	48	28-412	210	68-1342

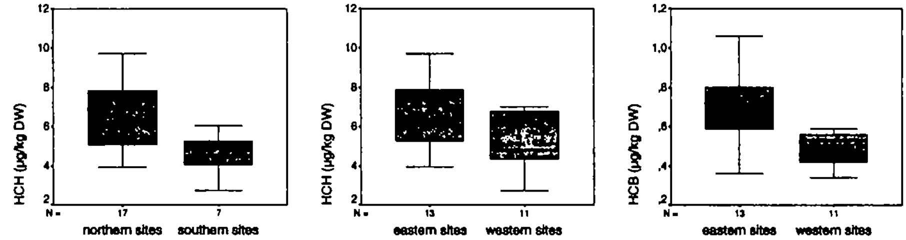

Figure 1: Significant regional differences of HCH and HCB concentrations in spruce needles

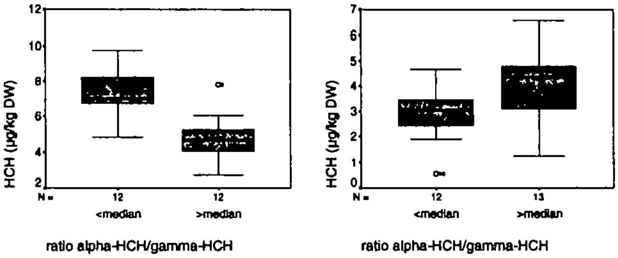

Figure 2: HCH concentration in the spruce needles (left) and humus layer (right) separated into groups of sites with a α-HCH/γ-HCH ratio lower and higher than median of these ratios for spruce needles (0.23) and humus layer (0.44), respectively

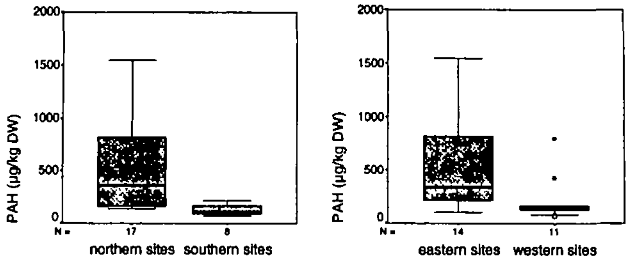

Figure 3: Significant regional differences of PAH concentrations (sum of all 18 investigated PAH) in the humus layer

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