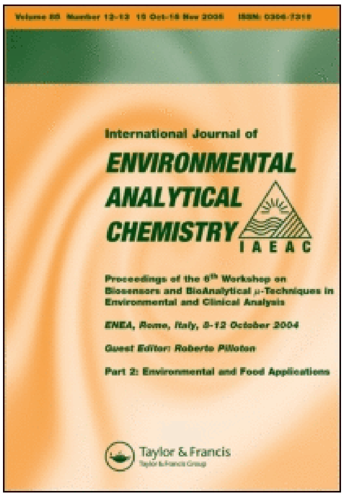

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ANALYSIS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN PENTACHLOROPHENOL TREATED POLES

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The analysis of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) from pentachlorophenol (PCP) treated jack pine poles is described. The concentration of PCDD and PCDF was found to change dramatically with the age of poles. The older jack pine pole produced in 1956 was found to have a total PCDD/PCDF content of 15 μg/g in the 0–20 mm assay zone of its' ground-line, while a corresponding jack pine pole treated in 1979 contained up to 239 μg/g PCDD/PCDF in the same assay zone.

Keywords: Polychlorinated dibenzo-*p*-dioxins; dioxins; polychlorinated dibenzofurans; dibenzofurans; pentachlorophenol; GC-MS; wood preservative; utility poles; treated wood waste

INTRODUCTION

Chlorophenols are probably the most important industrial source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs). Pentachlorophenol (PCP) has been extensively used as a wood preservative. It remains one of the main treatments for utility poles and is known to lose chemical to the environment[1]. It is well known that the technical grade PCP used in preservative formulations has, depending on its source, various levels of PCDDs and PCDFs. The fate of these highly toxic chemicals in PCP treated wood probably causes more concern than PCP itself. Dobbs and Grant[2] reported that dioxin concentration in PCP treated wood was within the range expected from the initial PCP retention. The real long-term changes in PCDD and PCDF concentration in

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PCP treated poles after prolonged weathering during service, has not been well studied. While the PCDDs and PCDFs could be lost from the treated wood by evaporation, leaching, migration with carrier oil, and photochemical degradation[3], they could also be generated from PCP[2–5] and predioxins[6] via photochemical transformation. PCP treated utility poles have an anticipated service life of 35 to 50 years, after which they are removed for disposal. The residual concentration of the PCDDs and PCDFs is an important factor limiting the options available for the way in which poles can be disposed. To assess the possible health and environmental risks that arise when PCP treated poles are disposed, the residual concentrations of PCDDs and PCDFs in seven jack pine poles after 13–37 years in service were studied using GC-MS.

EXPERIMENTAL

Materials

All solvents used in this experiment were omnisolv® (spectral grade) solvents from BDH. Brockman Activity I basic alumina from Fisher Scientific was activated at 130 °C over night before use. Deactivated alumina was prepared by thoroughly mixing activated alumina with 5% distilled water. Florisil™ from Aldrich was washed with methylene chloride and hexane and then activated at 130 °C. Sea sand from BDH (acid purified) was extracted with acetone and dried. $^{13}C_{12}$-OCDD was purchased from Cambridge Isotope Laboratories and the dioxin and dibenzofuran mixtures were from Chromatographic Specialties Inc. All other chemicals were of analytical grade.

Sections from seven jack pine (*Pinus banksiana* Lamb.) poles removed from service after 13–37 years, were provided by Bell Canada to enable the analyses of the residual chemical contents. The first group of samples provided, were recovered from poles treated in 1956, 1960, 1967, and 1976, respectively and removed in 1989. These samples were stored indoors between 1989 and the time of analysis in 1991–1992. The remaining sections were recovered from poles treated in 1955, 1977, and 1979, respectively, and removed in 1992. This second group of samples was analyzed soon after they were received. The sections were recovered from the ground-line, brand or top of the poles. In the ground-line care was taken to avoid the region which may have received any remedial treatment.

Extraction

PCDD and PCDF extraction efficiency from incinerator fly ash using various extraction methods has been studied[7]. It was concluded that Soxhlet extraction with toluene was the most effective with an average efficiency of 98% after 24 hour extraction. Other extraction methods gave efficiencies range from 1% to 44%[8]. No data is available on the extraction efficiency of PCDD and PCDF from treated wood. Soxhlet extraction with toluene was used in this study. Small wood pieces were cut from the pole sections[9] and ground into sawdust. One gram of sawdust was Soxhlet extracted with 100 mL toluene for 24 hours and evaporated on a Rotavapor at 40 °C and cleaned up as described below.

Sample clean up

Numerous methods are available to purify samples for PCDD and PCDF analyses. Two methods were tested in this study. The first method[10] involved a two step process. The toluene (10 mL) extract was added to a column (40 cm × 1.5 cm) containing successive layers (from top to bottom) of 1 g sodium sulfate (anhydrous, to remove any water in the extract), 2 g deactivated alumina (to remove pentachlorophenol and polar wood extractives), 1 g sodium sulfate, 10 g 44% sulfuric acid on silica gel (to remove any oxidizable impurities), 1 g 1:4 potassium carbonate/sodium sulfate, and 1 g sodium sulfate. The column was then washed with 50 mL toluene. The toluene eluent, an almost colorless solution, was collect and evaporated on a Rotavapor to dryness. Hexane (2–3 mL) was added to the residue and blown dry with nitrogen to remove any remaining toluene. The residue was then transferred to another column (30 cm × 0.7 cm) containing 2 g activated Florisil. The Florisil column was then washed with 200 mL of hexane to remove polycyclic aromatic hydrocarbons, polychlorobiphenyl ethers and any polychlorobiphenyls that were possibly present[11]. The PCDD and PCDF was then eluted with 30 mL methylene chloride. The methylene chloride eluent was evaporated, dissolved in toluene and analyzed on GCMS.

The second method involved a one step clean up[8]. The toluene extract was evaporated to dryness, dissolved in minimum amount of methylene chloride and mixed with purified sea sand. After evaporating all the methylene chloride with a stream of nitrogen, the sea sand was added to the top of a column (30 cm × 0.7 cm) containing 5 g of activated basic alumina with the help of small amount of hexane. The column was then washed with 30 mL of 3:97 methylene chloride/hexane (volume ratio), 15 mL of 20:80 methylene chloride/hexane, and 10 mL of methylene chloride. As analyzed by GC-MS, fraction one contained no dioxins, while fraction three contained small amount of OCDD that was only 0.5% of that in fraction two. The second fraction was evaporated and dissolved in 1 mL toluene. The toluene solution (0.1 mL) was mixed with 0.5 μg $^{13}C_{12}$-OCDD (internal standard) in 0.1 mL toluene and diluted to 0.5 mL. The resulting solution was subjected for GC-MS.

Comparing the two procedures described above, the second method was less time consuming and gave cleaner samples than the first method. The second procedure was therefore used for all the analysis.

GC-MS analysis

The instrument used was a VG Trio-1000 GC-MS system operating in EI mode. The column was a 30 meter J & W DB-5 column with an internal diameter of 0.25 mm and a film thickness of 0.25 micron. The operating conditions are summarized in Table I. The quantification of PCDD and PCDF was carried out using $^{13}C_{12}$-OCDD as internal standard. The responses of different congeners of PCDD and PCDF relative to $^{13}C_{12}$-OCDD were determined by injecting a mixture containing 0.5 ng each of $^{13}C_{12}$-OCDD, OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,7,8-pentachlorodibenzo-p-dioxin (PnCDD), 2,3,7,8-tetrachlorodibenzo-p-dioxin, OCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,7,8-PnCDF, and 2,3,7,8-tetrachlorodibenzofuran. Because of the large concentration difference between OCDD and lower chlorinated dibenzo-p-dioxins (five chlorine and less), no effort was made to quantify dibenzo-*p*-dioxins and dibenzofurans substituted by five chlorine atoms or less. The lower chlorinated dioxins, however, were detected in some samples.

TABLE I GC-MS Operating Conditions

Injection temperature	300°C	Rate B	4 °C/minute
Interface temperature	270 °C	Final temperature B	280 °C
Ion source temperature	260 °C	Final time B	15 minutes
Initial oven temperature	100 °C	Electron current energy	70 eV
Initial time	2.0 minute	Multiplier voltage	550 V
Rate A	15 °C/minute	Ionization Mode	EI
Final temperature A	240 °C	Operating mode	Selected ion recording
Final time A	0.0 minute		

RESULTS AND DISCUSSION

There are 75 PCDD congeners and 135 PCDF congeners in total. Congeners having the same number of chlorine atoms are called isomers. Octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF) each has only one possible isomer, while heptachlorodibenzo-p-dioxin (HpCDD) has two isomers. Two mixed standards, a PCDD mixture and a PCDF mixture, were used in this study. The PCDD mixture contained OCDD, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD), 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PnCDD), and 2,3,7,8-tetrachloro-*p*-dioxin (TCDD) and the dibenzofuran mixture contained OCDF, 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF), 1,2,3,4,7,8-HxCDF, 1,2,3,7,8-PnCDF, and 2,3,7,8-TCDF. The use of these two standards allows us, therefore, to quantify OCDD, OCDF, and the two HpCDDs as individual isomers. All the remainder will be given in total isomer concentrations such as total HxCDDs. PCDDs and PCDFs are dechlorinated when irradiated by ultraviolet light[12]. All samples were thus protected from light as much as possible. It has been reported that PCDDs are unstable in strong alkali solutions. OCDD has a half life of only 4.5 minutes in boiling potassium hydroxide[13]. PCDFs are even less stable under basic conditions. A strong alkaline condition was therefore avoided. Another reason to avoid an alkaline condition, is that some polychlorophenoxyphenols, sometimes called predioxins, can be cyclized to give dioxins under these conditions[14,15].

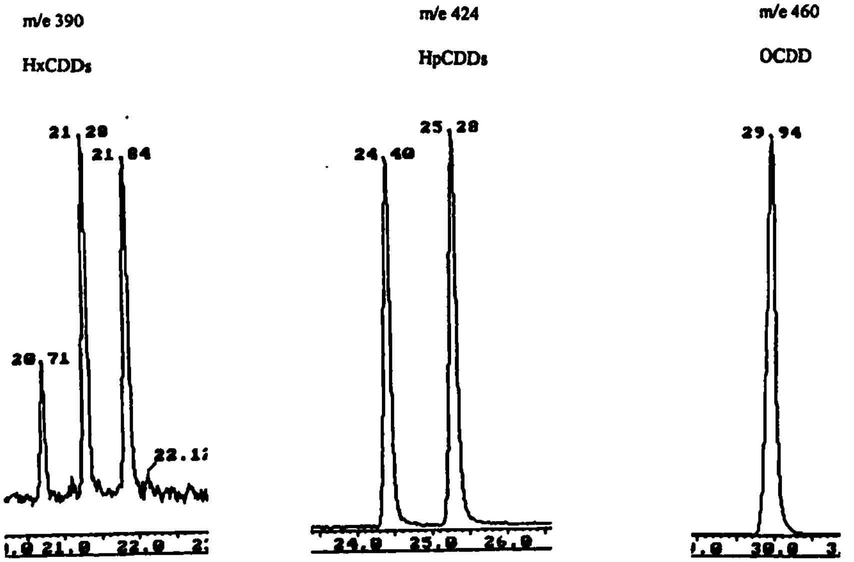

FIGURE 1 Typical ion chromatogram of PCDDs recorded in selected ion recording mode

Seven pole samples from six age groups were analyzed for their PCDD/PCDF content. Each pole was sampled using 0 – 20, and 20 – 40 mm assay zones respectively, from the surface at the ground-line and brand/top section. Figures 1 and 2 show typical ion chromatograms of PCDDs and PCDFs. The results are summarized in Table II. OCDD, OCDF, HpCDFs, both isomers of HpCDDs, HxCDDs, HxCDFs, and some pentachloro-substituted dibenzo-*p*-dioxins and didenzofurans were detected.

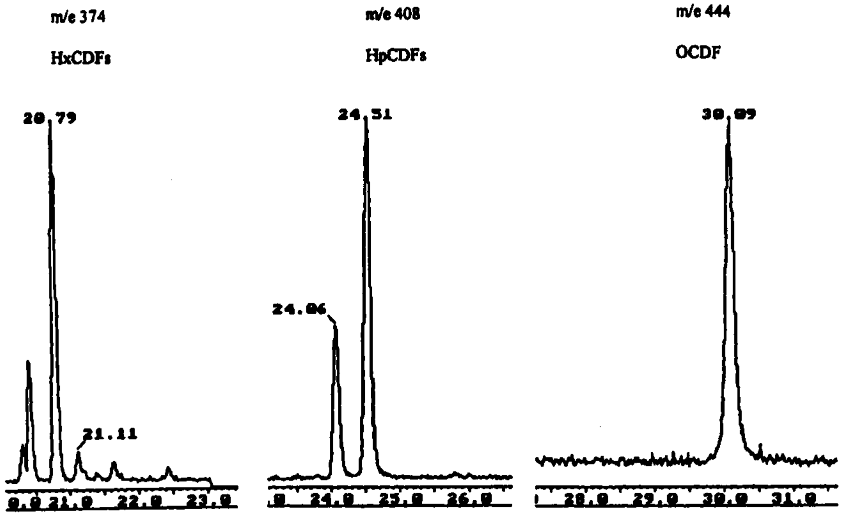

FIGURE 2 Typical ion chromatogram of PCDFs recorded in selected ion recording mode

For easy comparison, the results are also presented in the bar graphs in Figure 3. As expected, the concentration of the OCDD contaminant was the highest in all of the samples analyzed. It ranged from 6.79 ppm in a pole treated in 1955 and removed after 37 years of service, to as high as 216 μg/g in a pole treated in 1979 and removed after only 13 years (Figure 3). Since OCDD accounted for about 80% of the total PCDD/PCDF in most of the samples analyzed, the trend of changes in the total PCDD/PCDF levels was similar to that of OCDD. Because the initial PCDD/PCDF content in the poles was unknown, care was needed to identify trends in the changes in PCDD/PCDF content with time. The data shown in Table II and Figure 3 however, seems to show a trend of decreasing total PCDD/PCDF content with increasing service life. The 0–20 mm assay zone in the ground-line section of a 1979 jack pine pole contained the highest total PCDD/PCDF concentration, close to 240. The 1955 and 1956 jack pine poles contained less than 20 μg/g total PCDD/PCDF. As shown in Table II, the total PCDD/PCDF contents were higher in the 0–20 mm zones, than in the corresponding 20–40 mm zones, in all the poles treated prior to 1967. In the older 1956 and 1960 poles, the total PCDD/PCDF concentrations in the 0–20 mm and 20–40 mm assay zones, were similar. In the 1955 pole that had been in service for 37 years, the total PCDD/PCDF content was higher in the 20–40 mm assay zones than the 0–20 mm zones (Table II).

TABLE II PCDD/PCDF concentration (ppm) in various assay zones in jack pine poles recovered after selected service lives

Year Treated	*# of Years in Service*	*Assay Zone*[a]	*OCDD*	*1,2,3,4,6,7,8-HpCDD*	*1,2,3,4,6,7,9-HpCDD*	*Total HxCDD*	*OCDF*	*Total HpCDF*	*Total HxCDF*	*Total PCDD/PCDF*
1955	37	G1	10.1	0.86	0.46	0.21	1.90	1.66	0.21	15.4
		G2	14.7	0.67	0.53	0.05	1.14	1.16	0.12	18.4
		T1	6.79	0.64	0.38	0.08	1.41	1.47	0.13	10.9
		T2	16.3	0.79	1.00	0.05	0.68	0.81	0.07	19.7
1956	33	G1	12.7	0.94	0.65	0.05	0.47	0.98	0.12	15.9
		G2	13.4	0.90	0.65	0.06	0.46	0.95	0.12	16.5
1960	29	G1	40.3	3.93	2.53	0.29	1.42	8.12	0.53	57.1
		G2	50.4	1.65	1.55	0.07	0.62	2.24	0.53	57.1
1967	22	G1	98	22.7	10.9	0.86	0.87	1.61	0.90	136
		G2	50.4	2.23	2.51	0.08	0.40	0.77	0.07	56.5
1977	15	G1	50.7	3.06	2.27	0.19	1.18	1.13	0.12	58.7
		G2	32.7	2.60	1.47	0.15	1.33	1.17	0.09	39.5
		T1	45.8	2.01	1.50	0.09	0.57	0.36	0.01	50.3
		T2	19.8	1.01	0.61	0.05	0.39	0.36	0.04	22.3
1976	13	G1	124	5.14	4.42	0.45	0.42	1.79	0.70	137
		G2	27.7	1.59	1.12	0.13	0.47	1.36	0.34	32.7
1979	13	G1	216	6.06	5.35	0.31	4.95	5.51	0.29	239
		G2	177	11.0	32.1	1.17	2.40	3.40	0.34	227
		B1	140	6.34	4.11	0.42	4.86	6.98	0.75	164
		B2	134	6.56	12.6	0.47	2.06	2.94	0.25	159

a. Assay zone abbreviations G1: Groundline 0–20 mm; G2: Groundline 20–40 mm; T1: Top section 0–20 mm; T2: Top section 20–40 mm; B1: Brand section 0–20 mm; B2; Brand section 20–40 mm.

Regarding the distribution of different congeners, the level of PCDD decreased with decreasing chlorine substitution, *i.e.* [OCDD] > [HpCDD] > [HxCDD]. On the other hand, the concentration of HpCDF was higher than that of OCDF in most samples. The PCDFs were present in much lower concentrations than the PCDDs. The level of HpCDD and HxCDD were found to be highest in the 1979 sample (0–20 mm layer) and lowest in the 1956 sample. The distribution of PCDF in different samples was different from that of PCDD with more being found in the poles treated in 1979 and 1960.

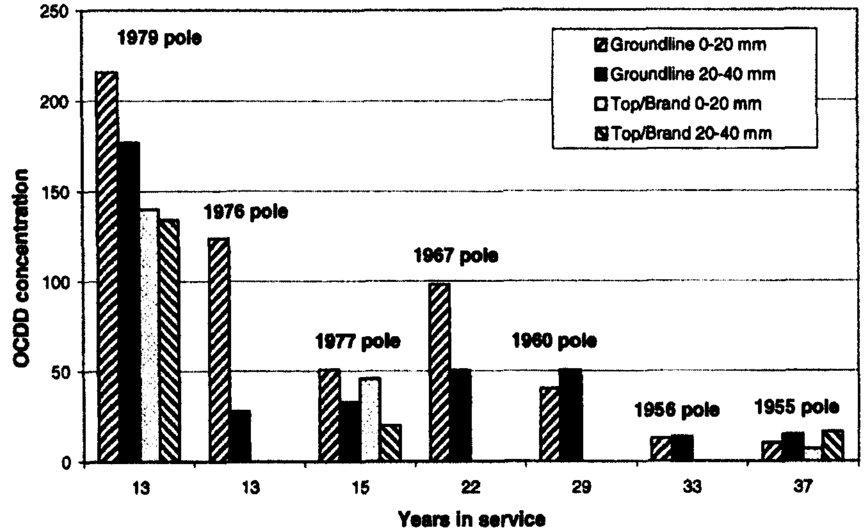

FIGURE 3 OCDD concentration (μg/g) in various assay zones at the ground-line and above ground (Top or Brand) sampling sections of jack pine poles recovered after selected years in service

Chlorophenols are probably the most important industrial source of PCDD and PCDF. Analyses of PCDD and PCDF in various chlorophenols and derivatives, especially technical grade pentachlorophenol, have been widely studied. The levels of different PCDD/PCDF congeners can vary significantly in technical grade pentachlorophenol from different sources, with OCDD ranging from as low as 210 μg/g, to as high as 3300 μg/g. The HpCDD concentration was reported to vary from 125 μg/g to 870 μg/g in different samples[16]. This high degree of variation in PCDD and PCDF concentration in the preservative will be reflected in the concentration of PCDD and PCDF in utility poles treated with pentachlorophenol from different sources. In addition, when pentachlorophenol treated poles are exposed to different weathering conditions, their PCDD and PCDF concentrations will change by different degrees. To minimise this, the poles in this study were all selected from the same geographical region, and would have had similar effects of weathering. The long term changes of PCDD/PCDF concentration in treated poles have not been extensively studied. Available data[3,5] indicated photolytic reactions of PCDD, both photo-destruction and photo-formation, occur only in the outer 0.5 mm layer. For wood samples treated with technical PCP in oil, no change in OCDD concentration was observed after exposure to sunlight for up to 2 years. The results from this current study, however, suggest a significant change in PCDD/PCDF level with the age of the poles. The PCDD/PCDF concentration tended to decrease with age, as shown in Table II. The 0–20 mm assay in the 1976 and 1967 pole contained 2 to 4 times more PCDD/PCDF than the 20–40 mm assay, while the two assays in the 1956 and 1960 pole contained similar amounts of PCDD/PCDF (Table II). Further, the total PCDD/PCDF concentration was higher in the 20–40 mm assay than in the 0–20 mm assay, in the pole treated in 1955. This would suggest that with extended time the dioxins and furans tended to decrease in both assay zones and the rate of decrease was faster in the outer assay zone.

PCDDs and PCDFs may be lost from the poles through physical processes such as evaporation, leaching, and migration with carrying oil. Their changes can also be affected by chemical processes, such as photochemical degradation[3] and photochemical formation from PCP[2–5] and predioxins[6]. It is extremely difficult to assess the physical and chemical changes of PCDDs and PCDFs in the treated poles, since the initial PCDD/PCDF concentrations were unknown. In addition, the influence of weathering is different from year to year, while the climatic/geological conditions where the poles were in service, were slightly different. A hypothesis of the chemical and/or physical changes of PCDDs/PCDFs with time can, however, be proposed from a careful examination of the results of this study.

It is reasonable to assume that the distribution of the different PCDD congeners in the various assay zones of the same pole sample, was uniform when the pole was first treated. Therefore, changes in the congener distribution with time can provide evidence of PCDD/PCDF changes through chemical or physical pathways. It is known that OCDD has a vapor pressure of 2.4×10^{-5} Pa while that of HxCDD is 8.8×10^{-5} Pa. It is also known that the less chlorinated HxCDD are more soluble than the highly chlorinated OCDD. Therefore, if the physical processes such as evaporation, leaching, and migration with carrier oil were the dominate pathways of PCDD/PCDF loss, the ratio of OCDD/HxCDD should be higher in the outer surface assay zones of the treated wood, than the inner assay zones. Photochemical formation of OCDD would also result in a higher OCDD/HxCDD ratio in the outer surface layer. On the other hand, if photochemical dechlorination of highly chlorinated PCDDs/PCDFs dominated, the

OCDD/HxCDD ratio should be lower in the outer surface assay than the inner assay zone of the pole.

According to Crosby[16], the HxCDD:HpCDD:OCDD ratio in technical PCP is 1:10–70:50–625. As shown in Figure 4, the OCDD/HxCDD ratios in 22–37 year-old poles are much lower in the 0–20 mm assay compared to that at 20–40 mm, suggesting extensive photodechlorination. One exception, is a 33 year-old pole that has a slightly higher OCDD/HxCDD ratio in the 0–20 mm assay zone, than in the 20–40 mm layer. This exception may be explained if that the particular sample was taken from a location of the pole where photochemical reactions are minimum. This might result if the pole ground-line section had been lower than indicated, in which case soil would have prevented photoexposure. As can also be seen from Figure 4, the OCDD/HxCDD ratios in the 0–20 mm assay zone were higher than the corresponding 20–40 mm layer, in the 13–15 year-old poles. This observation suggested that in the early years of service, preferential loss of less chlorinated dioxins and/or photochemical formation of OCDD are the more important pathways of change, compared to the photochemical dechlorination pathway. The HxCDD:HpCDD:OCDD ratios in various zones of poles recovered after different service lives are listed in Table III. HpCDD:HxCDD concentration ratios showed a trend of change similar to that of the OCDD/HxCDD ratios.

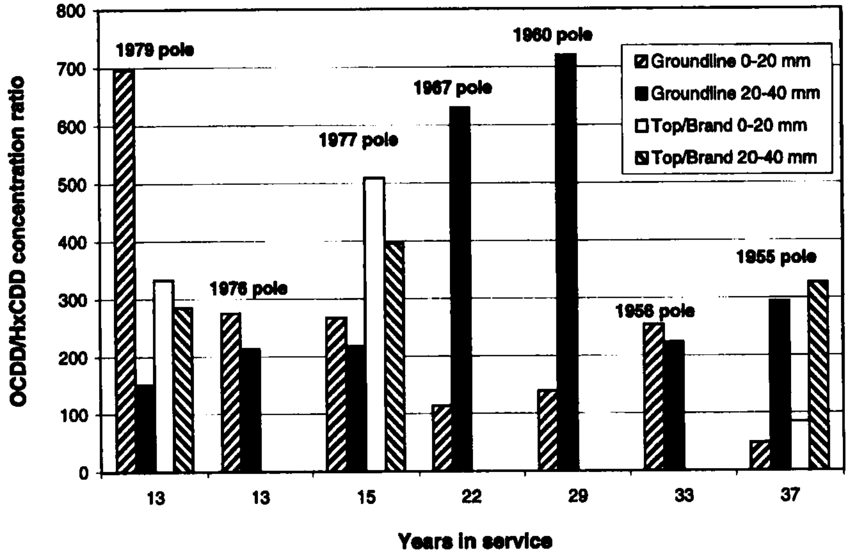

FIGURE 4 OCDD/HxCDD concentration ratio in various assay zones at the ground-line and above ground (Top or Brand) sampling sections of jack pine poles recovered after selected years in service

TABLE III Ratios of Cl_6-, Cl_7-, and Cl_8-substituted PCDDs in various assay zones[a] in PCP-treated jack pine poles recovered after selected service lives

Year Treated	*# of Years in Service*	*Assay Zone*	*HxCDD:HpCDD:OCDD*
1955	37	G1	1:6:50
		G2	1:24:294
		T1	1:13:85
		T2	1:36:326
1956	33	G1	1:32:254
		G2	1:26:223
1960	29	G1	1:22:139
		G2	1:46:720
1967	22	G1	1:39:114
		G2	1:59:630
1977	15	G1	1:28:267
		G2	1:27:218
		T1	1:39:509
		T2	1:32:396
1976	13	G1	1:21:276
		G2	1:21:213
1979	13	G1	1:37:697
		G2	1:37:151
		B1	1:25:333
		B2	1:41:285

a. Assay zone abbreviations same as Table II.

A sample of technical PCP used at a wood preserving plant in British Columbia, Canada was analyzed and found to contain about 1600 μg/g OCDD. Assuming that the poles were treated to have an initial PCP concentration of 35,000 μg/g (15 kg/m^3), the OCDD concentration in the pole would be 56 μg/g, much lower than the highest values obtained in this study. Taking into account the fact that earlier technical PCP products tend to have higher concentrations of PCDD and PCDF than those of today, the surprising 216 μg/g OCDD found in the 1979 jack pine pole is still hard to justify. More extensive studies are needed to establish the exact long-term changes of PCDD/PCDF content in PCP-treated wood waste.

CONCLUSIONS

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDF's) in pentachlorophenol treated jackpine utility poles were analyzed using a GCMS method. Octachlorodibenzo-*p*-dioxin (OCDD), heptachlorodibenzo-*p*-dioxins (HpCDDs), hexachlorodibenzo-*p*-dioxins, (HxCDDs) octachlorodibenzofuran (OCDF), heptachlorodibenzofurans (HpCDFs), and hexachlorodibenzofurans (HxCDFs) were identified and quantified. HxCDDs, HpCDF's, and HxCDF's were quantified as total congener concentrations, due to a lack of standards for all isomers. No effort was made to identify or quantify PCDDs and PCDFs contain five chlorines or less due to their much lower concentration compare to the higher chlorinated compounds.

OCDD was by far the most dominant form of PCDD/PCDF and accounted for 66%, to as high as 91%, of total PCDD/PCDF in the samples analyzed. PCDD/PCDF content in the poles seemed to change dramatically with service life. One pole was found to contain 11–20 μg/g of total PCDD/PCDF in various assay zones after 37 years in service. In comparison, another pole contained up to 240 μg/g of total PCDD/PCDF after 13 years of service.

Data from this study suggested that in the first years of service, dioxins, especially the lower chlorinated congeners, were lost mainly through physical processes. After prolonged service, photochemical dechlorination resulted in a relatively higher content of the lower chlorinated dioxins in the outer surface layers of the poles.

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