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Original Scientific Paper

ARE PINE NEEDLES BIOINDICATORS OF AIR POLLUTION? COMPARISON OF ORGANOCHLORINE COMPOUND LEVELS IN PINE NEEDLES AND AMBIENT AIR

Snježana HERCEG ROMANIĆ and Blanka KRAUTHACKER
Institute for Medical Research and Occupational Health, Zagreb, Croatia

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Levels of six PCB congeners and seven organochlorine pesticides were investigated and compared in ambient air and in pine needle samples. The applied methods are suitable for the analysis of PCBs and organochlorine pesticides in environmental samples and for their detection in recent intakes. DDE, HCB, lindane, PCB-28, PCB-52, PCB-101, PCB-138 and PCB-153 were found in all pine needle and air samples. The highest median values were found for PCB-28, PCB-101 and γ-HCH, and the lowest for PCB-180 and DDD. The median value of α-HCH/γ-HCH ratios was 0.2 in both matrices. DDE/DDT ratios were close to or below 1 in some pine needle and ambient air samples. The results showed a correspondence between air and pine needle pollution; the same compounds were present in the highest or in the lowest levels in both types of matrices. These results suggest that pine needles are passive biomonitors of air pollution.

KEY WORDS: *atmospheric pollution, biomonitor, biota, conifer, foliage, PCB*

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) belong to a group of persistent organic pollutants (POPs), which are toxic and tend to persist in the environment. Due to their lipophilic properties and resistance to metabolic breakdown, they tend to accumulate in fatty tissue and body fluids of animals and humans.

PCBs and OCPs directly enter the air from different sources. A part of PCBs and OCPs bind to particles while the other part is in gaseous phase. Weather conditions such as wind direction, wind velocity and ambient temperature determine PCB and OCP levels in air (1). They can reach far away from the source due to long-range atmospheric transport.

Vegetation has an important role in the biomonitoring of lipophilic compounds. PCBs and OCPs, present in the gaseous phase and particle-bound from surrounding air, sorb to wax which covers leaves (2, 3). Intake via plant root seems to be of minor relevance for lipophilic compounds (4). This is why vegetation can serve as a passive sampler and show the level of pollution at a particular site. Conifers have widely been accepted as reliable bioindicators due to their high leaf wax content. In addition, they are widespread and can be found over large areas. One conifer tree branch has several year-classes of needles, which makes it possible to obtain a pollution profile for more than one year (5).

This study compared previously published results of the levels and the distribution pattern of PCBs and OCPs in air (6) and pine needles (7, 8).

MATERIALS AND METHODS

Ambient air samples were taken at two different sites in Zagreb, Ksaver and Jakuševec. Ksaver is a residential area to the north and Jakuševec is an area

near a landfill and the industrial zone to the south of the city. The air distance between these two sites is about 9 km. The Ksaver series of 47 samples was collected from June 1999 to February 2000 and the Jakuševec series of 33 samples was collected from June 2000 to June 2001. Samples (≈1,000 m^3) were collected on polyurethane foam and quartz micro fibre paper (6). During January-March 1998, 19 pine needle samples were collected at urban and semiurban sites in Croatia (Jastrebarsko, Kamanje, Ludbreg, Bednja, Krapina, Čakovec, Koprivnica, Požega, Županja, Vinkovci, Dubrovnik, Kaštel Sućurac, Plomin and at six locations in Zagreb: Savska Opatovina, Kraljevački Novaki, Odra, Ksaver, Markuševačka Trnava, Jakuševec). Branches were collected at approximately 1.5 m above the ground and one- and two-year-old needles from the same branch were separated (7, 8).

The methods and results have been described in full by Herceg Romanić and Krauthacker (6, 7). Qualitative and quantitative analyses were done on a "UNICAM" 610 SERIES gas chromatograph with a ^{63}Ni electron capture detector. Two capillary columns were used: 1) SPB-5, 60 m x 0.25 mm, film thickness 0.25 μm, temp. programme 100 °C, then 4 °C min^{-1} to 240 °C, 50 min isothermally. 2) SPB-1701, 30 m x 0.25 mm, film thickness 0.25 μm, temp. programme 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. Each sample was analysed on both columns. Only compounds identified on both columns were evaluated.

The following organochlorines were analysed: organochlorine pesticides/metabolites HCB (hexachlorobenzene), α-, β-, γ-HCH (alpha-, beta-, gamma-hexachlorocyclohexane), DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane, DDE (1,1-dichloro-2,2-di(4-chloro phenyl)ethene and DDD (1,1-dichloro-2,2-di(4-chloro-phenyl)ethane and six indicator PCB congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180; numbered according to International Union for Purred and Applied Chemistry).

RESULTS AND DISCUSSION

Table 1 shows the summarized results of organochlorine compound measurements in ambient air and pine needle samples. The presented PCB and OCP measurements total both particulate matter and gaseous phase.

All compounds were present in more than 50 % of air and pine needle samples. Levels in the air and needles could not be compared directly. Mass concentrations of organochlorine pesticides in ambient air samples were in the range from below the determination limit for β-HCH, DDD and DDT to 247

Table 1 *Mass concentration (γ) of organochlorine compounds in ambient air samples collected in Zagreb during 1999/2001 (6) and compound mass fraction (w) in pine needle samples collected at urban sites in 1998 (8).*

Compound	Air (N=80)		One-year pine needles (N=19)		Two-year pine needles (N=19)	
	γ / pg m^{-3}		w / ng g^{-1} dry needles			
	range	median	range	median	range	median
HCB	1.1-36.3	10	0.24-1.38	0.64	0.14-2.81	1.0
α-HCH	0.6-60.5	10	0-1.06	0.31	0.05-2.62	0.68
β-HCH	0-40.0	5	0-2.28	0.38	0.13-5.54	1.0
γ-HCH	5.6-247	64	0.06-4.00	0.94	0.22-10.4	2.06
DDT	0-36	10	0.22-2.40	0.26	0.24-3.70	0.56
DDD	0-101	4	0-0.73	0.18	0.15-0.78	0.38
DDE	0.8-143	16	0-2.89	0.67	0.12-7.57	1.14
PCB-28	3.0-312	58	0.51-4.23	1.54	0.89-8.17	2.81
PCB-52	1.6-173	13	0.27-5.83	0.79	0.32-9.91	0.92
PCB-101	1.2-223	21	0.13-3.57	1.02	0.87-5.20	2.81
PCB-138	0.7-128	9	0.33-2.88	0.81	0.58-3.48	1.16
PCB-153	0.5-92	7	0.21-1.92	0.54	0.39-2.16	0.81
PCB-180	0-23	2	0-0.46	0.23	0.15-1.15	0.31

0 - below determination limit

pg m^{-3} for γ-HCH. HCB, α-HCH, γ-HCH and DDE were found in all samples at both sites, and γ-HCH had the highest levels. The mass concentrations of the six PCB congeners ranged between below the determination limit and 312 pg m^{-3}. At both locations PCB-28, PCB-52, PCB-101, PCB-138 and PCB-153 were found in all samples, and PCB-28 had the highest levels (6). In ambient air, concentration medians follow the order: γ-HCH>DDE>HCB≈α-HCH≈DDT>β-HCH>DDD; indicator PCBs - PCB-28>PCB-101-PCB-52>PCB-138>PCB-153>PCB-180.

As it was published earlier (7), no marked difference in the OCP and PCB levels and incidence was observed in pine needle samples with respect to different locations. Therefore, our results were combined and showed that mass fractions of organochlorine pesticide in one-year-old needles ranged between below the determination limit and 4 ng g^{-1}, while in two-year-old needles they ranged between 0.05 ng g^{-1} and 10.4 ng g^{-1}. Mass fractions of indicator PCBs in one-year-old needles ranged between below the determination limit and 5.83 ng g^{-1}, while in two-year-old needles they ranged between 0.15 ng g^{-1} and 9.91 ng g^{-1} (8). The levels of organochlorine compounds in two-year-old needles were higher, but the distribution pattern of medians in one-year and two-year-old needles were similar: γ-HCH>DDE>HCB>β-HCH>α-HCH>DDT>DDD; indicator PCBs-PCB-28>PCB-101>PCB-138>PCB-52>PCB-153>PCB-180. The same distribution patterns of organochlorine compounds found in two generations of needles indicated the same air pollution over two years (8).

DDE/DDT and α-HCH/γ-HCH ratios are often used to indicate a fresh input of DDT or γ-HCH in the environment. In pine needle samples, the median value of α-HCH/γ-HCH ratios was 0.2, which indicated a recent input of γ-HCH (7). The median value of α-HCH/γ-HCH ratios was also 0.2 in ambient air samples at both locations (6). DDE/DDT ratios close to or below 1 were also observed in six samples, but the median value of DDE/DDT ratios for all samples was 2.58 (7). The DDE/DDT ratio in ambient air samples is lower at Ksaver than at Jakuševec (0.8 vs 2.2) (6). Low DDE/DDT ratios were found before in samples of snow and rain collected in 1990/92 (9) and air collected in 1997 in Zagreb (6). Over the past three decades, there has been no evidence of DDT use in Croatia. The only explanation for the observed decrease in the DDE/DDT ratio is the long-range air transport. In Croatian neighbourhood, Di Guardo and co-workers (10) published data about DDT levels in spruce needles collected in 1999 close to a chemical plant in Italy which produced DDT from 1960s to 1996. Another explanation for the presence of DDT in our samples is air transport from areas where it is used to control malaria vectors (11).

Median PCB and OCP levels in ambient air and pine needle samples are shown in Figure 1. In order to present the levels of organochlorine compounds in pine needles and air in the same scale, medians of organochlorine concentrations in air have been multiplied by the factor of 10^{-1}. The profile of concentration medians was the same in one- and two-year-old needles. Figure 1 gives an example with concentration medians in one-year-old needles. The profile of concentration medians was similar for both matrices. The highest median values were measured for PCB-28, PCB-101 and γ-HCH, and the lowest for PCB-180 and DDD. These results suggest a correspondence between pine needles and air pollution; the same compounds are present in the highest and in the lowest levels in both types of matrices. In addition, fresh inputs of organochlorine

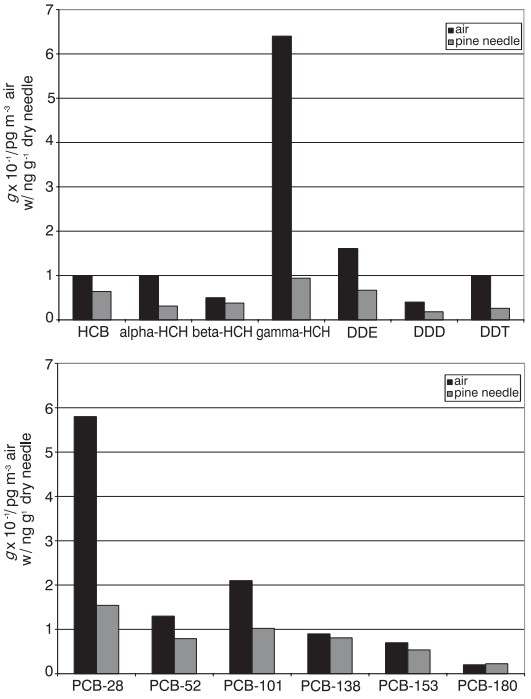

Figure 1 *Mass concentration (γ) medians of organochlorine compounds in ambient air samples (N=80) collected in Zagreb in 1999/2001 (6) and compound mass fraction (w) medians in one-year-old needles (N=19) collected at urban sites in Croatia in 1998 (8).*

compounds DDT and γ-HCH in air reflect on their levels in pine needles.

Some researches experienced difficulties while trying to calculate absolute air concentrations of pollutants on the basis of plant analysis. Tremolada and coworkers (12) showed that a comparison between calculated and measured air PCB concentrations provides useful evidence of good predictions of mean air concentrations from the pine needle data through the use of bioconcentration factors (BCF) based on *n*-octanol: air partition coefficients (K_{oa}). They obtained better predictions for PCB congeners with log K_{oa}<8.5 than for PCB congeners with log K_{oa}>8.5. Ockenden and coworkers (4) found that different plant species accumulated contaminants differently. They also found that pseudo-plant/air partition coefficients indicated sorption of PCBs in vegetation at lower temperature and favoured plant accumulation for less volatile congeners. However, they pointed out that although they tried to relate plant levels of analysed compounds to temperature, temperature could actually be masking other effects in biological processes, snow cover and actual atmospheric concentrations. Hellström and coworkers (5) propose that pine needles can be used to map the distribution of lipophilic airborne pollutants and clearly show local hot spots. They suggest, however, that we may never be able to calculate absolute air concentrations because of difficulties caused by biological factors affecting the uptake. Wyrzykowska and coworkers (13) in their study confirmed the suitability of pine needles as passive samplers for PCBs in air, reflecting current pollution sources and also historical production, storage and use of PCBs. They also pointed out that further studies should be undertaken to improve the understanding of factors affecting organochlorine levels in air and pine needle such as air-surface exchange, seasonal and spatial differences, atmospheric transport and fate, and life span of the foliage.

Our findings support the thesis that pine needles are useful for monitoring average profile of ambient air pollution and recent inputs of organochlorine compounds into the air, as they reflect on their levels in pine needles.

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Sažetak

JESU LI BOROVE IGLICE BIOINDIKATORI ONEČIŠĆENJA ZRAKA? USPOREDBA RAZINA ORGANOKLOROVIH SPOJEVA U BOROVIM IGLICAMA I ZRAKU

Ispitane su i uspoređene razine šest indikatorskih kongenera PCB-a i sedam organoklorovih pesticida u uzorcima zraka i borovih iglica. Primijenjene metode prikladne su za analizu PCB-a i organoklorovih pesticida u uzorcima iz okoliša te za određivanje njihova unosa u okoliš. DDE, HCB, lindan, PCB-28, PCB-52, PCB-101, PCB-138 i PCB-153 nađeni su u svim uzorcima zraka i borovih iglica. PCB-28, PCB-101 i γ-HCH prisutni su u najvišoj, a PCB-180 i DDD u najnižoj razini. U obje matrice omjer α-HCH/γ-HCH je 0.2. Omjer DDE/DDT jednak je ili manji od jedinice u nekim uzorcima zraka i borovih iglica. Iz prikazanih rezultata vidljivo je da je onečišćenje zraka i borovih iglica slično, tj. da su isti spojevi prisutni u najvišim odnosno najnižim razinama u obje matrice. Rezultati upućuju na to da su vrste i razine organoklorovih spojeva u borovim iglicama dobar pokazatelj prosječnog profila onečišćenja zraka.

KLJUČNE RIJEČI: *bilje, biomonitoring, biota, crnogorica, PCB, onečišćenje atmosfere*

CORRESPONDING AUTHOR:

Snježana Herceg Romanić
Institute for Medical Research and Occupational Health
P.O. Box 291, HR-10001 Zagreb, Croatia
E-mail: *sherceg@imi.hr*