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Distribution of Persistent Organochlorine Compounds in One-Year and Two-Year-Old Pine Needles

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides belong to a group of persistent organic pollutants. They have been found all over the abiotic and biotic environment. In air, part of PCBs and organochlorine pesticides adsorb on the surfaces of airborne particles and another part occurs in the gaseous phase.

Vegetation is used in many studies as an indicator of a site pollution (Blais et al. 2003; Di Guardo et al. 2003; Hellström et al. 2004). Leaves are covered with wax which acts as a passive sampler for lipophilic compounds from the surrounding air. Pine needles are probably the most studied vegetation species in this respect, due to their worldwide distribution and high lipid content, which effectively accumulates lipophilic compounds. Needles can be used to monitor atmospheric pollution on global, regional and local scales. It has been suggested that it should be possible to infer differences in atmospheric concentrations through differences in vegetation concentrations (Blais et al. 2003; Di Guardo et al. 2003). Pollutant uptake depends on many factors such as plant species, temperature and physico–chemical properties of compounds. When surveying an area, intraspecies comparison is important because different plant species accumulate pollutants differently (Ockenden et al. 1998). Furthermore, coniferous trees can have one- and two-year-old needles on the same branch. It is likely that needles of different age have different pollutant concentrations. This can confound data interpretation.

The aim of this study was to investigate the distribution of organochlorine pesticides and PCBs in pine needles and to evaluate differences in one- and two-year-old needles.

MATERIALS AND METHODS

Nineteen pine needle samples were collected in urban and semiurban areas across Croatia during January-March 1998. Branches were collected at approximately 1.5 m above the ground level, and one-year-old needles were separated from the two-year-old from the same branch. Needles were dried at room temperature to constant weight and then analyzed.

The following organochlorine compounds were measured: HCB (hexachlorobenzene), α-,β-,γ-HCH (alpha-, beta-, gamma-hexachlorocyclohexane),

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DDE (1,1-dichloro-2,2-di(4-chlorophenyl)ethene), DDD (1,1-dichloro-2,2-di(4-chlorophenyl)ethane, DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane and seventeen PCB congeners (PCB-28, PCB-52, PCB-60, PCB-74, PCB-101, PCB-105, PCB-114, PCB-118, PCB-123, PCB-138, PCB-153, PCB-156, PCB-157, PCB-167, PCB-170, PCB-180, PCB-189; numbered according to IUPAC).

Organochlorine compounds were extracted from dried and ground needles (15 g) using dichloromethane. Due to the complex composition of wax, multistage cleanup was required. Waxes were repeatedly precipitated by cooling. The cleanup of extracts was continued by saponification under alkaline conditions and by adsorption chromatography on a multilayer silica column (containing silica gel with sulphuric acid and silica gel with sodium hydroxide). Purified extracts were evaporated and polychlorinated biphenyls and organochlorine pesticides determined using a "UNICAM" 610 SERIES gas chromatograph with a ^{63}Ni electron capture detector. The method has been described in full by Herceg Romanić and Krauthacker (2004).
Two capillary columns were used: 1) 60 m × 0.25 mm, SPB-5 film thickness 0.25 μm, temp. program 100 °C, then 4 °C min^{-1} to 240 °C, 50 min isothermally and 2) 30 m × 0.25 mm, SPB-1701 film thickness 0.25 μm, temp. program 110 °C, then 4 °C min^{-1} to 240 °C, 50 min isothermally. Carrier gas was nitrogen. The injector temperature was 250 °C and the detector temperature 270 °C. Qualitative and quantitative analyses were done by comparison with external standards. Each sample was analysed on both columns. Only compounds identified on both columns were evaluated. The determination limit was 0.03 ng g^{-1} dry needles for each compound.

RESULTS AND DISCUSSION

Table 1 shows the concentration ranges and the percentage of positive samples. Organochlorine pesticides and indicator PCBs (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-180) were measured in 19 pairs of one- and two-year-old needle samples, while 11 other PCB congeners were measured in 14 pairs of samples.
HCB, γ-HCH, DDE, PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 and PCB-118 were found in all one- and two-year-old needle samples. The ranges of compounds are wider in the two-year-old needle samples than in one-year-old needles. Organochlorine pesticides and indicator PCBs concentration ranges overlap while the ranges of the remaining PCB congeners are lower than the organochlorine pesticides and indicator PCBs. The concentration of organochlorine pesticides ranged between 0 (below determination limit) and 4 ng g^{-1} in one-year-old needles and between 0.05 and 10.4 ng g^{-1} in two-year-old needles. The concentration of indicator PCBs in one-year-old needles ranged between 0 (below determination limit) and 5.83 ng g^{-1} and between 0.15 and 9.91 ng g^{-1} in two-year-old needles. The remaining PCB congeners ranged between 0 (below determination limit) and 1.49 ng g^{-1} in one-year-old needles and between 0 and 2.49 ng g^{-1} in two-year-old needles.

Table 1. Concentration range (ng g^{-1} dry needles) and incidence of organochlorine compounds expressed as the percentage of positive samples in one- and two-year-old needles.

Compound	ONE-YEAR-OLD NEEDLES		TWO-YEAR-OLD NEEDLES	
	Range	%	Range	%
	Organochlorine pesticides (N=19)			
HCB	0.24-1.38	100	0.14-2.81	100
α-HCH	0-1.06	95	0.05-2.62	100
β-HCH	0-2.28	89	0.13-5.54	100
γ-HCH	0.06-4.00	100	0.22-10.40	100
DDE	0.22-2.40	100	0.24-3.70	100
DDD	0-0.73	63	0.15-0.78	100
DDT	0-2.89	84	0.12-7.57	100
	Indicator PCBs (N=19)			
PCB-28	0.51-4.23	100	0.89-8.17	100
PCB-52	0.27-5.83	100	0.32-9.91	100
PCB-101	0.13-3.57	100	0.87-5.20	100
PCB-138	0.33-2.88	100	0.58-3.48	100
PCB-153	0.21-1.92	100	0.39-2.16	100
PCB-180	0-0.46	95	0.15-1.15	100
	Other PCB congeners (N=14)			
PCB-60	0-0.58	86	0-0.92	93
PCB-74	0-1.27	71	0-2.53	79
PCB-105	0-0.39	86	0.16-0.86	100
PCB-114	0-0.87	43	0-0.66	57
PCB-118	0.17-1.46	100	0.32-2.58	100
PCB-123	0-1.49	79	0.45-2.49	100
PCB-156	0-0.23	21	0-0.36	57
PCB-157	0-0.39	7	0	0
PCB-167	0-0.42	14	0-0.1	14
PCB-170	0-0.75	64	0-0.46	86
PCB-189	0-0.4	7	0-0.23	7

N – number of samples; 0 – below determination limit

Figures 1 and 2 show the concentration medians of organochlorine pesticides, indicator PCBs and other PCB congeners in one- and two-year-old needle samples. The incidence of 3 PCB congeners (PCB-157, PCB-167, PCB-189) was below 50% in all samples and they are not shown in Figure 2. Also, the incidences and the medians of all compounds are higher in two-year-old needles. In all needles medians follow the same order: organochlorine pesticides - γ-HCH>DDE>HCB> β-HCH>α-HCH>DDT>DDD; indicator PCBs - PCB-28>PCB-101>PCB-138> PCB-52>PCB-153>PCB-180; other PCB congeners – PCB-118, PCB-123>PCB-60> PCB-74>PCB-105>PCB-170. The medians of the remaining PCB congeners are 0 with the exception of PCB-156 and PCB-114, whose medians in two-year-old needles are higher than 0.

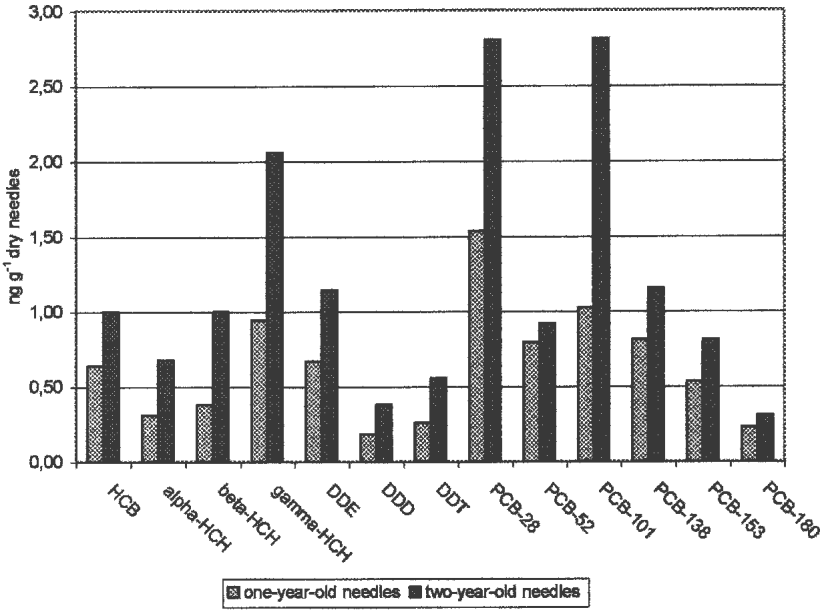

Figure 1. Median concentrations of organochlorine pesticides and indicator PCBs in one- and two-year-old needle samples.

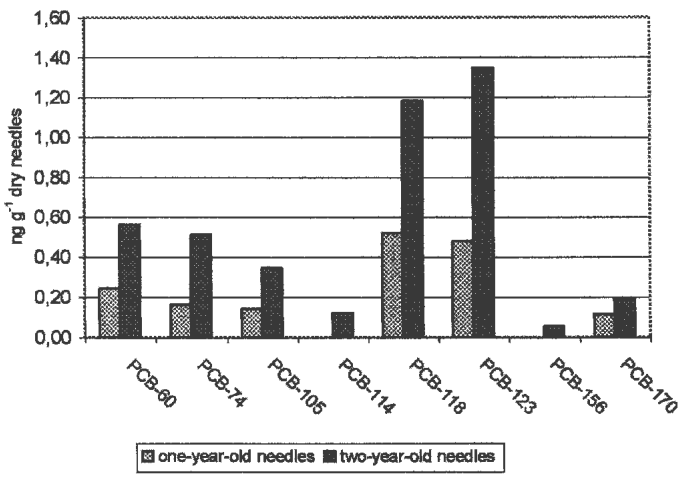

Figure 2. Median concentrations of eight PCB congeners in one- and two-year-old needle samples.

Our results suggest that the patterns of organochlorine compounds in one- and two-year-old needles are similar, but the levels of organochlorine compounds in two-year-old needles are higher due to longer exposure to air pollution. Also, our results suggest that over the two years, air pollution was the same because the same patterns of organochlorine compounds were found in two generations of needles.
As published before (Herceg Romanić and Krauthacker 2004), levels of PCBs and OCPs in samples of pine needles collected in urban and semi-urban sites in Croatia could be characterized as typical for urban areas and no sampling site with high or low levels of all analysed compounds was observed. The distribution of PCBs and OCPs is not influenced by the differences in climate, but rather by the long-range transport (DDT) and the proximity of pollution sources (lindane).
However, a comparison with published regional (or global) data is sometimes difficult because samples are not of the same age. It is therefore necessary to collect samples of the same age, to be able to make a reliable comparison of coniferous burdens between sites. An alternative could be a comparison of the compound pattern.

The levels of mono-*ortho* PCB congeners (PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189) were calculated as toxic equivalents (TEQ) which, in turn, were calculated using the toxic equivalency factors (TEFs) recommended by the World Health Organization (WHO) (Ahlborg et al. 1994). The greatest contribution to TEQs is by PCB congeners which are most often detected: PCB-105, PCB-118 and PCB-123. TEQ in one-year-old needles ranged between 0 and 0.5 pg WHO-TEQ g^{-1} dry needles and the median was 0.2 pg WHO-TEQ g^{-1} dry needles, while in two-year-old needles TEQ ranged between 0.2 and 0.8 pg WHO-TEQ g^{-1} dry needles and the median was 0.4 pg WHO-TEQ g^{-1} dry needles.

There are not many published data about non-*ortho* and mono-*ortho* PCB congeners but they overlap with our findings. Weiss et al. (2000) investigated PCB-77, PCB-126 and PCB-169 in spruce needles, but their levels were below detection limit. In Osaka, Japan, levels of PCB-77, PCB-126 and PCB-169 in pine needles collected in 1995 ranged between 2.28 and 115 pg g^{-1}, 0.12 and 42 pg g^{-1}, and 0.8 and 9.44 pg g^{-1} respectively. When expressed as TEQs, these levels ranged between 0.04 and 5.4 pg TEQ g^{-1} (the TEF model was not mentioned) (Aozasa et al. 1996). Mono-*ortho* PCBs were detected in pine needles collected in Germany in 1989 at two rural locations. The respective ranges of PCB-118, PCB-156 and PCB-170 were 0.6-2.43, 0.07-0.27 and 0.11-0.85 ng g^{-1} dry needles (Kylin et al. 1994). The respective ranges of PCB-118, PCB-156 and PCB-170 found in pine needles at four rural locations in Sweden were 1-2.95, 0.1-0.16, and 0.09-0.17 ng g^{-1} dry needles (Kylin et al. 1994). Our results are similar with these results.

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