

SEMIVOLATILE ORGANIC COMPOUNDS AT REMOTE FOREST SITES OF SLOVENIA AND CARINTHIA

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Introduction

Previous investigations gave evidence that several semivolatile organic compounds (SOCs) with problematic environmental properties are ubiquitously detectable even at remote forest sites of the Alps¹. The results for an altitude profile in the northern limestone Alps² showed higher concentrations of accumulating organic compounds at the higher-altitude site. The present study represents a continuation of these monitoring activities and provides results on the recent load with semivolatile organic compounds of international concern at remote forest sites of the south-eastern Alps.

Methods and Materials

Nine Slovenian and Carinthian forest sites located remote from emission sources were selected (Figure 1). At all sites Norway spruce needles of the 1st needle age class (½-year old) and at five of these sites the complete humus layer were sampled in October 2000. In addition, an altitude profile located in the border region between Slovenia and Carinthia (Koralpe) was set up where Norway spruce needles of the 1st age class at five sites, needles of the 2nd age class (1½-year old) and the humus layers at three sites of different altitudes were taken. The samples were analysed for the following compounds: polychlorinated dibenzodioxins and -furans (PCDD/F), polychlorinated biphenyls (PCB), hexachlorobenzene (HCB), hexachlorocyclohexans (HCH), DDT plus metabolites (DDX), aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, chlordecone, pentachlorophenol (PCP), polybrominated diphenylethers (PBDE) and polycyclic aromatic hydrocarbons (PAH). A detailed description of the methods is given in ^{1,3}.

Results and Discussion

The results of the present study give evidence of a continued load with semivolatile organic compounds at remote forest sites of the Alps. Particularly remarkable is the continued detection of pesticides that have not been used in Austria and neighbouring countries for many years (e.g. DDT, aldrin, dieldrin). Some results for the individual compounds are as follows (Table 1):

PCDD/F: The humus layer concentrations, which are an indication of the total long-term input of PCDD/F by dry and wet deposition and litterfall, did not give evidence of any major decrease in the PCDD/F load of this compartment. The recent concentration range is similar to the one measured in the 1993 humus layer samples from southern Austria¹.

PCB: The needle concentrations for the six frequently investigated PCB ("PCB6") were the only exception in that the concentrations in the recent study were higher than in the previous one¹. The

range of humus layer concentrations was similar to the one of the previous study. A common observation of the PCDD/F and PCB based on the toxic equivalent concentrations for both groups of compounds suggests that the current ubiquitous PCB load in terrestrial ecosystems should receive equal attention as the current PCDD/F load (Table 1).

Table 1: Medians and concentration ranges (in brackets) of semivolatile organic compounds in spruce needles of the 1st age class (N1, ½-year old) and in the humus layer (O) from the Slovenian and Carinthian sites. From the sites of the altitude profile (Figure 1) only the site located at mean altitude was included. (PCB6: sum of IUPAC no 28, 52, 101, 138, 153, 180; TE-PCB: sum of all PCB with TEQ-factors; HCH: sum of α -, β -, γ -, δ -isomeres; PAH: sum of 15 PAH – all EPA-PAH except naphthalene; all concentrations are based on dry weight)

		N1 (n = 9)	O (n = 5)
PCDD/F	ng/kg	8.5 (2.8 – 16.9)	222 (144 – 628)
	ng ITEQ/kg	0.10 (0.03 – 0.23)	2.7 (1.5 – 8.8)
	ng TEQ-WHO/kg	0.10 (0.03 – 0.23)	2.9 (1.7 – 9.3)
PCB6	$\mu\text{g}/\text{kg}$	1.2 (0.2 – 2.0)	4.5 (2.9 – 8.1)
TE-PCB	$\mu\text{g}/\text{kg}$	0.23 (0.18 – 0.28)	1.71 (0.51 – 3.30)
	ng TEQ-WHO/kg	0.21 (0.19 – 0.27)	2.4 (0.8 – 5.4)
HCB	$\mu\text{g}/\text{kg}$	0.6 (0.5 – 0.9)	0.8 (0.6 – 1.9)
HCH		1.7 (1.1 – 2.5)	2.7 (1.9 – 4.1)
DDX		0.3 (n.n. – 0.7)	4.9 (3.1 – 12.7)
Aldrin		(<0.1)	0.7 (<0.1 – 1.4)
Dieldrin		(<0.3)	1.5 (0.3 – 1.5)
Endrin		(<0.3)	(<0.3)
cis-Chlordan		<0.1 (<0.1 – 0.1)	0.1 (0.1 – 0.2)
trans-Chlordan		<0.1 (<0.1 – 0.4)	<0.1 (<0.1 – 0.2)
Heptachlor		(<0.1)	<0.1 (<0.1 – 0.1)
Mirex		<0.1 (<0.1 – 0.3)	<0.1 (<0.1 – 0.3)
Chlordecon		(<0.1)	<0.1 (<0.1 – 0.1)
PCP		<0.4 (<0.4 – 0.5)	<0.4 (<0.4 – 0.5)
PAH		19 (13 – 107)	85 (56 – 144)

HCB: The HCB concentration ranges in the needles and humus layers are similar to the ones of the previous investigation of needles and humus layers¹.

HCH: The HCH needle concentrations are clearly lower than in a previous investigation¹, which fits in with the decreasing use and actual ban of lindane in Austria. The HCH concentration ranges in the humus layer of the present study were similar to those of the humus layers sampled in 1993.

DDX: A comparison with data from previous investigations suggests that the DDX humus layer concentrations decreased during the last years. The results for the needles do not allow such an assumption.

Other chloropesticides: In most needle samples the pesticides aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, chlordecone and pentachlorophenol were below the detection limits. Single concentrations above the detection limits were up to 0.5 µg/kg. In the humus layer almost all of these compounds were detectable in single or in several samples (Table 1).

PBDE: Only in some humus layer samples single PBDE (PBDE 47, PBDE 99, PBDE 155) were above the detection limit (> 0.3 µg/kg). It is assumed that the recent PBDE concentration ranges which are ubiquitously detectable at remote terrestrial ecosystems lie between those for the PCDD/F and PCB.

PAH: The concentration ranges in the needles and humus layer samples were similar to those detected in southern Austria for the year 1993¹. Therefore, no evidence can be given for any substantial decrease in the PAH load of remote areas in the investigated region.



Figure 1: Location of the investigated sites

Regional differences: Almost no regional differences in the concentrations were identified. The concentration ranges for the Slovenian sites were similar to the ones for the Carinthian sites. Only site 7 in the south-west of Slovenia (Figure 1) showed higher concentrations in the humus layer for most compounds. It is known that this part of Slovenia has a higher annual precipitation and higher inputs of sulphur and nitrogen compounds which originate from long-range transport from the Italian industrial regions and the Po valley⁴. The higher precipitation and the barrier effects may also be responsible for the higher concentrations of SOCs in the humus layer of this site.

Altitudinal differences: The results for the altitude profile Koralpe confirm previous findings which show a tendency of higher concentrations at higher-altitude sites². For almost all investigated compounds (particularly the pesticides), the highest concentrations were found at the highest-altitude site of the Koralpe profile (examples in Figure 2). The changes of pollutant patterns with different altitudes suggest different reasons and origins for the detected concentrations at the individual sites of the altitude profile.

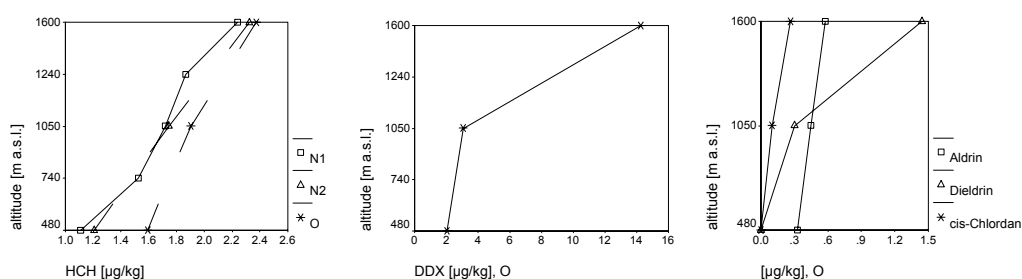


Figure 2: Chloropesticides in the spruce needles (N1: 1/2-year old, N2: 1 1/2-year old) and in the humus layer (O) of the altitude profile Koralpe

Like in the previous investigation of remote forest sites¹, several compounds are positively correlated. Remote forest sites with a higher load are always contaminated with a complex mix of several organic compounds from different sources. This aspect should receive particular attention, because nothing is known about the possible effects of a mixture of these compounds (synergies, additive effects etc.).

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