

## PCB and organochlorine pesticides in one-year and two-year old pine needles

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### Introduction

Vegetation is used in many studies as an indicator of a site pollution<sup>1</sup>. 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 plants due to their worldwide distribution and the 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<sup>2,3</sup>. 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<sup>4</sup>. Furthermore, coniferous trees, can have one- and two-year old needles on the same branch. It is likely that needles of different ages have different pollutant concentrations. This can confound data interpretation.

The aim of this study was to investigate a pattern of organochlorine pesticides and PCBs in pine needles and to evaluate time-dependent differences in levels. The organochlorine pesticides and PCB contents were determined in one- and two-years 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- and two-year old needles from the same branch were separated.

The following organochlorine compounds were measured: HCB (hexachlorobenzene),  $\alpha$ -, $\beta$ -, $\gamma$ -HCH (alpha-,beta-,gamma-hexachlorocyclohexane), 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).

Organochlorine compounds were extracted from dried grounded needles by dichloromethane. Due to the complexity of wax composition, multistage clean up was required. Waxes were repeatedly precipitated by cooling. The clean up of extracts was continued by saponification under alkaline conditions and adsorption chromatography on a multilayer silica column (containing silica gel impregnated with sulphuric acid and silica gel with sodium hydroxide). Purified extracts were evaporated and polychlorinated biphenyls and organochlorine pesticides determined by HRGC/ECD. The method used has been described in full by Herceg Romanić and Krauthacker<sup>5</sup>. The analysis was done on an "ATI UNICAM" 610 SERIES gas chromatograph with a <sup>63</sup>Ni electron capture detector. Compounds were separated on two capillary columns: 1) 60 m × 0.25 mm, SPB-5 film thickness 0.25 µm, flow 14 mL min<sup>-1</sup>, temp. programme 100 °C, then 4 °C/min to 240 °C, 50 min isothermally. 2) 30 m × 0.25 mm, SPB-1701 film thickness 0.25 µm, flow 15 mL min<sup>-1</sup>, temp. programme 110 °C, then 4 °C/min 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 standard. Each sample was analysed on both columns. Only compounds identified on both columns were evaluated. The detection limit was 0.4 ng/ml for each compound.

## Results and discussion

Concentration ranges and percent of positive samples are shown in Table 1. Organochlorine pesticides and indicator PCBs (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153 i PCB-180) were measured in 19 pairs of samples while 11 other PCB congeners were measured in 14 pairs of one- and two-year old needle samples.

**Table 1.** Concentration ranges (ng/g dry needle) and the incidence of organochlorine compounds expressed as percent of positive sample in one- and two-year old needle.

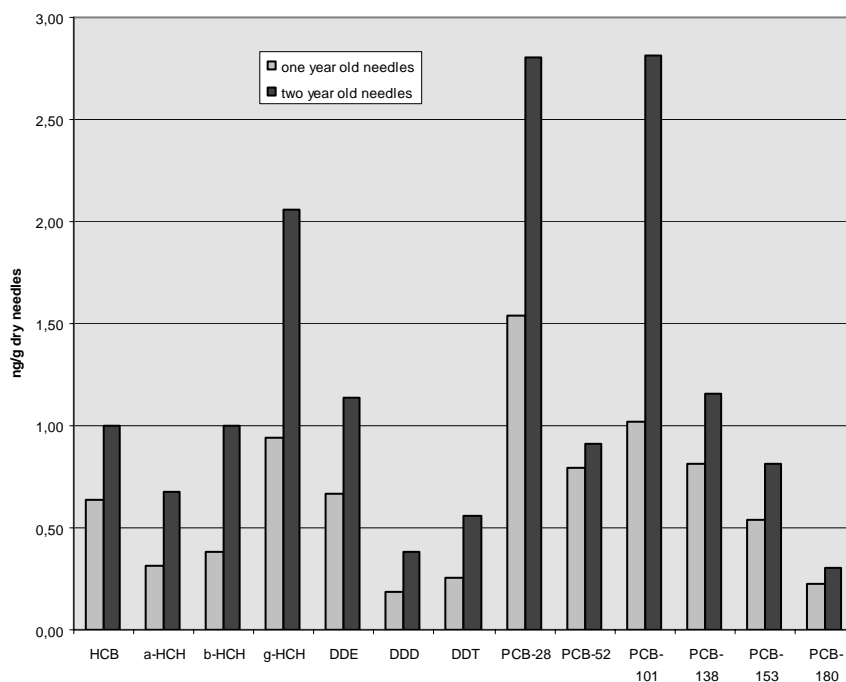
Compound	ONE YEAR-OLD NEEDLES		TWO-YEAR OLD NEEDLES	
	Range	%	Range	%
Organochlorine pesticides (N=19)				
HCB	0.24-1.38	100	0.14-2.81	100
$\alpha$ -HCH	0-1.06	95	0.05-2.62	100
$\beta$ -HCH	0-2.28	89	0.13-5.54	100
$\gamma$ -HCH	0.06-4.00	100	0.22-10.40	100
DDE	0.22-2.40	100	0.24-3.70	100
DDD	0-0.73	63	0.15-0.78	100
DDT	0-2.89	84	0.12-7.57	100
Indicator PCB (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 detection limit

HCB,  $\gamma$ -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 two-year old needle samples than in one year-old needles.

Figures 1 and Figure 2 show 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.

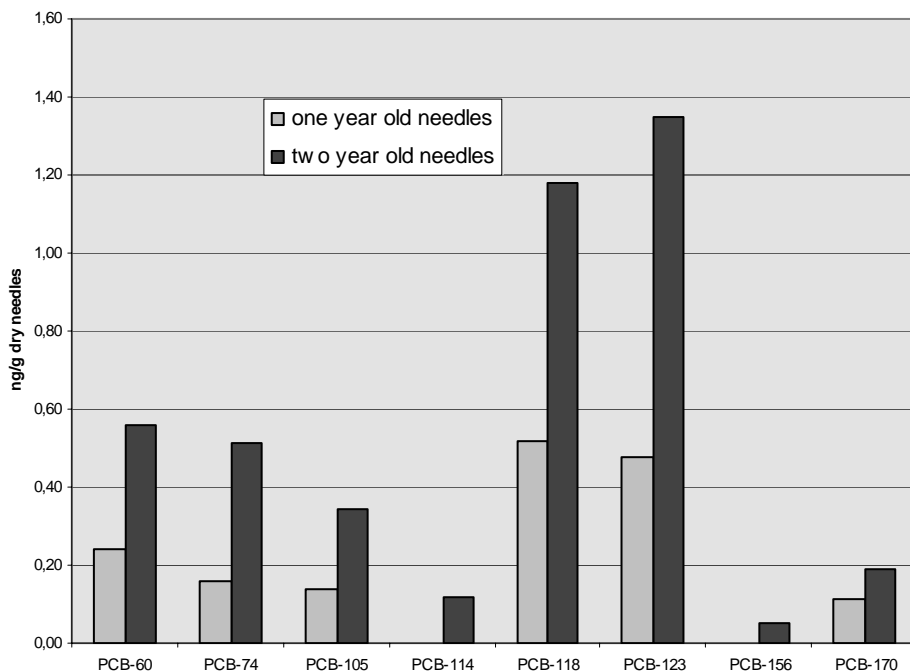
**Figure 1.** Median concentrations of organochlorine pesticides and indicator PCBs in one- and two-year old needle samples.



The incidence and median of all compounds are higher in two-year old needles. In both, one- and two-year old needles medians follow the same order: organochlorine pesticides -  $\gamma$ -HCH>DDE>HCB> $\beta$ -HCH> $\alpha$ -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 exception of PCB-156 and PCB-114 whose medians in two-year old needles are higher than 0.

Our results suggest that the patterns of organochlorine compounds in one year 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. It is therefore necessary to collect samples of the same age, to be able to make a reliable comparison of coniferous burdens between sites. However, it is sometimes difficult to compare organochlorine compound levels from samples of the same age on a large regional (or global) scale. An alternative could be a comparison of compound pattern.

**Figure 2.** Median concentrations of remaining 8 congener PCBs in one- and two-year old needle samples.



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