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CHLORINATED PHENOLS AND THEIR DERIVATIVES IN SOIL AND GROUND WATER AROUND WOOD-PRESERVING FACILITIES IN FINLAND

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INTRODUCTION

Tri-, tetra- and pentachlorophenols are widely used for protecting wood against blue staining and rot. The active ingredients of the cocktail used in Finland are 2,3,4,6-tetrachlorophenol (TeCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) with some minor chlorophenols (Table 1). Several chlorinated phenoxyphenols occur as impurities of the chlorophenol formulation (Table 2). A dipping method, where wood is soaked in a 2 % alkaline solution of chlorophenols is commonly used in preservation. The treatment solution will spread in the environment by dripping, evaporation or wash during transport and storage of the treated wood. Chlorophenols are eventually either leached through the soil column to ground water or washed via ditches to adjacent watercourse. We studied the spread of a commercial wood-preserving agent around 5 wood-preserving facilities at sawmills in different parts of Finland. We analyzed soil, ground water and surface water for the presence of chlorophenols and chlorinated phenoxyphenols. Heavy pollution of soil, water and even ground water was observed at most of the sawmills studied. The different chemical constituents of the wood- preserving cocktail differed in their environmental behaviour.

EXPERIMENTAL

Chlorophenols in water samples were concentrated for analysis by adsorption onto Sep-Pak C_{18} cartridges followed by elution with acetone. Soil samples were extracted with dietyl ether at pH 2 for 8 hours. The chlorophenols were acetylated and analyzed by electron capture gas chromatography and gas chromatography mass fragmentography as described earlier (1).

RESULTS AND DISCUSSION

The situation proved to be very different at each individual sawmill, depending on the age of the mill, local wood-preserving practices (such as presence of dripping basin for freshly dipped wood) and hydrogeological factors. Tables 3 and 4 show, as an example chlorophenols and table 5 chlorinated phenoxyphenols found as contaminants at one sawmill. The sampling was performed in October 1983 when the mill had been in operation for 3 years on the same location. There was no drained dripping basin and the treated lumber was transported to the storage area (unprotected soil) only a few minutes after it had been soaked.

The tables show that relatively high amounts of chlorinated phenols were found in soil and water. Soil around the dipping basin contained up to 145 mg chlorophenols kg-1wet weight and contamination reached the level of 200 cm. Ground water at this point (-2.3 m) was also heavily contaminated, containing 0.2 mg chlorophenols litre-1. At other locations more distant from the preserving facility, the ground water was much less contaminated, 0.012 mg (-1.0 m) and 0.025 mg (-3.4 m) chlorophenols litre-1 225 and 350 m from the preserving facility, respectively. The results indicate that ground water movement was slow in this area.

Three of the 9 ground-water wells (table 4) located within 300 m from the wood-preserving facility and in the actual use for drinking water contained chlorophenols in the same ratio as the wood preservative. The concentrations were low, 1 µg litre -1 or less. However, also these concentrations are of concern because the odour and taste threshold for chlorinated phenols is very low, in the range of 0.1 µg litre-1 and the possible long time effect of small amounts of chlorophenols in drinking water are unknown. WHO recommends that the concentration of 2,4,6-trichlorophenol in potable water should be below 0.1 µg litre -1 and that for pentachlorophenol below 10 µg litre-1(2).

Table 4 shows that also surface waters were contaminated; the small river that flows through the sawmill area contained 0.04 µg chlorophenols litre-1. The small ditch (ON 4) flowing to the nearby lake contained 35 µg chlorophenols litre-1 at the point of discharge.

An interesting finding was the occurence of 2,4,5-trichlorophenol in soil samples. In one case (MN 1, 100-120 cm) its amount exceeded that of pentachlorophenol, although the preserving cocktail contained 7.5 % of pentachlorophenol and only 0.06 % of 2,4,5-trichlorophenol. 3,4-Dichlorophenol, 3,4,5-trichlorophenol and 2,3,4,5-tetrachlorophenol were found in soil samples but not in the wood preservative solution (<0.01 %). We do not know the origin of these chlorophenols. They may have originated from biological, photochemical or chemical degradation of pentachlorophenol, 2,3,4,6-tetrachlorophenol, 2,3,4,5-tetrachlorophenol or 2,3,4-trichlorophenol. These chlorophenols are formed during the biodegradation of pentachlorophenol (3). 3,4-Dichlorophenol and 2,3,4,5-tetrachlorophenol were found in µg/l amounts in water samples.

Soil quality, such as organic matter content, pH and water holding capacity, may greatly influence the leaching of chlorophenols into ground water. At the wood-preserving facility here discussed chlorophenols were accumulated in clay-rich sand at the lower end of a pH gradient where pH changed from 7.5 to 5.7 (pH of heavily contaminated soil is often 8-10).

The distribution of chlorinated phenoxyphenol (table 5) was different from that of chlorinated phenols. They accumulate strongly in the surface layers; at 0-5 cm the amount was 3-5 mg/kg and decreased gradually to less than 0.5 mg/kg below 20 cm. Tables 2 and 5 show that the ratio of each chlorinated phenoxyphenol isomer is the same in soil as in the wood preservative solution. This indicates that none of the isomers is degraded to a noticeable amount.

Our results, some of which were discussed above, show that chlorophenols have the capability of leaching through soil, and contamination of soil, which has been found a threat for surface water (3,4), is therefore an equal threat for ground water.

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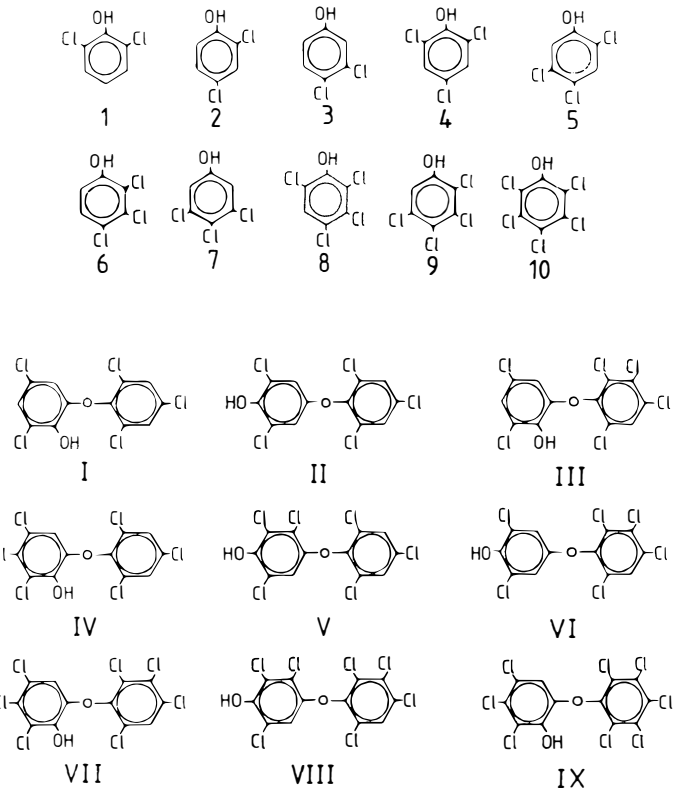

Figure 1. Chlorophenols (1-10) and chlorinated phenoxyphenols (I-IX) found as contaminants of the sawmill area.

TABLE 1. Chlorophenol composition of the preservative (Ky-5)

chlorophenol	%
2,6-dichlorophenol	0.01
2,4-dichlorophenol	0.96
2,4,6-trichlorophenol	10.85
2,4,5-trichlorophenol	0.06
2,3,4-trichlorophenol	0.04
2,3,4,6-tetrachlorophenol	80.61
PCP	7.47

TABLE 2. Chlorinated phenoxyphenols found as contaminants in the wood-preservative Ky-5. For I-IX see Fig 1.

Phenoxyphenol	mg/kg
I	580
II	640
III	1100
IV	750
V	730
VI	1230
VII	1980
VIII	2150
IX	150

TABLE 3. Chlorophenols (µg/kg fresh weight) detected in soil 20 m from the dipping basin. Symbols of 2-10 are shown in Figure 1.

Depth(cm)	2	3	4	5	6	7	8	9	10
0-5	4275	-	5164	2171	2126	-	32335	1033	103020
5-20	143	-	187	-	-	-	900	-	1575
20-40	760	-	1145	230	280	-	3705	55	7900
40-60	855	-	2335	240	185	-	12475	-	6110
60-80	645	-	2360	1850	280	-	17505	90	5455
80-100	310	4595	895	1490	260	505	6245	180	1910
100-120	595	4405	1554	2915	360	495	9980	170	2025
120-140	95	1110	-	115	-	-	2200	-	450
140-160	-	-	-	-	-	-	60	-	30
160-180	-	-	-	-	-	-	65	-	30
180-200	-	-	-	-	-	-	115	-	40

-=chlorophenol was not detected.

TABLE 4. Chlorophenols (µg/l) detected in surface water and ground water in the sawmill area. See Figure 1 for structures of compounds 1-10.

Sample[a]	1	2	3	4	5	6	8	9	10	Distance[b] (m)	Water-level[c]
SOK 1	14.50	390.00	-	957.00	46.70	20.90	14300.00	6.38	6080.00	1	
SOK 2	-	0.34	-	4.83	0.42	0.17	63.30	0.30	13.10	10	
ON 4	0.06	0.48	1.25	3.15	1.25	0.38	23.10	2.48	5.29	310	
VN 1	-	-	-	-	-	-	0.03	-	0.01		
VN 2	-	-	-	-	-	-	0.25	-	0.07		
PVP 1	-	0.20	-	5.67	0.28	0.16	179.00	0.04	23.30	5	-2.3
PVP 2	-	0.19	-	0.79	0.09	0.03	8.45	0.04	2.64	225	-1.0
PVP 3	-	0.62	0.54	1.27	6.25	0.03	12.40	1.24	3.03	350	-3.4
W 1	-	-	-	0.01	-	-	0.57	-	0.07	305	-5.2
W 2	-	-	-	0.03	-	-	0.10	-	0.02	225	-1.0
W 3	-	-	-	-	-	-	0.06	-	0.04	175	+2.7
W 4	-	-	-	-	-	-	0.01	-	0.01	110	+3.2
W 5	-	-	-	0.01	-	-	0.13	0.02	0.30	195	+1.3
W 6	-	-	-	-	-	-	0.31	-	0.17	195	+2.3
W 7	-	-	-	-	-	-	0.11	-	0.17	225	+1.2
W 11	-	-	-	0.12	-	-	0.14	-	0.05	270	+2.2
W 12	-	-	-	0.02	-	-	0.24	-	0.16	200	+2.4

[a]SOK, blind drain; ON, ditch from the mill area; VN, water from river flowing by the mill area; PVP, ground water inside the mill area; w; groundwater in the neighbourhood of the sawmill.
[b]Distance from dipping basin to sampling point.
[c]Difference in groundwater level (m) between dipping basin and sampling point.

TABLE 5. Chlorinated phenoxyphenols (mg/kg fresh soil) detected in soil 20 m from the dipping basin. For structures of I-IX see Figure 1.

Depth(cm)	I	II	III	IV	V	VI	VII	VIII	IX
0-5	2.99	3.21	3.94	2.70	2.65	3.93	4.76	0.45	0.19
5-20	0.69	0.49	0.67	0.66	0.53	0.54	0.91	0.68	0.06
20-40	0.30	0.12	0.18	0.28	0.16	0.12	0.19	0.13	0.03
40-60	0.09	0.04	0.07	0.10	0.05	0.08	0.08	0.09	0.02
60-80	0.05	0.05	0.07	0.07	0.04	0.08	0.22	0.16	0.02
80-100	0.03	0.04	0.01	0.02	0.02	0.05	0.02	0.05	-