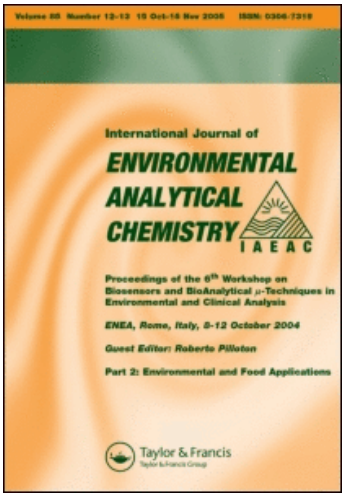

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F. Cui[ab]; J. N. R. Ruddick[a]
[a] Department of Wood Science, Faculty of Forestry, The University of British Columbia, Vancouver, B.C., Canada [b] Forintek Canada Corp., Vancouver, B.C.

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A NEW PROCEDURE FOR THE ANALYSIS OF CHLOROPHENOLS IN PRESERVATIVE TREATED UTILITY POLES

F. CUI* and J.N.R. RUDDICK†

Department of Wood Science, Faculty of Forestry, The University of British Columbia, 270–2357 Main Mall, Vancouver, B.C., Canada V6T 1Z4

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Preservative concentration in pentachlorophenol (PCP) treated wood has been traditionally determined in the industry using x-ray spectrometry or titrametric analysis of chloride. Although the methods are simple and inexpensive, they have a number of drawbacks. One of the main limitations is that the individual concentration of PCP, tetrachlorophenol (TCP), and other chlorinated chemicals cannot be determined. They are also sensitive to interferences. In the present study, procedures were developed to analyze PCP, TCP, pentachloroanisole (PCA) and trichlorophenols using gas chromatography-mass spectrometry (GC-MS). The wood to be analyzed was ground into sawdust and extracted with methanol/acetic acid in a sonicator. The extract was then pre-purified using either a Florisil™ column (for softwood samples) or an ion exchange column (for heartwood samples) before GC-MS analysis. No PCA or trichlorophenols were detected in eight jackpine poles which has been in service for 13–37 years. The concentration of PCP in the surface 0–20 mm assay zone ranged from 5,200 to 27,000 μg/g, while that in the 20–40 mm zone was 13–60% of the 0–20 mm zone. The lower chlorinated 2,3,4,6-tetrachlorophenol was found at 90–1500 μg/g. No other tetrachlorophenol isomers were detected.

KEY WORDS: Pentachlorophenol, GC-MS, wood preservative, utility poles, analysis.

INTRODUCTION

Pentachlorophenol was the wood preservative most widely used by the utility pole industry, from the 1950s to the 1970s. About 80% of all poles installed during this time period were treated with PCP. With more and more poles reaching the end of their service life, the disposal of PCP-treated wood waste has now become an environmental concern. PCP-treated wood contains a complex mixture of chemicals, some of which originate from the technical grade PCP used in the treating process, while the rest come from the carrier oil. Depending upon the manufacturing procedure, technical grade PCP contains various amounts of toxic impurities, such as polychlorodibenzo-p-dioxins (PCDDs), and polychlorodibenzofurans (PCDFs).

*Present Address: Forintek Canada Corp., 2665 East Mall, Vancouver, B.C. V6T 1W5
†Corresponding author

Other chlorinated phenols such as tetrachlorophenols (TCP), trichlorophenols, and higher chlorophenols (polychlorophenoxyphenols etc.) may also be present. The composition of technical grade PCP from a number of sources has been reported[1,2]. Although the amount and composition of the technical PCP and treating oil present in freshly treated poles might be known, the concentration of the various chemicals will change during service, due to chemical and physical processes. The chemical reactions include photochemical and biochemical degradation of the chlorophenols and biochemical transformation of PCP to other toxic chemicals such as PCA. The degree to which photodegradation of PCP and TCP occurs in utility poles is uncertain. However, the photochemical formation of octachlorodibenzo-*p*-dioxin from PCP has been reported[3–5]. No information is available regarding the biochemical degradation by bacteria and fungi of PCP and other chlorophenols in poles during service, however, the presence of known metabolites of the chlorophenols in the poles could identify the importance of biochemical activities. PCP and other chemicals can also be lost by physical processes such as volatilization, and migration with the oil solvent or rain water. TCP is more volatile and more soluble than PCP and therefore should be lost more rapidly from the pole surface. This, however, must be verified by experiment.

Previous studies[6] have shown that recovered poles still have high levels of PCP. Traditionally, the PCP content in treated poles has been determined by extracting the chemical and titrating the extract to measure the chloride content using the Volhard procedure[7]. More recently, the use of x-ray spectrometers has become the standard quality control method for the treating industry, largely because of its ease of use. In this paper, we report our studies on the level of chlorophenols in eight jackpine poles determined using a GC-MS method. Pre-purification procedures developed for sample clean-up prior to GC-MS analysis are also reported.

EXPERIMENTAL

Materials

All solvents used in this experiment were Omnisolv (spectral grade) from BDH. PCP (99%) was purchased from Aldrich. 2,3,4,6-Tetrachlorophenol standards were from Fluka. 2,4,6-Tribromophenol from Eastman Kodak was recrystallized in hexane/diethyl ether before use. All other chemicals were analytical reagents. Florisil from Aldrich (60–100 mesh, reagent grade) was washed with methylene chloride and hexane, and activated at 130 °C for 24 hours. The ion exchange resin was Amberlite CG400 anion exchange resin (analytical grade). The dry resin (200 g, in chloride form) was allowed to swell in water overnight before packed into a glass column. The column was eluted with 10% sodium acetate until no chloride ion was detected with silver nitrate. The resin was first washed in the column with deionized water until the eluent was neutral, and then with 1 liter of glacial acetic acid and finally with 1 liter of methanol. The column was allowed to drain after methanol washing and the resin was stored in a tightly sealed bottle to prevent the wet resin from drying.

Sections from eight jackpine (*Pinus banksiana* Lamb.) poles were provided by Bell Canada to enable the determination of the residual chemical after 13–37 years of service.

The first sections provided were recovered from poles treated in 1956, 1957, 1960, 1967, 1974, and 1976, respectively and removed in 1989. These samples were stored indoors between 1989 and the time of analysis in late 1991. The rest sections were recovered from poles treated in 1955, 1977, and 1979, and removed in 1992. These second group of samples were analyzed as soon as they were received.

Each pole to be analyzed was sampled at two locations, the groundline section and the "brand" section which was approximately 3 meters from the butt of the pole. The "top" section was used when the "brand" section was unavailable. At each section two analytical zones, 0–20 mm and 20–40 mm from the pole surface were studied. The choice of these two zones was made based upon the limited preservative penetration normally achieved in jackpine poles. A second factor was the effect of any biological activity on the chemical composition in the groundline should be observed in these zones. Care was taken that the sampled area was at least 0.5 cm away from any "check" to ensure homogeneity of the sample. The samples were cut into small pieces and ground to sawdust in a Wiley Mill fitted with a 20 mesh screen. After milling, each sample was mixed thoroughly and its PCP concentration estimated on an ASOMA™ X-Ray Fluorescence Analyzer. The amount of sample to be used for the extraction step described below was based on this estimated PCP concentration.

All analyses were carried on a VG Trio-1000 GC-MS system operating in electron ionization (EI) mode at 70 ev. The ion source temperature was 240 °C and the interface temperature was 250 °C. All quantitation were calculated based on peak area of the following ions: TCP acetate m/z 230, 232, and 234; PCP acetate m/z 264, 266, and 268; tribromophenol acetate m/z 328, 330, and 332. The GC column was a 25 meter HP-5 column (0.2 mm ID, 0.32 μm film thickness) from Hewlett Packard. The GC conditions were as follows: initial oven temerature 85 °C, initial time 2 minutes, rate 15 °C/minute, final temperature 265 °C, final time 2 minutes, injector temperature 250 °C.

Extraction

The extraction method used was a modification of a published procedure[8]. It involved sonication of sawdust in acidified methanol. For a jackpine sapwood sample treated with 500 ppm PCP, the extraction efficiency was 99.5%. A small amount (0.1–0.5 g, depending on approximate PCP content) of PCP containing sawdust was placed in a 10 mL screwcap (Teflon-lined) test tube after which 10 mL methanol and 0.1 mL glacial acetic acid were added. The test tube was shaken briefly and sonicated at room temperature for 15 minutes. The test tube was again shaken briefly and centrifuged. The clear solution was transferred to a 25 mL volumetric flask. The sawdust residue was further extracted twice with 5 mL methanol and 0.05 mL glacial acetic acid as above and the clear solution transferred to the same volumetric flask. The sawdust residual was finally shaken with 5 mL methanol, centrifuged, and clear solution transferred to the volumetric flask. The combined extract was diluted to exactly 25.00 mL.

Florisil column clean-up

Sapwood samples contain mainly chlorophenols and oil, which are of different polarity. A Florisil column was needed to separate the polar chlorophenols from the nonpolar oil carrier solvent. A small volume of the extract (accurate to 0.010 mL, containing 10–20 μg PCP) was mixed with the internal standard tribromophenol (20 μg) in a 5 mL vial and evaporated to dryness with a stream of nitrogen. The residue was transferred with the help of a small amount of 1:1 hexane/methylene chloride (1–2 mL) to a column (30 cm × 0.1 cm) containing 1 gram of Florisil. The column was eluted with 10 mL 1:1 hexane/methylene chloride. The eluent which contained mainly oil was discarded. The column was then eluted with 10 mL 1:9:0.1 diethyl ether/hexane/acetic acid (volume ratio) and the eluent collected. One mL of the eluent was transferred into a test tube and evaporated to dryness with nitrogen. This fraction contained mainly PCP, TCP, and tribromophenol. To the residue was added 1 mL pH 9.9 sodium bicarbonate buffer. The mixture was derivatized with 100 μL acetic anhydride at room temperature for 30 minutes. All PCP, TCP, and tribromophenol were converted to their acetates during the derivatization. The acetates were then extracted with 1 mL isooctane and 1 μL of the extract injected for GC-MS analysis. The pre-purification procedure for PCA analysis was similar to that for PCP analysis using Florisil column. The oil fraction was removed by washing with hexane and the anisole was recovered by eluting the column with methylene chloride. Tribromoanisole was used as the internal standard for PCA quantification.

Ion exchange column clean-up

Heartwood samples contain wood extractives in addition to the chlorophenols. Although chlorophenols and the wood extractives have similar polarity, they have significantly different acidity and ion exchange columns can easily separate the two components. A small volume of the extract (accurate to 0.010 mL, containing 10–20 μg PCP) was mixed with the internal standard tribromophenol (20 μg) and added to a column (30 cm × 0.7 cm) containing 0.5 g BDH CG-400 anion exchange resin (acetate form). The column was washed with 10 mL methanol and the eluent discarded. The column was then washed with 10 mL acetic acid and the eluent collected. One mL of the eluent was transferred to a 10 mL screwcap test tube and evaporated at 40–50 °C with a stream of nitrogen. The residue was derivatized as described above.

RESULTS AND DISCUSSION

Extracts of PCP treated wood contain, in addition to PCP and TCP, large amounts of wood extractives and oil. Although analysis parameters can be selected such that the contaminants do not interfere with the determination of PCP and TCP, the GC column and ion source of the mass spectrometer could become heavily contaminated in a short time. The C-18 cartridge clean up procedure reported by Goewie and Berkhof[9] was found to be unsatisfac-

tory in our study, probably due to the high oil content present in the pole material. Florisil column and ion exchange column clean-up procedures was used to pre-purify sapwood and heartwood extracts, respectively. Florisil (magnesium silicate) is a very polar material which is useful for separating chemicals of different polarity. It is particularly useful for purifying PCP samples extracted from sapwood, since the major impurity, the treating oil, is nonpolar while PCP is a polar compound.

The use of a Florisil column for the purification of PCP samples was reported previously by Wagner *et al.*[10]. It was found, however, that the column irreversibly bound free PCP and was therefore unsuitable for quantitative analysis. This difficulty can be overcome by treating the sample with diazomethane, to convert the PCP to PCA, before Florisil column clean-up. This strategy is impractical for two reasons. Firstly, diazomethane is an extremely toxic and potentially explosive chemical, so that it cannot be used in a normal laboratory on a routine basis. The second drawback was that PCA could not be distinguished and analyzed in the same sample, since all the PCP was converted to PCA. In the present study, it was demonstrated that the addition of 1% glacial acetic acid was able to quantitatively recover PCP from Florisil column. As can be seen from Figure 1, the pre-purified sample was free from interference and contaminants. Consequently, the lifetime of the GC column was significantly extended, and frequent cleaning of ion source of the mass spectrometer was avoided.

Ion exchange has been previously used to purify PCP containing samples extracted from wood, contaminated soil, and water[8,11,12]. It was particularly useful for separating PCP from phenolic wood extractives. The Florisil column, on the other hand, could not separate these two components, since they are of similar polarity.

X-ray spectrometry is a simple, fast, and inexpensive method for the estimation of total chlorinated compounds in treated wood. This method, however, does not have the sensitivity and specificity for many purposes where PCP and anisoles or lower chlorinated phenols need to be differentiated, or when high sensitivities are required. The GC-MS method used in this study can detect low levels of any interested compounds with high specificity and accuracy. Detection of PCP, PCA, and TCP at 1 μg/g level was achieved without difficulty. Since PCP and TCP were present in high levels in all of our samples, and PCP, PCA, and other possible chlorinated compounds have similar toxicity, the detection of these compounds at lower levels were not pursued. As shown in Figure 2 the results from x-ray and GC-MS analyses are in some cases similar, with the x-ray results always being lower than the more specific GC-MS analyses. It was found in this study, that the presence of the sulfate ion can strongly interfere with the determination of PCP in treated wood, resulting in an underestimation of the chlorophenate concentration. It was also noted that when high levels of carrier oil are present in the sample, the preparation of a pressed ground wood pellet resulted in some loss of oil during the process, which also caused depletion of the PCP and TCP again resulting in a low value. This is not a major concern to the industry since the technique is only employed to determine whether the treatment has achieved the threshold value required for the treated wood to perform adequately. In practice, commodities are treated to retentions in excess of the target, since the cost involved in re-treating the product should it fail to achieve the standard retention is much greater than the cost of the additional chemical. The differences were not consistent, particularly for the lower concentrations of

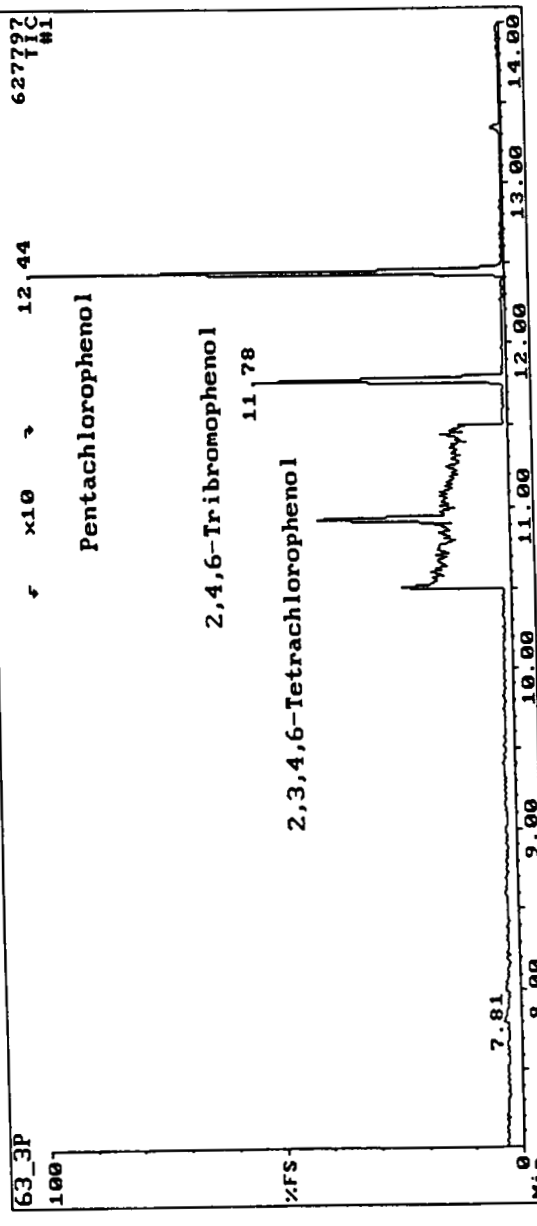

Figure 1 Typical total ion chromatogram (TIC) of a sample extracted from a jack pine pole after florisil clean up.

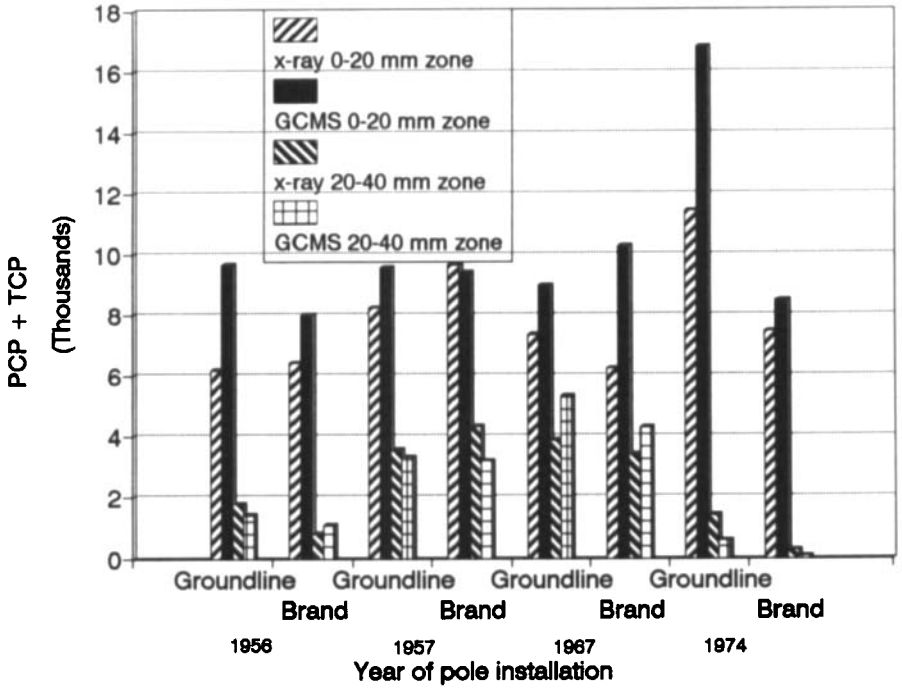

Figure 2 Comparison of the total chlorophenol concentrations (in μg/g) as determined by x-ray spectrometry and the GC-MS method.

chlorophenols. The PCDDs and PCDFs, which belong to a class of highly toxic compounds, will be discussed in a future publication.

Listed in Table 1 are concentrations of TCP and PCP in sections removed from eight different poles. The PCP concentration in the surface 0–20 mm assay zone varied from 27,000 μg/g to 5,200 μg/g, while the corresponding concentration at 20–40 mm was (with two exceptions) only 13–60% of that in the 0–20 mm zone. In one 15 year old pole the PCP content in the 20 to 40 mm zone is actually greater than that in the outer 0 to 20 mm zone. One explanation for this, would be the excessive loss (bleeding) of preservative from the pole surface, which occasionally occurs. Previous studies of more than eighty PCP-treated jack pine poles[6,13] have suggested that freshly treated jack pine poles contain approximately 16 kg/m^3 (or 38,000 ppm) in the outer 20 mm of treated wood. This is somewhat higher than the 27,000 μg/g measured after 13 years (Table 1) and when combined with the data from this study, suggests a trend of decreasing PCP concentration with the increasing service life, with the greatest loss occurring during the early years in service. This confirms observations made in an earlier study of PCP depletion in southern pine poles[14].

The TCP concentration expressed as a percentage of the total PCP + TCP content varied from 1 to 17% (Figure 3), although the majority of the data fell within the range 4 to 14%. At the groundline, the TCP percentage measured in both the outer and inner assay zones

Table 1 Pentachlorophenol and tetrachlorophenol content in recovered jack pine utility poles.

Year Pole was Produced	Year Pole was Removed	No. of Years in Service	Sampling Location on Pole	Chemical Concentration (μg/g)			
				0-20 mm assay zone		20-40 mm assay zone	
				PCP $\times 10^3$	TCP $\times 10^2$	PCP $\times 10^3$	TCP $\times 10^2$
1955	1992	37	Ground	5.2	2.5	2.6	2.0
			Top	5.8	6.4	3.5	3.5
1956	1989	33	Ground	9.0	6.5	1.3	1.3
			Brand	7.5	4.9	1.0	0.9
1957	1989	32	Ground	8.9	6.7	3.1	2.2
			Brand	9.3	1.1	2.9	3.1
1967	1989	22	Ground	8.3	6.8	4.9	4.5
			Brand	9.4	8.7	3.8	5.1
1977	1992	15	Ground	6.1	3.6	8.9	5.7
			Top	5.2	7.1	3.0	5.1
1974	1989	15	Ground	16	8.1	0.5	1.0
			Brand	7.8	6.9	0.58 (1.2)*	0.08 (0.07)*
1979	1992	13	Ground	17	2.8	9.2	5.9
			Top	14	3.3	7.3	6.6
1976	1989	13	Ground	27	15	13	7.2
			Brand	18	8.2	6.6	4.9

was between 4 and 9%. This is typical for commercial technical grade PCP[1,2]. This suggests that at the groundline, preservative depletion is strongly influenced by physical factors, which is consistent with the proposed importance of ground-water movement on chemical depletion[6]. Turning to the above ground results, the TCP content generally ranges from 6 to 14%. Why the proportion of TCP is higher in the above ground portion of the poles, is not clear. However, photochemical reduction of PCP to TCP can be ruled out, since such reactions would only occur at the surface. Although evaporation plays an important role in depleting chlorophenates from the above ground portion of poles[6], the higher vapour pressure of TCP, compared to that of PCP, would lead to more rapid loss of TCP from the pole surface. With the exception of the 37 year old pole, the percent TCP assayed at the "Brand" or top of the poles, was lower in the outer assay zone than in the inner zone, supporting the proposed mechanism of preservative depletion.

No conclusion can be reached from this study about the possibility of PCP biodegradation at the groundline of poles during service, since no common metabolites of PCP biodegradation were detected. The outer assay zone at the groundline failed to show any tendency to decrease with time over the 15 to 37 years suggesting that any biodegradation process is slow. Neither do the results support the gravitational migration of oil into the groundline from the above ground part of the pole. The outer 0–20 mm assays did not show any significant increase when the PCP level of the 13–15 year old poles was compared to that of poles which had been in service for 22–37 years. Instead a marked reduction of PCP retention was found in the older poles.

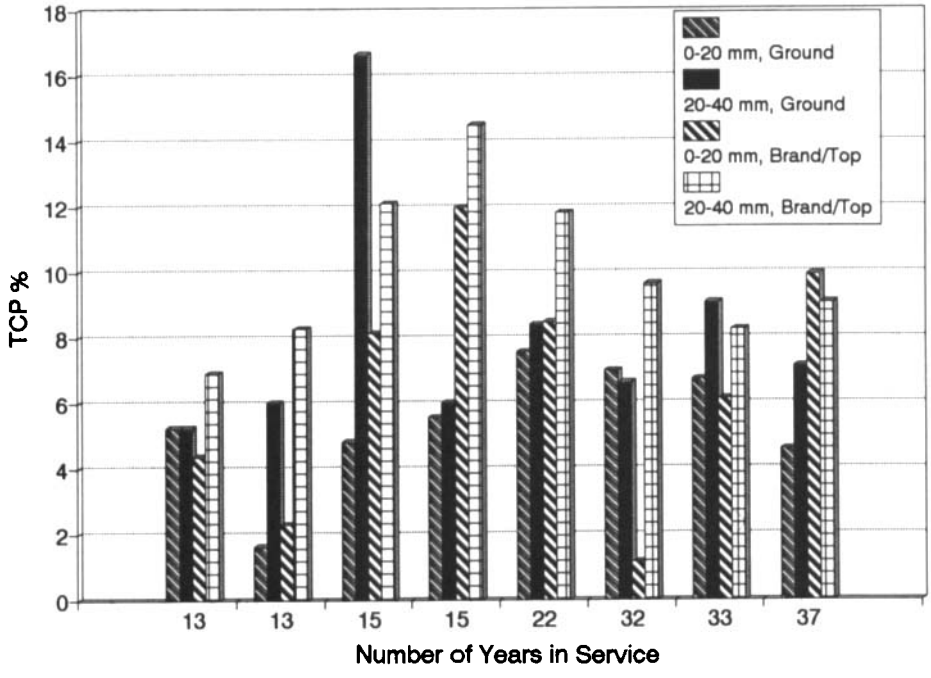

Figure 3 The TCP remaining in samples removed from the groundline and "Brand" (or top) of jack pine poles, expressed as a percentage of the total TCP and PCP content after various service lives.

CONCLUSIONS

Prior to GC-MS analysis of chlorinated compounds in eight jackpine poles with service lives of 13–37 years, sample clean-up was required, because of the presence of large amounts of oil in the sapwood and extractives in the heartwood. A Florisil column could eliminate virtually all contaminants from sapwood extracts, with quantitative recovery of PCP and TCP. An ion exchange column was found suitable for removing wood extractives from heartwood extracts. The PCP concentration varied from 27,000–5,200 μg/g in the outer 0–20 mm, and 1,000–13,000 μg/g in the 20–40 mm zone. When this data is compared to other data on PCP content in freshly treated jack pine poles, a trend of decreasing PCP level with increasing service life was confirmed, with the majority of the PCP being lost during the early years of service. Only one isomer of TCP, 2,3,4,6-tetrachlorophenol was detected. At the groundline the percent TCP, expressed as a fraction of the total chlorophenate content, was similar to that reported for technical grade PCP. In the above ground sections, the PCP content appeared to be depleted. For the above ground portion of the pole, the lower percentage of TCP in the outer assay zone compared to that for the inner zone, probably arises from differences in the rate of evaporation of TCP and PCP from poles in service. PCA, trichlorophenols and other lower chlorinated phenols were not detected in any of the samples.

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