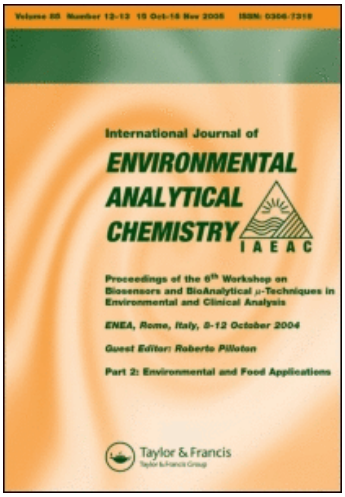

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Analysis of Chlorinated Phenols, Phenoxyphenols and Dibenzofurans Around Wood Preserving Facilities†

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Until presently chlorophenol containing wood preservative has been widely used in Finland to protect timber, lumber, plywood and fiberboard against rot and blue-staining fungi at saw mills. We analysed soil, ground water, runoff and workers' urine at several saw mills for the presence of the various chemical components of the commercial wood preservative.

We found serious local contamination of soil with chlorophenols and also with the minor, potentially very toxic minor constituents of the commercial product, namely polychlorinated phenoxyphenols and dibenzofurans. Chlorophenols were observed to contaminate soil at great depth. Ground water, surface water and also workers' urine was found contaminated by chlorophenols. Polychlorinated phenoxyphenols and dibenzofurans were found in great quantity (equal or close to that of chlorophenols) in the topmost 5 cm of soil at the sawmill area, but these compounds had not penetrated into the soil at such great depth as did chlorophenols.

KEY WORDS: Soil contamination, wood preservative, chlorophenols, polychlorinated phenoxy phenols, polychlorinated dibenzofurans (PCDF).

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INTRODUCTION

In Finland there are over 300 saw mills and factories producing timber, lumber, plywood and fiberboard. Their total production was 9.3 million m^3 in 1983. In order to protect the wood products against blue staining fungi and soft rot during storage and shipping, the products are treated with fungicides, of which a technical cocktail of chlorophenols has been the most widely used in Finland as well as in most other countries for the past 40 years.

Many studies have shown that chlorophenols are persistent in water environment (for a review, see References 1, 2), but few studies have been carried out to look for persistence in soil. We analysed samples of soil, ground water, surface water and of human origin (urine) from saw mills using technical chlorophenol as wood preservative.

We have reported earlier on the spread of chlorophenols in soil, surface water and ground water around saw mills.[3,4] In this paper we report studies on the occurrence of the potentially toxic impurities of the technical chlorophenol, namely the polychlorinated biphenyl ethers (polychlorinated phenoxy phenols, PCPP) and dibenzofurans (PCDF) in saw mill surroundings. We report on the persistence of these chemical compounds and also of chlorinated phenol as soil contaminant. At every saw mill we studied, the soil was found heavily contaminated by chlorophenols. Also the minor constituents of the technical chlorophenol product, polychlorinated biphenyl ethers and dibenzofurans were found in soil at parts per million level. All of these compounds were found to be persistent to degradation *in situ*.

MATERIALS AND METHODS

Samples to be analysed were collected from three different (A, B, C) saw mills at different parts of Finland. Saw mill A had been for 3 years in operation, saw mill B 20 years and saw mill C more than 40 years. Mill A produced 25 000 m^3 of sawn timber and lumber per year, of which about 5000 m^3 used to be treated with a commercial chlorophenol containing wood preservative (Ky-5). 600 g kg^{-1} of the pre-

servative (by weight) was sodium salt of pentachlorophenol (5–9%), 2,3,4,6-tetrachlorophenol (78–83%) and 2,4,6-trichlorophenol (7–15%), and the annual use of this product at saw mill A was approx. 1000 kg. Saw mill B's annual production was approx. 42 000 m^3, of which 15 000 m^3 was treated involving the use of approx. 5300 kg of Ky-5. Saw mill C produced 250 000 to 300 000 m^3 of timber and lumber per year and used for this approx. 20 000 kg of Ky-5. The figures for Ky-5 use are based on information given by the mill representatives.

The preserving solution was 0.5 to 2% (by weight) solution of Ky-5 in water and the sawn wood was submerged in this solution for approx. 1 minute, after which it was allowed to drain 5–10 minutes on a roll trail above a trickling basin. Mills A and B had no trickling basin.

Samples of soil and water were collected both near (approx. 20 metres) the treatment basin and also at storage area of treated wood (several hundred meters away from the treatment facility). The samples were analysed for chlorophenol as described previously[3] using 2,3,6-trichlorophenol and 2,6-dibromophenol as internal references. Urine samples were hydrolysed in 3 M H_2SO_4 by incubating in stoppered bottles 2 h at water bath 90° to 100°C, before extraction and analyses to recover possible glucuronyl conjugates.[5,6]

Polychlorinated phenoxy phenols were extracted with acetone at pH 2 under mechanical shaking (20 min) and then in ultrasound bath (1 h) with occasional shaking. Irgasan DP 300 (5-chloro-2-(2,4-dichlorophenoxy)phenol, Bayer AG) was added to the samples as internal reference. The recovery of Irgasan DP 300 was 70 to 100%. The results given in the tables and figures have been corrected for the recovery. The phenoxyphenols were identified and quantitated as acetates[7] using gas liquid chromatograph equipped with SE-30 fused silica capillary column and 31 authentic reference compounds, synthesized by T. Humppi at Jyväskylä University as described in Reference 7.

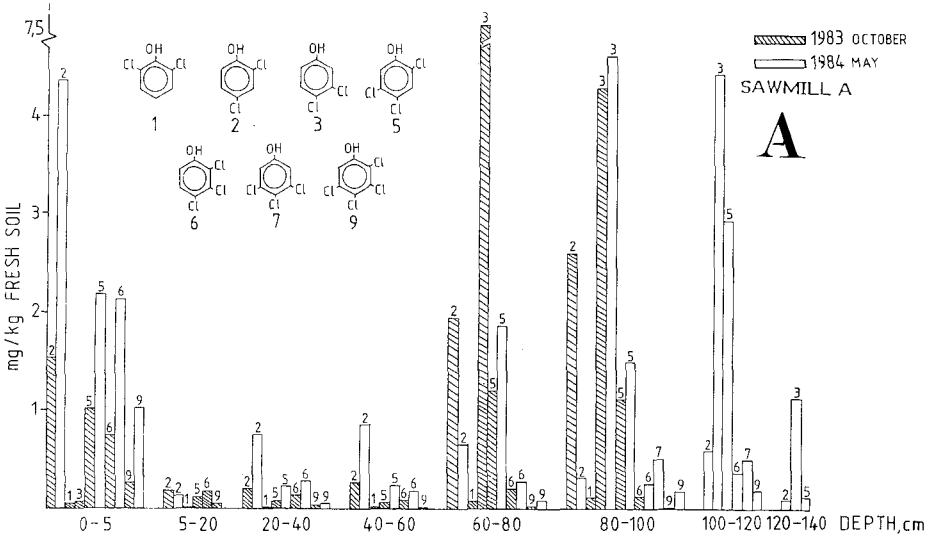
Chlorinated dibenzofurans were extracted with a soxhlett apparatus into acetone/hexane (50/50, by vol.). The extract was washed 3 times with 1 M aqueous NaOH solution and purified over a silica gel/Al_2O_3 column.[8] Identification and quantitation was done by GC-MS using 14 authentic model compounds as external standard (obtained from T. Humppi).

RESULTS

Polychlorinated phenols

Fig. 1 A–C shows the results on the analyses of chlorinated phenols in soil at saw mill A in samples taken at two subsequent years. The topmost layers consisted of sand together with organic matter like sawdust, bark, wood chippings and a little oil from the engines of working machines. The other layers were mostly sand and gravel[3] except for the layer below 80 cm which contained clay.

The figure shows that ten different chlorophenols were found in soil, and that the concentrations for some of them were quite high. The clay layer has accumulated chlorophenols so that the concentration at 60–120 cm is as high as at the soil surface. 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol were found in almost the same ratio as in the preservative used (Ky-5). This confirms the stability of those compounds in soil. Another interesting thing is to see that there are new chlorophenolic compounds which were not found in Ky-5: 2,3,4,5-tetrachloro-, 3,4,5-trichloro- and 3,4-dichlorophenol. These may represent products of (bio)degradation.



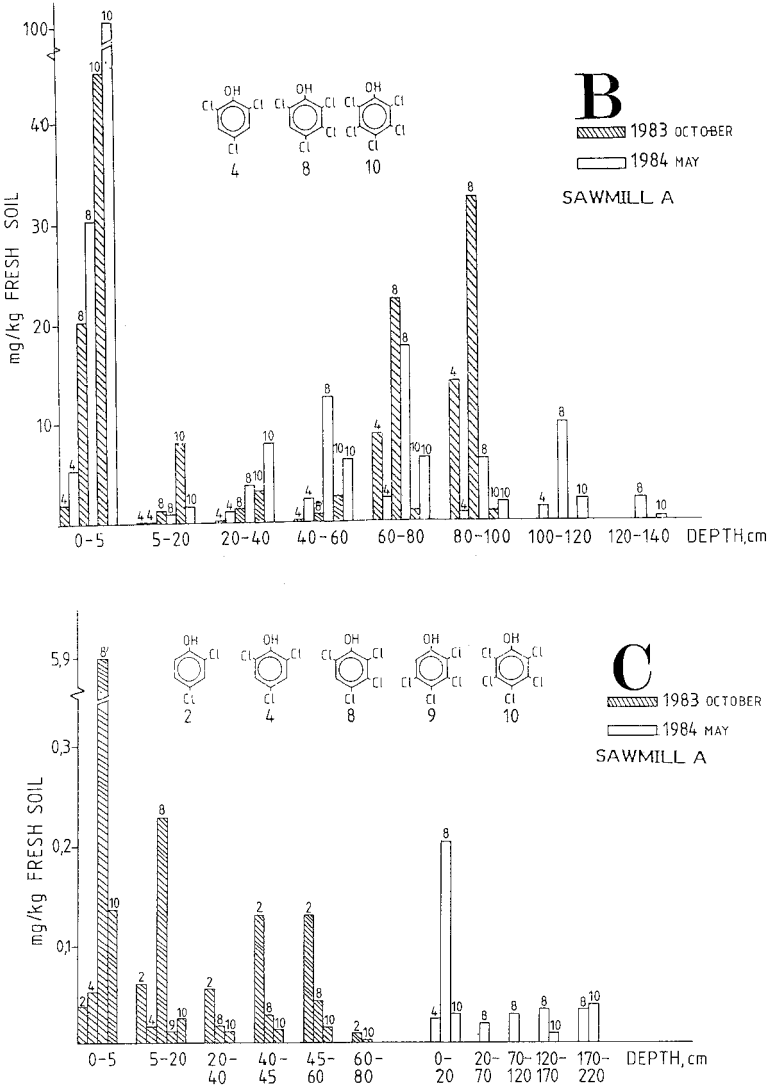


FIGURE 1 Chlorinated phenols found in soil sampled at the area of saw mill A. Figures A and B show the results obtained near (20 m) the wood protection treatment facility; Fig. 1C shows the results at the storage area (200–300 metres apart from the treatment facility).

The use of chlorophenol was discontinued at this mill at the time of the first sampling. Yet the soil concentrations of chlorophenol in the next year were in the same order of magnitude (the sampling site in 1984 was not exactly the same, but close to, that in 1983). This was true at various locations at the saw mill area (compare Figure 1A, B to Figure 1C). This result shows that the chlorophenols, although water soluble compounds, were not easily washed away.

The results for mill B were very similar to those at mill A and have been described elsewhere.[3] Mill C, which exceeded in production mills A and B by an order of magnitude, surpassed the other mills also in the level of chlorophenol contamination of soil. Table I shows the results of chlorophenol analyses from soil sample near the location where slurry and sawdust from the dipping basin had been stored. Note that the concentrations are given in mg rather than μg per kg. The concentration of 2,4,6-tri- and 2,3,4,6-tetrachlorophenol went up to 1–3 grams per kg of fresh soil.

Figure 2 shows the results of urine analysis for chlorophenols in 2 different saw mill employees and 3 workers of Ky-5 plant. It shows that all (randomly selected) employees had significant amounts of chlorophenol in urine, both the minor (Figure 2A) and the major (Figure 2B) components were seen. This shows that not only the soil and water, but also the people have become contaminated by the wood preserving chemical.

Polychlorinated phenoxyphenols

Figure 3 shows the gas chromatographic separation of polychlorinated phenoxyphenols (PCPPs) reference compounds and various samples. Table II shows the quantities of PCPP's present in two different lots of the type of wood preservative Ky-5 used by the saw mills A, B, and C. The 8 main PCPP components in the Ky-5 made up to 1% by weight (Table II). When the minor PCPPs were taken into account, the total sum was approx. added up to 1.5% by weight.

Figure 4 shows the distribution of PCPP's in soil at saw mill A. It is seen that there were PCPP's in soil, in concentrations up to 25 mg (sum) kg^{-1}, and that 80–90% of all phenoxyphenols were retained by the topmost 5 cm of soil. The reason for the strong adsorption of PCPPs may be the poor solubility in water. The situation at saw mills B and C was similar, except for that Mill C again surpassed

TABLE I

Chlorophenols (mg/kg fresh weight) detected in soil inside saw mill C

Sample	Depth (cm)	2,6-DCP	2,4-DCP	3,4-DCP	2,4,6-TCP	2,4,5-TCP	2,3,4-TCP	3,4,5-TCP	2,3,4,6-TeCP	2,3,4,5-TeCP	PCP
mn 1	0–5	—	5.7	5.3	73.0	4.2	0.9	1.7	994.6	0.9	73.8
mn 1	5–20	—	10.0	41.1	136.5	14.2	2.1	3.8	1120.0	2.2	50.8
mn 1	20–40	—	47.4	18.2	1258.3	15.7	3.8	0.5	1776.4	—	14.9
mn 1	40–50	—	17.6	16.0	451.3	5.7	1.4	0.4	736.4	—	9.1
mn 1	50–60	—	4.7	7.0	152.7	1.9	0.2	—	348.2	—	6.0
mn 1	60–70	—	2.7	3.3	79.4	0.8	—	—	231.0	—	5.0

—, isomer not detected.

DCP, dichlorophenol; TCP, trichlorophenol; TeCP, tetrachlorophenol; PCP, pentachlorophenol.

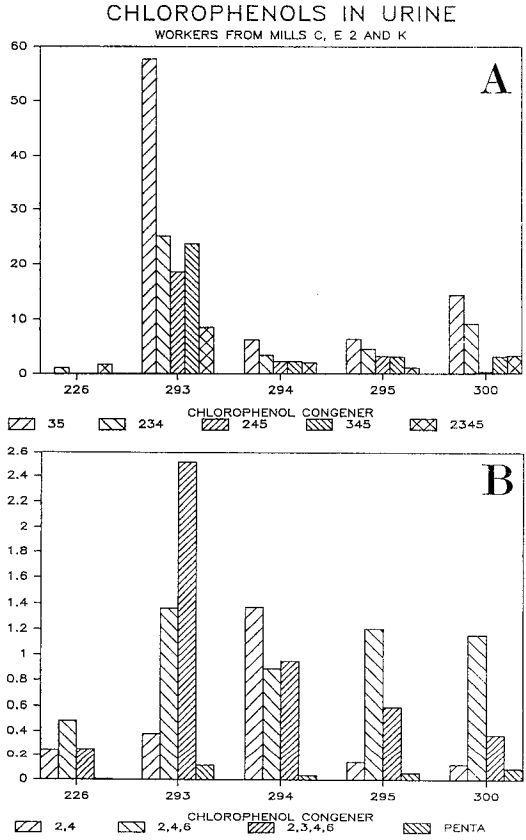


FIGURE 2 Analysis of 5 randomly selected saw mill workers' urine for polychlorinated phenols. The results are expressed as $\mu g l^{-1}$ (A) and $mg l^{-1}$ (B). Worker number 300 was employed by saw mill C (see Table I). The urine samples were collected late 1983.

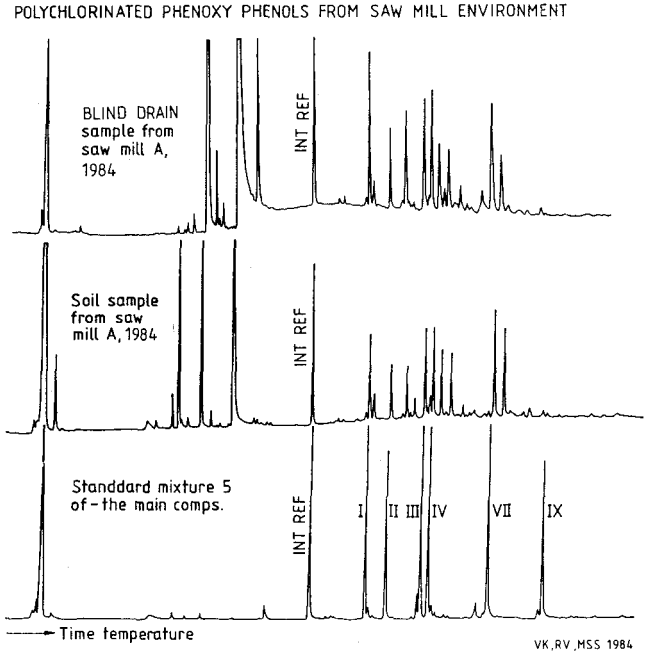


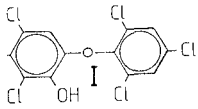
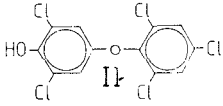
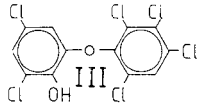
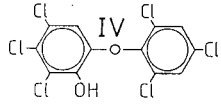
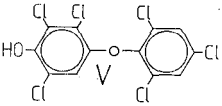
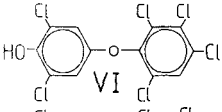
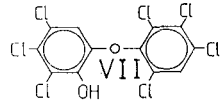
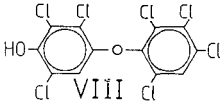
FIGURE 3 Three chromatograms of polychlorinated phenoxyphenols (PCPP). Column SE-30, 25 m × 0.3 mm I.D., with H_2 as the carrier gas and temperature gradient for the column from 60° to 280°C at 10°C min^{-1}, and then run at 280°C.

the mills A and B in the degree of contamination: the PCPP's added up to 60 mg per kg of fresh soil. At the time of sampling (May 1984) no chlorophenol had been used at saw mill A in 6 months. The fact that ample PCPPs were nevertheless found, shows that PCPPs are persistent in soil.

The water samples, both surface water (nearby creek) and ground water, were found clean in respect to PCPP's, although there was ample chlorophenols (up to 20 mg per litre, presented in Reference 3) to be found. Only one heavily contaminated blind drain, near the treatment facility, contained water with a sum of 1 mg of PCPP's $litre^{-1}$ (Figure 3). The reason for the relative immobility of the phenoxyphenols may be their poor solubility in water. No PCPPs were found in the urine samples.

TABLE II

Chlorinated phenoxyphenols detected in two different lots of the commercial chlorophenol formulation, Ky-5 (μg/g)

Formula	Name	I	II
	4, 6-dichloro-2-(2, 4, 6-trichlorophenoxy)phenol	551	610
	2, 6-dichloro-4-(2, 4, 6-trichlorophenoxy)phenol	686	591
	4, 6-dichloro-2-(2, 3, 4, 6-tetrachlorophenoxy)phenol	1188	1009
	4, 5, 6-trichloro-2-(2, 4, 6-trichlorophenoxy)phenol	849	598
	2, 3, 6-trichloro-4-(2, 4, 6-trichlorophenoxy)phenol	804	650
	2, 6-dichloro-4-(2, 3, 4, 6-tetrachlorophenoxy)phenol	1407	1050
	4, 5, 6-trichloro-2-(2, 3, 4, 6-tetrachlorophenoxy)phenol	2260	1726
	2, 3, 6-trichloro-4-(2, 3, 4, 6-tetrachlorophenoxy)phenol	1986	2318

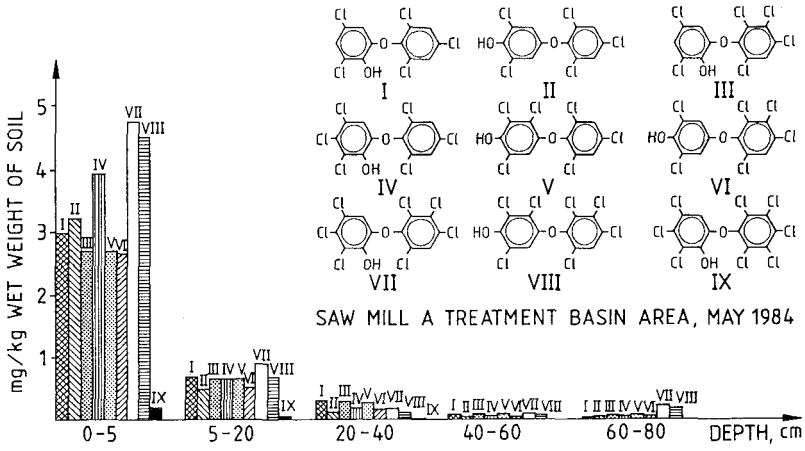


FIGURE 4 The occurrence of polychlorinated phenoxyphenols (PCPP's) in soil at saw mill A. The chlorophenol content of the same samples is shown in Figures 1A and B (May 1984). Only the main components are shown.

Polychlorinated dibenzofurans

Figure 5 shows the total ion chromatogram of the neutral fraction of Ky-5, and Table III summarizes the peaks that were identified. Six different PCDF congeners were identified, namely octa-, 1,2,3,4,6,8,9-hepta-, 1,2,3,4,6,7,8-hepta-, 1,2,4,6,8,9-hexachloro-, 1,2,4,6,7,8-hexachloro- and 1,2,3,4,6,8-hexachlorodibenzofurans. It is seen in the chromatogram (Figure 5) that there is also material, although less than in the hexa-heptaCDF region, in the area of pentaCDF (area of peaks 10–14) and tetraCDF (area of peaks 6 to 9) but these were not well enough resolved to give mass spectra of a single congener.

Figure 6 shows results of analysis when Ky-5 and soil samples from saw mill A were analysed for the quantity of the six above-mentioned PCDF compounds. It shows that 100 to 200 ppm of these congeners were found in Ky-5 and that in soil samples the same congeners were found and the isomer ratios are very much the same as in Ky-5. It further shows that the top most 5 cm layer of soil has

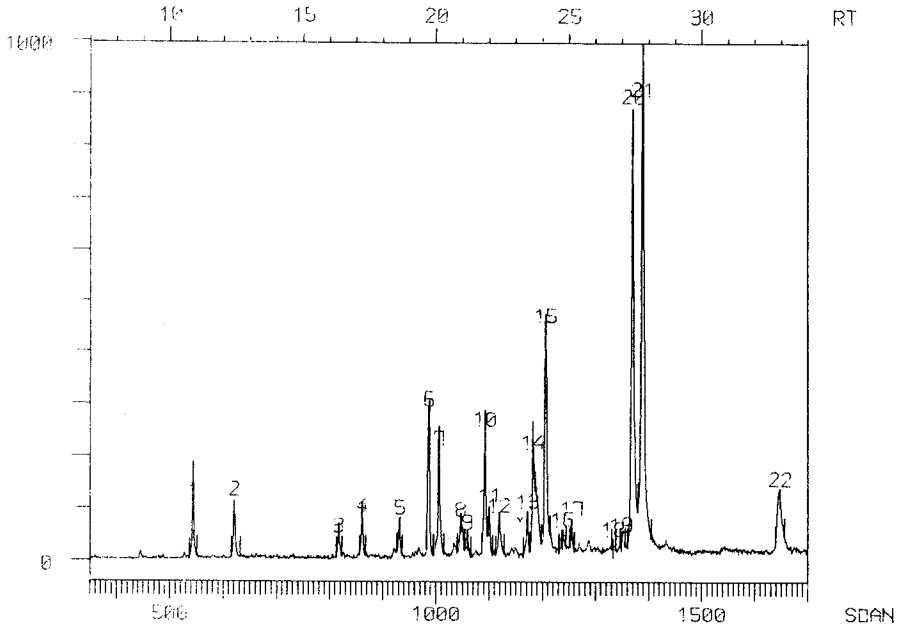


FIGURE 5 Total ion current chromatogram of the neutral fraction of the wood preservative Ky-5. The capillary column used for the GLC was SE-30. The identified peaks are listed in Table III.

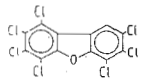
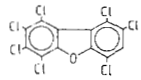
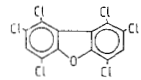
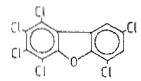
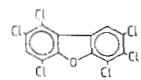
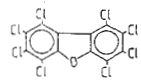
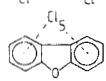
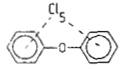
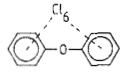
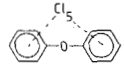
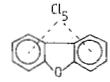
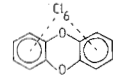
adsorbed almost all the PCDFs, leaving very little to leach deeper into the soil: the quantity found between 5 and 40 cm was less than 10% of that in the top 5 cm. The accumulation onto surface soil seems even more predominant than was the case of PCPPs. It can also be concluded that these chemicals are persistent in the environment, since at the time of the sampling no new spillage had taken place in the past 6 months (chlorophenol use ended at this mill November 1983).

DISCUSSION

The results of this study show that the use of technical chlorophenol for protecting wood products against fungi, has led to serious chemical contamination of soil, water and humans at the workplace.

TABLE III

The identified compounds of the neutral fraction of Ky-5

Compound	Peak number	M^{+2}
	20	408
	21	408
	15	374
	14	374
	14*	374
	22	442
	10	340
	4	342
	5	376
	3	342
	13	340
	16	390

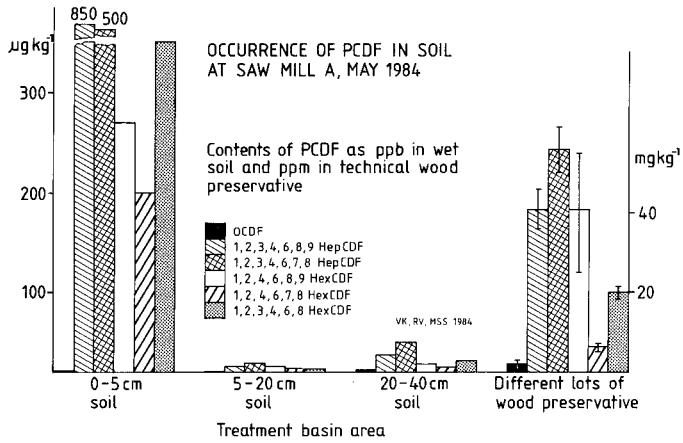


FIGURE 6 Results from analysis of technical chlorophenol Ky-5 and soil from saw mill A for selected PCDF congeners. The soil samples were taken May 1984; the use of Ky-5 ceased at the saw mill in November 1983.

We studied so far 6 saw mills (coded: A, B, C, E1, E2 and K), and saw in each a similar pattern of contamination: chlorophenols have penetrated deep into soil, often in ground water also, whereas PCPPs and PCDFs have accumulated themselves in the topmost 5 cm of soil.

The concentration of chlorophenols in urine of the employees was 100 to 1000 fold higher than reported for non-occupationally exposed persons.[6,9] When the saw mill was resampled 6 months after discontinuation of chlorophenol use at the mill, the soil concentrations of chlorophenols had not decreased compared to the first sampling. Chlorophenols thus are persistent in soil conditions. Chlorophenols are probably also spread by air in the saw mill area, as acid rain and acid wood extractives gradually convert the phenolates into phenols on treated wood surface.

The 8 major components of PCPPs, which observed to have contaminated saw mill soil, were found in Ky-5 also by Humppi and co-workers.[7] The amount of these compounds in soil was very high (up to 60 mg kg^{-1}), sometimes exceeding the amount of chlorinated phenols in the same soil. The PCPPs are not very volatile and probably do not spread by air. The risks caused by their accumulation to the environment and health are difficult to estimate at present, since little is known on the possible harmful effects of these

compounds. One tri-chloro phenoxyphenol is a widely used bactericide (Irgasan DP 300, see Methods) and this group of compounds may therefore possess biocidic activity of some kind. Since the PCPPs stick to soil surface, ground water contamination or leaching are not very likely. However, the working environment may contaminate people by direct skin exposure.

We report here the presence of ppm quantities of PCDF compounds in soil in the vicinity of wood treatment facility. The main components so far identified were hexaCDF and heptaCDF which are not supertoxic. We intend to search further to see if lower concentrations of more toxic congeners are also present. Dowicide 7, which is a wood preserver consisting for 90% of pentachlorophenol, has been reported[8,9,10] to contain similarly hexaCDF, heptaCDF and octaCDF as we describe here for Ky-5, and components as we found for Ky-5. These are probably universally present in technical chlorophenols and are thus probably found in environments where such chemicals have been in technical use.

The contamination of soil by the chemical components in the wood preservative was more serious than we had expected. The reason for this can partially be seen in the careless working habits by which the wood protecting chemicals are being utilized at the saw mills, e.g. (1) the treatment basin is usually located outdoors, on bare soil, (2) with no runoff collecting facility; (3) the treated wood—still drip wet—is often transported directly after dipping to storage area (usually outdoors on bare soil); (4) the sludge that accumulates on bottom of the treatment basin (saw dust, wood extractives, bark) during the preserving season, is often irresponsibly disposed of or stored with danger of leakage and leaching; (5) the employees do not always were protective clothing; we have e.g. observed them to continue working with gloves that were soaked with the preserving chemical.

The production of technical chlorophenol for wood protection was recently closed down in Finland and the expected development is that other wood preserving chemicals will replace chlorophenol in the future. However, our results indicate that the wood preserving chemicals already in soil today, may be a tedious environmental problem, because there seems to be little spontaneous (bio)degradation. Moreover, if the working practice remains as it is today, the chemicals replacing Ky-5 can be expected to contaminate the environment also.

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