SEMIVOLATILE ORGANIC COMPOUNDS IN NEEDLES OF NORWAY SPRUCE FROM AN URBAN-INDUSTRIAL ENVIRONMENT

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Abbreviations: EPA-PAH…15 of the 16 "priority pollutant" PAH (except naphthalene), non-TE-PCB…polychlorinated biphenyls without TE-factors, TE-PCB…coplanar and mono-ortho-substituted PCB with TE-factors, PCDD/F…polychlorinated dibenzo(para)dioxins /–furans, PCP…pentachlorophenol, PAH…polycyclic aromatic hydrocarbons

Introduction

Conifer needles are particularly suitable for the bioindication of atmospheric organic pollutants. Norway spruce, chosen for this study, is a frequently employed indicator species in Europe. In 1996, needle conditions were monitored in and around the Austrian city of Linz. In addition to the urban agglomerate (200.000 inhabitants), Linz harbours the largest Austrian steel works which, together with a number of chemical plants, occupy an area of intense industrial activity. Anatomical and chemical needle analyses included needle surface characteristics, nutrients, heavy metals, stress-related enzyme activities and semivolatile organic compounds (SOCs), the latter of which are subject of this article.

Methods and Materials

Norway spruce (*Picea abies* [L.] Karst.) needles ($1/2$-year and $1\frac{1}{2}$-year old) were sampled at 18 sites which were considered representative for the area under the immediate influence of urban and industrial emissions (Figure 1). Sampling period: Oct. 2nd – Oct. 4th, 1996. Samples were prepared as described earlier[1]. Chemical analysis included six non-TE-PCB (IUPAC no^s. 28, 52, 101, 138, 153, 180), PCDD/F, PCP, and PAH as reported elsewhere[1]. Additionally, the TE-PCB (IUPAC no^s. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) were determined with the isotope-dilution method and GC/HRMS. Uni- and multivariate statistical analysis was performed with SPSS Version 11.0.1 (SPSS Inc., Illinois, U.S.A).

Results and Discussion

Table 1 shows descriptives of SOC concentrations in needles of both age classes. Comparison with needle contents of Norway spruce growing at remote sites (i) throughout Austria[1] and (ii) in a combined Austrian / Slovenian monitoring region[2] shows that the investigated SOCs reached higher concentrations in the urban/industrial agglomerate of Linz. The PCDD/F concentrations were several times higher than those from remote Slovenian and Carinthian sites[2]. The PCDD / PCDF ratio (sample median) was near unity (1.16 and 0.96 in younger/older needles), indicating nearby sources rather than long-distance atmospheric influx[3]. The sum of non-TE-PCB was 3–18 times that of remote regions, and TE-PCB concentrations were almost sixfold increased (absolute values and TEQ WHO). Needle PCP content was below the quantification limit at most sites but reached peak values of 1.5–1.9 µg kg^{-1} which are 3–4 times higher than concentrations at remote sites. PAH concentrations were 4–10 times as high as values found in remote Austrian or Slovenian regions. The most abundant PAH were fluoranthene, phenanthrene, chrysene and pyrene. For the sum of PCDD/F (expressed in TEQ WHO), PCB (absolute values and TEQ WHO) and PAH, the highest concentrations were detected for sites which are close to the industrial area.

The highest absolute PCDD/F concentration in ½-year old needles was detected for a peripheral site. Except the highest PCP value at another peripheral site, elevated PCP concentrations occurred at locations close to the industry and the city center. PCP was used as a pesticide in Austria, but has been banned several years ago. Its spatial distribution and the presence of higher concentrations in the study area is therefore remarkable.

All PAH reached higher levels in the younger needles. For eight PAH species, the difference was significant ($\alpha \leq 0.05$). Likewise, the sum of TE-PCB as well as most of its member congeners attained significantly higher concentrations in the younger needles. PCDD- and PCDD/F-sums were also lower (though not significantly) in the preceding year's needles, while total PCDF-content was slightly higher (by median) in the older needles. As opposed to the majority of analysed SOCs, levels of all non-TE-PCB were increased in the older needles (for congener no. 28 this difference was significant). Needle contents of TE-PCB generated higher toxic equivalent-concentrations (TEQ WHO for humans / mammals) than those of PCDD/F combined.

Upon multivariate analysis, the accumulation patterns of some SOCs exhibited spatial differences which were related to differences in the physico-chemical properties of the substances.

(i) In both needle age classes, approx. 78% of the variation of the concentrations of individual PAH was reproducible by two principal components. The respective factor loadings depended on size (ring count), lipophilicity (octanol/water partition coefficient K_{OW}), and volatility (vapour pressure p_S) of the respective PAH species. Moreover, the factor values of the sampling sites showed contrasting spatial distributions. Close to the city center and the industrial territory, needles scored high at the first factor which had high loadings of the large, less volatile PAH with a high K_{OW} (Figure 2). The complementary second factor (high-loading PAH have few rings, higher p_S, lower K_{OW}) increased towards the periphery and hillscape around the city.

(ii) Cluster analysis, based on the PCB-pattern (congeners' fractions of total PCB content) of the older needles resulted in a central and a peripheral site cluster. The PCB-pattern of samples from the central cluster had higher than average (all sites) amounts of the PCB congeners no. 138, 153, 180 and no. 118, 123, 126, 156, 157, 167, 189, all of which are higher chlorinated compounds and have higher octanol-air partition coefficients (K_{OA}). Those sites forming the peripheral cluster were dominated by the tri- to pentachlorinated biphenyls with lower vapour pressures (p_S). Clustering of needle PCB-patterns of the current year's needles was equally consistent concerning the cluster-specific prevalence of chlorination and K_{OA}, but not in a spatial context – sites with alternating affiliation were interspersed throughout the study area.

The manifestation of pronounced zonal gradients in the older needles may be influenced by a temperature-dependend phenomenon: fractionation of gaseous PCB by deposition-revolatilisation cycles has repeatedly been reported[4,5]. The average temperature for the period Dec. 95–Feb. 96 fell from ca. -1.2 to ca. -3.2 °C with increasing distance from the city center and altitude (location in the peripheral hills). Similar isothermes existed for the temperature sums (May – Oct. 96). The occurrence of the most volatile congener (no. 28) in the older needles agreed with the temperature trend, reaching highest concentrations in the colder zones.

Table 1: Concentration ranges (based on needle dry mass) of various organic compounds in spruce needles

	unit	yr	n	median	min	max	mean	s.d.
∑ PCDD/F	[ng / kg]	1	17	45.42	21.16	90.62	49.46	19.07
		2	11	45.75	18.30	79.46	46.97	17.74
	ITEQ [ng TEQ/ kg]	1	17	0.74	0.28	1.72	0.75	0.38
		2	11	0.94	0.27	2.43	1.08	0.56
	TEQ WHO [ng TEQ/ kg]	1	17	0.75	0.27	1.87	0.78	0.41
		2	11	1.01	0.29	2.54	1.13	0.57
∑ non-TE-PCB	[µg / kg]	1	17	3.62	1.89	12.49	4.55	3.25
		2	11	6.62	4.71	13.43	8.55	3.18
∑ TE-PCB	[µg / kg]	1	18	1.29	.78	4.16	1.82	1.15
		2	11	1.01	.64	1.42	.97	.27
	TEQ WHO [ng TEQ/ kg]	1	18	1.16	0.74	8.91	1.71	1.87
		2	11	1.18	0.70	2.55	1.29	0.49
∑ EPA-PAH *)	[µg / kg]	1	18	197.1	126.6	1511	282.5	313.0
		2	11	161.3	99.77	963.5	236.9	244.9
PCP	[µg / kg]	1	18	0.5	<0.5	1.9		
		2	11	0.5	0.5	3.0		

yr…needle age class (1 = ½-year old, 2 = 1½-year old), n = sample size, s.d.…standard deviation,
ITEQ…international toxic equivalents, TEQ WHO…WHO toxic equivalents for humans/mammals,
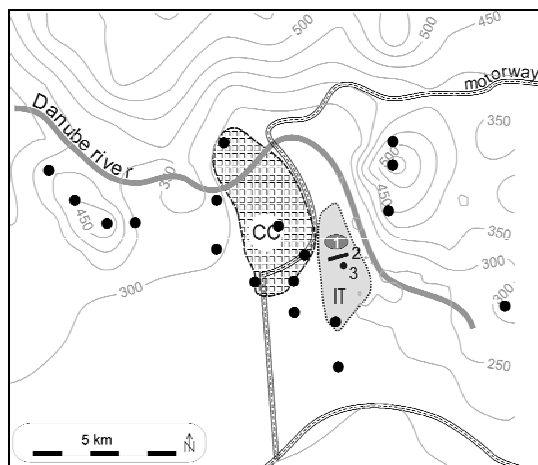(*) without naphthalene

Figure 1 (left): Map of the study area, showing location and area of the densely populated city center (CC), the industrial territory (IT), (1) a cluster of chemical plants, (2) a battery of coke-ovens, (3) the flue of the ore sintering unit, two highly frequented motorways and (●) the points where needle samples were collected. Grey isohypses show relief structure (increments of 50 m a.s.l, labels oriented uphill).
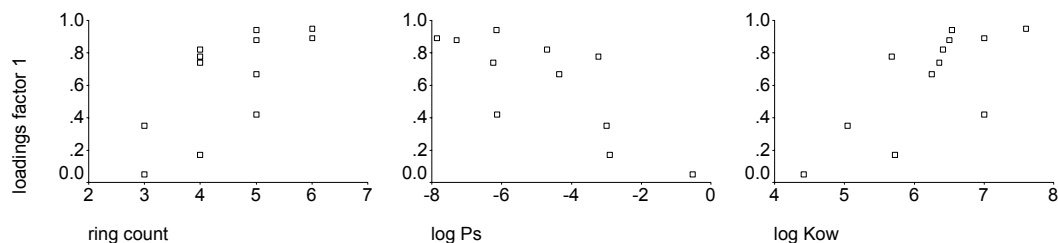
Figure 2: Factor loadings of 12 PAH found in ½-year old spruce needles, and their association with some physico-chemical parameters of the PAH. This factor attained its highest values in and near the urban center and the industrial territory.

(iii) Examination of the PCDD/F homologue patterns in the older needles yielded two clusters. One of them was dominated by the highly (hepta- and octo-)chlorinated compounds, the other by less substituted homologues, with hexachlorinated dibenzofuranes contributing most to the discrimination of clusters. The demarcation of the clusters roughly coincided with the main wind direction (WNW) and suggested a spatial connection with flue gases of the steel smelter's sintering unit. PCDD/F patterns in the younger needles, however, lacked consistency regarding spatial distribution and homologue composition of the derived clusters. This finding resembles the situation found for PCB.

Apart from possible temperature effects mentioned above, the regional partitioning of PAH and PCB congeners points at a distance-dependent separation between particle-bound and gaseous compounds. Compounds associated to particles prevail in the vicinity of the city center and heavy industry. This corresponds to large PAH with high K_{OW}[6,7] and PCB with a high degree of chlorination[8,9]. Compounds which are mainly present in the atmospheric gas phase make a higher contribution to PAH- or PCB-patterns at peripheral sites, indicating that these substances cover longer distances from their presumable source.

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