DEVELOPMENT AND APPLICATION OF AN INTEGRATED APPROACH TO THE ANALYSIS OF PCP AND ITS PETROLEUM SOLVENT IN WOOD, SOIL AND WATER MATRICES

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ABSTRACT

This analytical method allows the quantification of pentachlorophenol (PCP) by gas chromatography (GC-ECD) and that of its petroleum solvent by infrared spectrometry (FTIR) from soil, wood and water samples. Its particularity resides in the use of a unique sample from which are extracted both PCP and its petroleum solvent. Extraction of the analytes from wood or soil is made by ultrasonication in a mixture of methanol-freon 113. Recoveries for the different matrices range from 95 to 99%. After its extraction from the matrix, the oil is separated from the PCP by extraction with freon 113. Then, the PCP still in the buffered aqueous solution is derivatized by acetic anhydride, extracted by freon 113, and injected in the GC. Absolute detection limits (3σ) for the PCP and the petroleum solvent are respectively 28 ng and 0.1 mg for 1 g of solid sample. The radial and longitudinal PCP and oil concentration distributions have been established for several combinations of wood species and treating processes. In-service pole analyses are also presented.

RÉSUMÉ

Cette méthode d'analyse permet la quantification du pentachlorophénol (PCP) par chromatographie gazeuse et détection par capture d'électrons (GC-ECD) et de l'huile par spectrométrie infra-rouge (FTIR) dans des matrices d'eau, de sol et de bois. Sa particularité réside dans le fait qu'un échantillon unique est utilisé, duquel le PCP et l'huile sont extraits. L'extraction des analytes du sol ou du bois est effectuée par ultrasons dans un mélange de méthanol-fréon 113. Les pourcentages de récupération pour les différentes matrices varient entre 95 et 99%. Après son extraction de la matrice, l'huile est séparée du PCP par extraction avec le fréon 113 et le PCP demeuré sous forme de phénolate dans la phase aqueuse tamponnée est acétylé, extrait dans du fréon 113 puis injecté dans le chromatographe. Les limites de détection absolues (calculées selon 3σ) du PCP et de l'huile sont respectivement de 28 ng et 0,1 mg pour un échantillon de 1 g. Les distributions longitudinales et radiales du PCP et de l'huile ont été établies pour différentes combinaisons d'espèces de bois et de types de traitement. Des résultats d'analyse de poteaux en service sont également présentés.

INTRODUCTION

A comprehensive pentachlorophenol management program is being undertaken at Hydro-Quebec (1). Part of this program is the characterization of the migration pathways of PCP and oil in the environment. This specific project will lead to the development of modelization software able to predict to which extent the PCP and the oil might migrate from the pole under various climatic and soil conditions (2). The software uses a database which defines the PCP and oil concentrations under various experimental conditions. This database is being built using data obtained through the analytical method developed at the Institut de recherche d'Hydro-Québec. Concentration data are established for both PCP and oil in water, wood and soil samples. For this reason, a versatile analytical protocol was necessary to cope with the three matrices, and also to provide PCP and oil determinations from the same sample treatment.

The sample treatment can take up to seventy percent (70%) of the time necessary to perform an analysis. In order to reduce our sample treatment, we developed an integrated approach that allows PCP and oil to be determined from a unique sample, using the same sample treatment. In a way to further reduce the sample treatment and provided only PCP is to be quantified, its analysis is often done using elemental methods such as X-Ray fluorescence (3) and neutron activation analysis (NAA) (4). While these methods are useful, their lack of specificity for the PCP molecule gives place to severe interferences due to the chloride content of soil and water samples. Specific detection of the PCP molecule was mandatory and the method was developed in such a fashion.

This paper presents the development of an analytical method for the quantification of both PCP and oil from the same sample, using a single sample treatment. The analytical performances of the method are presented. The PCP and oil concentrations in freshly treated wood poles are characterized for jack pine and red pine, treated by Domtar and the Industrie de Préservation du Bois (IPB) and their radial and longitudinal distributions are established. The sampling procedures developed to obtain the wood borings for the PCP and oil radial and longitudinal distributions are presented. In-service poles are also analyzed for their PCP and oil contents.

EXPERIMENTAL

Analytical method. A block diagram of the analytical method is presented in Figure 1. This method is based on the one proposed by Abrahamsson and Xie (5) for the analysis of PCP in water samples. An internal standard (2,3,6-trichlorophenol) is added to each sample prior to the extraction step. The internal standard allows to correct for losses which can occur during the extraction, separation and derivatization steps. The standard chosen meets the following requirements: i) it has not been detected in in-service poles up to 35 in age. ii) it has been established that its derivatization efficiency is similar to that of PCP.

Wood and soil samples are first extracted with a mixture of freon 113 and methanol (20 mL of each solvent for 1 g of material). For water samples where high PCP concentrations (> 5 μg/L) are expected, the sample (100 mL) is buffered by adding 2.5 g of sodium phosphate (Na_2HPO_4). When the concentration in the water sample is expected to be low (< 5 μg/L), a 1 L-volume is acidified and the PCP and oil are preconcentrated by extraction in freon 113.

Following the extraction, an aliquot of the organic phase is mixed with 100 mL of a buffered aqueous phase at pH 9.3. At this pH level, the PCP is mostly in its ionic form (phenolate ion) and stays in the aqueous phase. The oil is extracted with three 5 mL-volume of freon 113 and the PCP still in the aqueous phase is acetylated using 5 mL of acetic anhydride, back-extracted in a 8-mL volume of freon 113 and injected (1 μL) in the GC.

Optimization Experiments. The extraction of PCP and oil from the wood and soil matrices is done by ultrasonication.. Different mixtures were evaluated and the freon 113-methanol mixture provided the optimal extraction efficiency with a PCP recovery of 98.4% after 40 min of ultrasonication. The oil recovery was 95.2%. The PCP and oil extraction recoveries reached 96% and 93% respectively after only 10 min of ultrasonication. Other mixtures not using freon 113 were also investigated and led to recoveries ranging from 82 to 95%. The recovery values presented are the average of six replicates. For the unspiked treated wood, the recovery values were calculated by successively extracting the same samples. The quality of the extraction has been further confirmed by NAA in the following manner: treated wood samples were analyzed for their chlorine content which was attributed after proper correction to the PCP molecule, prior to any extraction and after the first and second extractions. Sub-samples were taken from the same sample to avoid any bias in the determination.

The recoveries of PCP and oil for the whole analytical protocol have been validated at different concentration levels using treated and untreated wood, and spiked blank soil samples. The results are presented in Table 1.

Table 1. Validation of the analytical method for wood and soil samples

Sample	PCP			Oil		
	Added	Recovered[a]		Added	Recovered[a]	
	(mg)	(%)	RSD	(mg)	(%)	RSD
Spiked wood	0.095	94	7	8	114	32
	11	97	5	40	104	1
				240	101	1
Treated wood	0	98.5	0.5	0	N.A.	
Spiked soil	0.6	99	7	17	115	8
	6	103	15	130	101	4

(a) Based on 6 replicates

The level of recovery is satisfactory, for oil as for PCP, considering that both have been derived from the same sample. The high oil recovery RSD obtained for the 8 mg spike may be partly due to irreproducible contribution from wood extractives. For the soil, the values obtained are representative of the nature of the soil used, and further confirmations would be needed for different soils, particularly those with a high organic carbon content, as they are prone to adsorb PCP.

Standard Preparation. At first, the standards were prepared by adding appropriate aliquots of a standard solution of PCP in toluene to uncontaminated soil or wood samples (blank). The oil was added by weighing the appropriate volume. These standards were then submitted to the whole analytical protocol including ultrasonication. The purpose was to take into account the solvent losses which would occur during the ultrasonication and filtration steps. The accuracy of these steps has been improved by using erlenmeyers with screw caps and by filtering with a fritted glass filter immerged in the solvent mixture. The effectiveness of this approach was verified by comparing calibration curves obtained with standards prepared in wood or soil with others obtained by adding PCP and oil aliquots directly to the aqueous phase. The calibration curves obtained for the PCP are shown in Figure 2. The slopes of these curves show little variation with regard to their preparation mode. When all the data pertaining to the PCP are plotted on a single curve, the slope is 1.464 and the regression coefficient is 0.994. The same comparison was established for the oil, and the results are presented in Figure 3. The same conclusion applies for the oil.

These comparisons show that no losses occur during the extraction and filtration steps as the characteristics of the curves obtained for both PCP and oil are similar. The PCP and oil standards are therefore prepared by adding appropriate aliquots to the aqueous phase. Pipetted volumes of oil and a solution of PCP in methanol are used.

Instrumental conditions. The PCP is analyzed by GC-ECD and the operating conditions of the instrumentation are summarized in Table 2.

The oil is analyzed by FTIR, according to APHA method 503B (6). The samples and standards are scanned from 3200 to 2700 cm^{-1}. The solvent contribution is subtracted. The absorbance is measured by constructing a straight baseline over the spectral range scanned and by measuring the absorbance from the baseline to the peak maximum at 2930 cm^{-1}. A 1 cm path-length cell is used.

Table 2. Operating conditions for the GC-ECD

Instrument	HP5890 Gas Chromatograph
Detector	Electron capture detector
Gas flow rate	Column: He, 2.45 mL/min Detector: Ar-5%CH_4, 40 mL/min
Column	HP Ultra2, 25 m x 0.32 mm x 0.52 μm (film thickness)
Temperature Programmation	Initial Temperature: 120°C Heating rate: 10°C/min Final Temperature: 220°C for 1 min
Total Analysis Time	11 min
Injected volume	1 μL

The analytical performances presented in Table 3 are the same for the three matrices. The method, as described, provides appropriate detection limits and working ranges. These figures could be improved by changing the sample-to-solvent ratio, in order to preconcentrate the analytes.

Table 3. Analytical performances of the method

Parameter		PCP	Oil
Detection limit(a)	Relative	0.2 μg/L	2 mg/L
	Absolute	28 ng	0.1 mg
Working range (decades)		3	3

(a) For 1-g solid sample.

Quality Control Program. A quality control program has been developed to ensure that the data obtained are precise and accurate. This program includes three types of control. The first consists of reinjecting periodically two of the seven standards (the second and the sixth) to verify that the sensitivity of the detector is maintained during the analysis. The second control aims at verifying the accuracy of the method through the analysis of blank samples spiked with known quantities of PCP and oil. Finally, the third control establishes the precision of the method by the analysis of duplicate samples. At least 10% of the samples are reanalyzed.

Sampling and treatment of wood samples. The sampling procedure developed to obtain wood samples to establish PCP and oil longitudinal distribution is described in Figure 4. The zero position corresponds to the base of the pole while the 12.3-m position represents the top. The wood samples are obtained by using a Pressler borer. The pole is sampled over its entire diameter, and two borings are taken, perpendicular to each other. These borings are combined and their length and weight are noted to calculate the wood density. The samples are reduced in powder through a water-cooled grinder and homogenized. The effect of grinding has been assessed by submitting two halves of the same boring to analysis by NAA, one grinded and the other intact. The results have shown that the process has no significant effect on the chlorine content of the samples (i.e. PCP content).

For radial distribution (Fig. 5), the sampling is the same as for longitudinal distribution, except that the corresponding 1 cm long sections of borings A, B, C and D are combined. A small shaving is removed from each boring to prevent any bias in the determination due to a possible surface phenomenon (presence of contaminants, migration of preservative solution at the surface of the pole, etc.). The average density of the four 1 cm long sections is determined and these sections are then grinded and homogenized. The concentration values thus represent the average of borings A, B, C and D. This sampling procedure should ensure adequate representation of the concentration values obtained. After their treatment, the samples are stored in a freezer at -20°C overnight and analyzed the next day.

The density of each sample is calculated to account for its oil content which can contribute significantly to the accepted value (i.e. 384 kg/m^3 for dry jack pine and dry red pine).

Figure 6 shows the radial distribution of wood density, as obtained for jack pine (12.3-m, class-4) freshly treated by the Industrie de Préservation du Bois (IPB). This figure shows the important gap between the value normally used and the values obtained in our laboratory, which vary between 600 and 790 kg/m^3. These values are used to convert the PCP and oil concentrations from mg/g to kg/m^3.

RESULTS AND DISCUSSION

When put in service, the pole looses a fraction of the preservative solution and thus becomes the source of PCP and oil emission in the environment. It is thus important to establish the values initially in the pole in order to correlate these values to those obtained in the soil and water around the pole. Therefore, freshly treated poles have been characterized longitudinally and radially for their PCP and oil contents. The effect of pine species and treating processes have been evaluated. These findings have been compared with PCP and oil concentrations found in in-service poles.

Longitudinal Distribution. The effect of pine species on the PCP and oil longitudinal distributions has been investigated. Figure 7 shows the PCP longitudinal distributions obtained for IPB freshly treated jack pine and red pine. While the PCP concentration values range from 1.5 to 6 kg/m^3, the distributions show the same trend for both species. Three poles of each species and treating process have been analysed. Although only one curve of each is shown, to lighten the presentation, the three poles gave identical trends.

The PCP distribution in IPB jack pine is compared in Figure 8 with that obtained in a Domtar jack pine pole. Between 3 and 9 m, the distributions are comparable, but major differences are observed at both ends. This difference arises from the treating process used by these two companies and results from the preferential penetration of the fiber by the preservative, which is easier longitudinally than tangentially. Domtar uses an additional thermal step in its process to vaporize an important quantity of preservative solution when the final vacuum is applied. This contributes to making the concentrations of PCP and oil uniform throughout the entire length of the pole. It also leaves the surface of the pole cleaner.

However, this does not necessarily lead to lower oil concentrations, as seen in Figure 9. This figure shows the oil distribution along the length of the pole for IPB and Domtar. The concentrations vary between 50 and 175 kg/m^3 and the behavior observed is comparable to that of PCP. The concentrations of oil obtained contribute to the density of the wood and cause an underestimation of PCP concentrations when they are calculated based on the 384 kg/m^3 density value.

Radial Distribution. The IPB radial distribution of PCP and oil concentrations have been established for two longitudinal positions, namely 0.46 and 5.85 m. The results are presented in Figures 10 and 11. In both cases, the concentrations are higher at 0.46 m, due to the higher penetration of the preservative solution in the open end of the pole. For the Domtar jack pine pole, the PCP and oil concentrations are equivalent at 0.30 and 5.85 m and follow the behavior already observed in the longitudinal distribution.

Figure 12 presents various PCP radial distributions obtained for freshly treated and in-service poles. Except for the 1990 Domtar jack pine pole which shows high PCP levels, all the other poles have remarkably similar PCP concentrations. The 1983 IPB jack pine pole shows an unexpected high PCP level in the heart of the pole. The boring was dark at the time of sampling and it is presumed that its high concentration was possibly due to a cavity filled with preservative solution when treated.

The equivalent radial distributions for the oil are plotted in Figure 13. Oil concentrations are decreasing from 1990 to 1973 poles, and even the pattern of distribution over the radius is modified. The oil concentration at the periphery of the pole is depleted in the first two centimeters for the 1973 and 1983 poles. For the 1983 pole, the high oil concentration in the heartwood is in correlation with the high PCP concentration observed in the same location. For the 1973 pole, the oil concentration constantly increases between 0 and 13 cm. The borings sampled were clean, and the heartwood had a pine aroma. The radial distribution of an untreated pine was established to verify if other compounds were co-extracted with the oil. The lowest curve in Figure 13 shows that the contribution to the oil signal from compounds co-extracted from the untreated jack pine do not explain totally the behavior observed for the southern yellow pine. A lighter fraction of the petroleum oil may possibly migrate to the heart of the pole but the FTIR method used to quantify the oil is not sufficiently selective to verify this hypothesis since it is based on the aliphatic C-H bond vibration.

In-service Pole. Fifteen identical in-service poles have been analyzed. These jack pine 10.77-m class-4 poles were treated in 1983 by IPB and were installed on three neighboring streets the same year. They were sampled at 1.54 and 4.62 m above the ground, which corresponds to approximately 2.77 and 5.85 m from the base of the pole. These positions are called the base and the mid-pole respectively.

The PCP concentrations at the base and mid-pole are presented in Figure 14. These concentrations vary from 0.7 kg/m^3 to 2.6 kg/m^3 and the RSD for these pole-to-pole concentrations is 56% for the base samples and 30% for the mid-pole ones. The average concentrations, however, are the same at 1.16 kg/m^3. Therefore, no conclusion can be drawn as to a potential migration of the preservative inside the pole on the basis of these results.

The oil concentrations at the base and mid-pole are presented in Figure 15. These concentrations vary from 8 kg/m^3 to 80 kg/m^3 and the RSD for these pole-to-pole concentrations is 60% for the base samples and 50% for the mid-pole samples. Although the average concentrations are not the same, their difference is not statistically significant even if in 10 cases out of 15 the oil concentration at mid-pole is lower than that at the base.

The ratios of PCP-to-oil concentrations established for the base and the mid-pole samples are presented in Figure 16. In thirteen cases out of fourteen, the [PCP]/[oil] ratio is higher at mid-pole than its counterpart at the base. The average ratios are 4.2% and 6.2% for the base and mid-pole samples, and their RSD are 23% and 36% respectively. The difference between the average ratios obtained at these two positions is statistically significant at the 1% level. This means that the loss of oil at mid-pole is more important than that observed at the base, provided the concentrations of oil are normalized for the respective PCP concentrations.

From three longitudinal distributions obtained with different 1990 IPB poles, we have established the average [PCP]/[oil] ratios. These results presented in Figure 17 indicate that even when the PCP and oil concentrations vary along the length of the pole, as shown in Figures 8 and 9, their ratio remains constant at *ca.* 4.4%. In all cases, the poles were freshly treated.

On the basis of the [PCP]/[oil] ratios obtained with the 1983 IPB in-service poles, it is therefore possible to conclude that the [PCP]/[oil] ratios vary with the longitudinal position in ageing poles. The mechanisms by which the PCP and the oil are lost are under study.

CONCLUSION

An analytical method has been developed for the quantification of the PCP and oil in different matrices within a unique sample, using an integrated approach. This method includes interesting features such as the ultrasonication extraction, the integrated sample treatment and the density determination of each sample. This method constitutes a powerful tool to assess the behavior of PCP and oil in the environment from its point of origin, the pole itself.

The results obtained with in-service poles show that field experiments can be valuable for the evaluation of the preservative solution retention provided that the number of poles sampled is sufficiently large to establish a meaningful database. The importance of establishing correlations between the source of emission and the surrounding soil and groundwater should be emphasized, since the quantities of PCP and oil entering the environment are initially in the pole. It will permit to derive tendencies and to explain the discrepancies sometimes observed when working with natural matrices as wood poles.

The interest in longitudinal and radial characterization of poles has been demonstrated. It has been shown that the [PCP]/[oil] ratios vary with the longitudinal position in ageing poles. These findings will help to direct future experiments required for the development of the mathematical model.

ACKNOWLEDGMENTS

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REFERENCES

1. Beaulieu, G., Bériault A., Chénier, R. and L. Houde. 1991. Hydro-Québec Program for Better Environmental Management of PCP-Treated Poles. Paper presented at the CWPA Twelfth Annual Meeting, Vancouver, B.C., November 5 and 6.

2. Lefebvre, G. and J.C. Tessier. 1991. Decision support systems for management of PCP migration in the environment. Paper presented at the CWPA Twelfth Annual Meeting, Vancouver, B.C., November 5 and 6.

3. Kressbach, J.N., Tang, J. and J.E. Walker. 1987. Proceedings of the Annual Meeting of the AWPA, 83rd:273-283.

4. Slau, J.F. and J.A. Meyer. 1973. Wood Sci., 6(1):19-21.

5. Abrahamsson, K. and J. Xie. 1983. J. Chrom., 279:199-208.

6. American Public Health Association. Method 503B. Partition-Infrared Method (TENTATIVE). In: Standard methods for the examination of water and wastewater, 15th Edition, 1980. Washington DC.

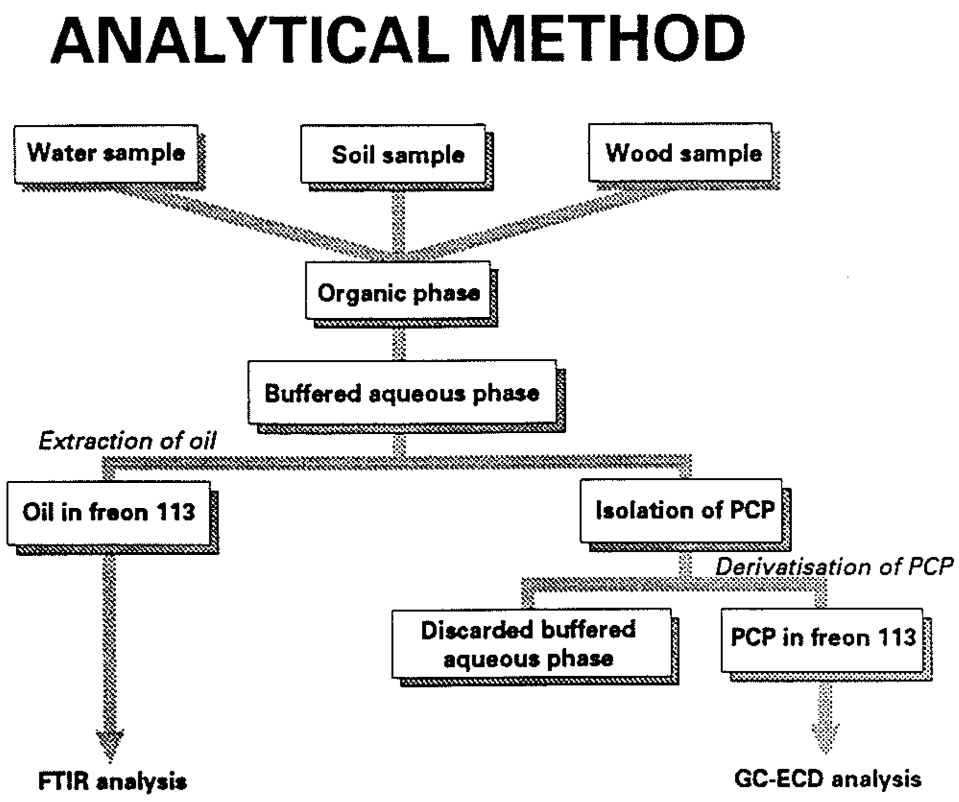


Figure 1. Basic steps of the analytical method

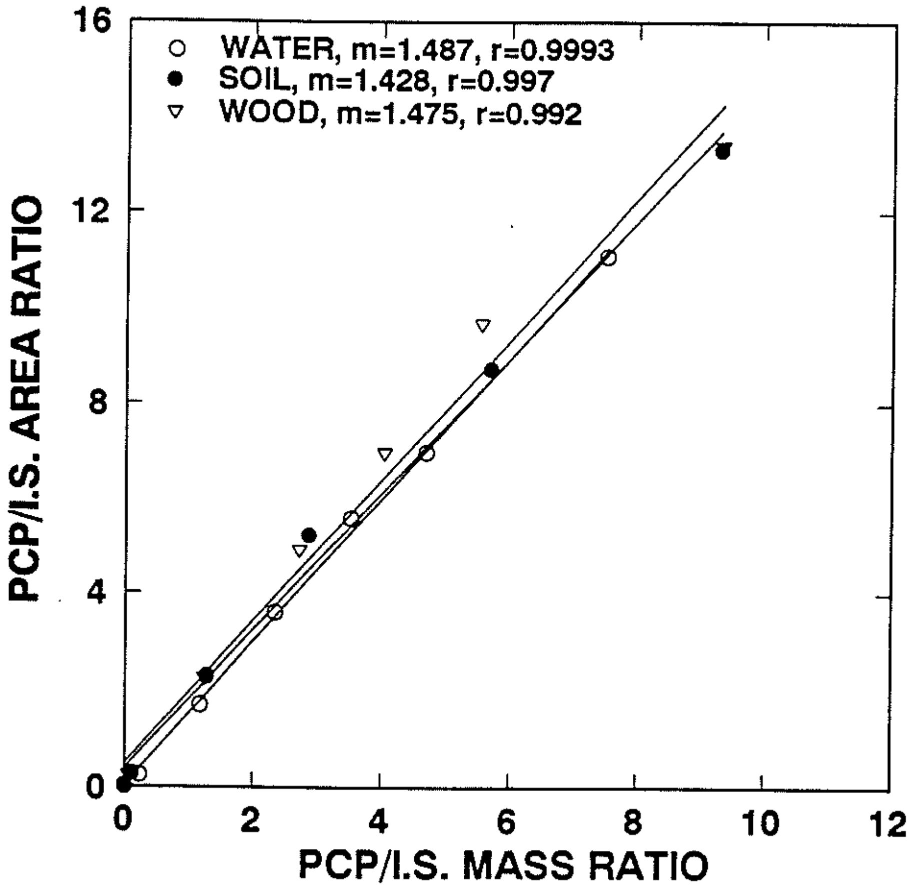


Figure 2. PCP calibration curves obtained by different preparation modes

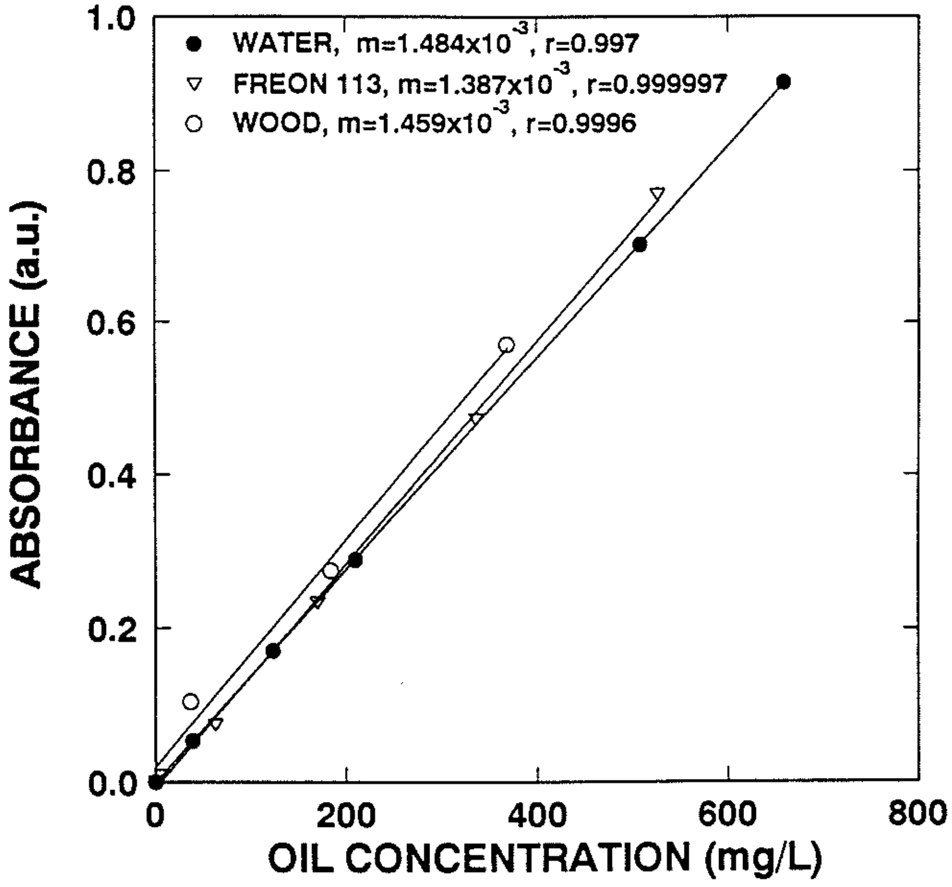
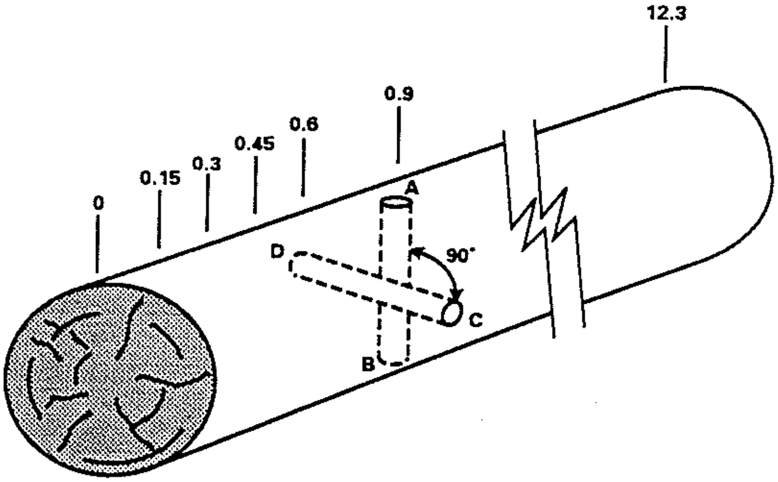


Figure 3. Oil calibration curves obtained by different preparation modes

LONGITUDINAL DISTRIBUTION

Sampling



Sample treatment

Density determination of boring
Boring splitting
Grinding
Storage

Figure 4. Wood sampling procedure for PCP and oil longitudinal distribution in poles

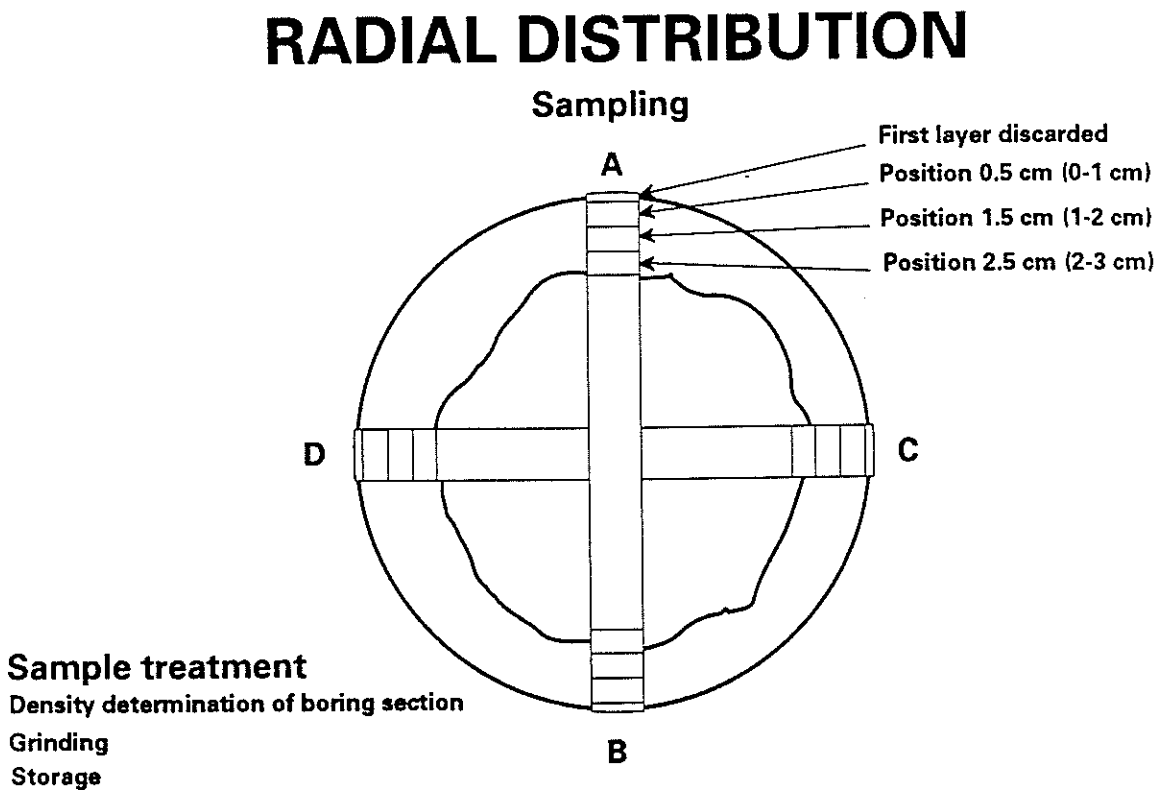


Figure 5. Wood sampling procedure for PCP and oil radial distribution in poles

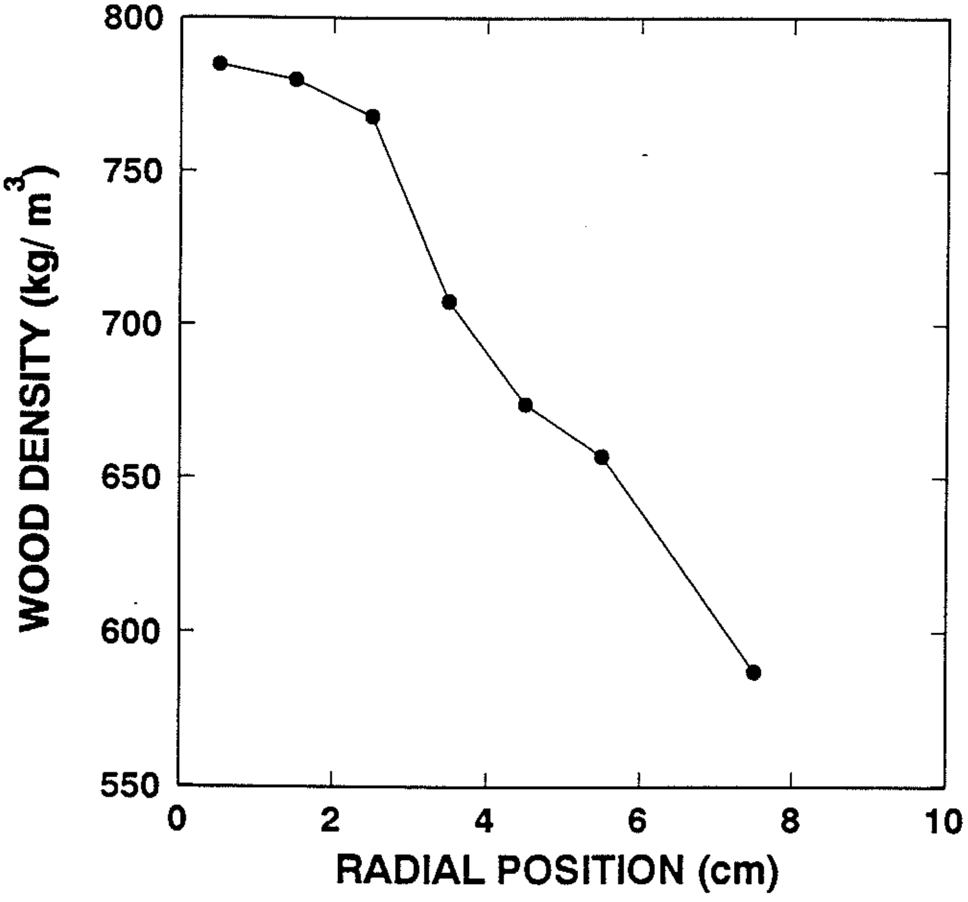


Figure 6. Variation of wood density along the radius of the pole

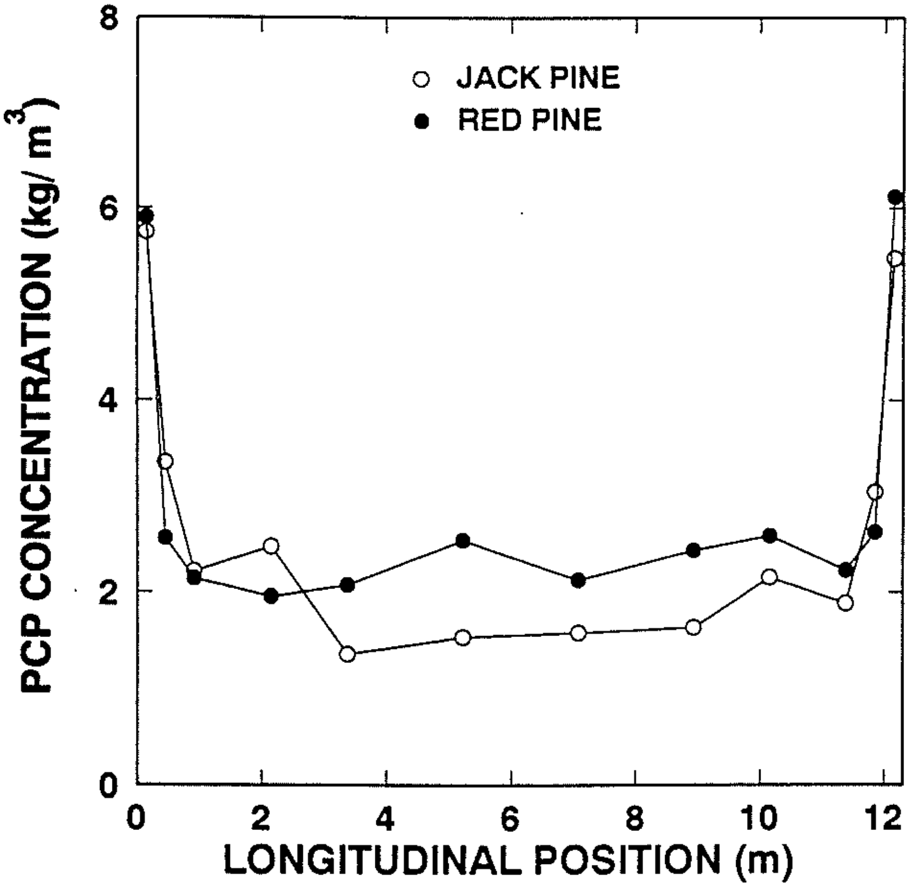


Figure 7. Pine species effect on PCP longitudinal distribution

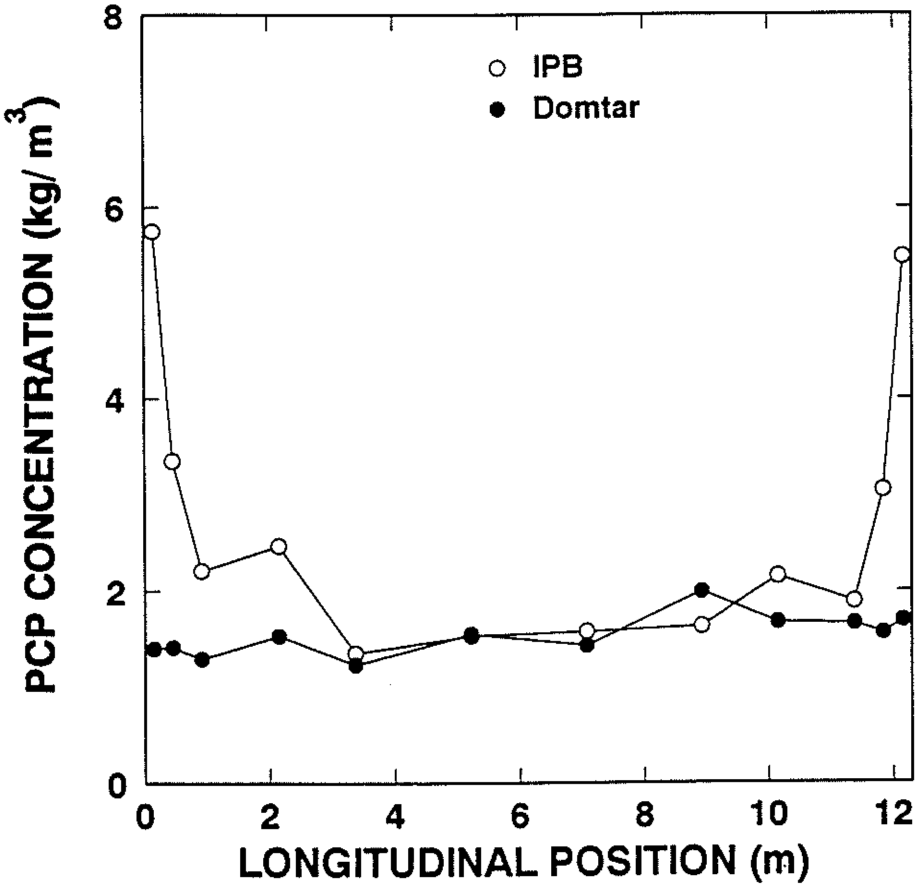


Figure 8. Treatment effect on PCP longitudinal distribution

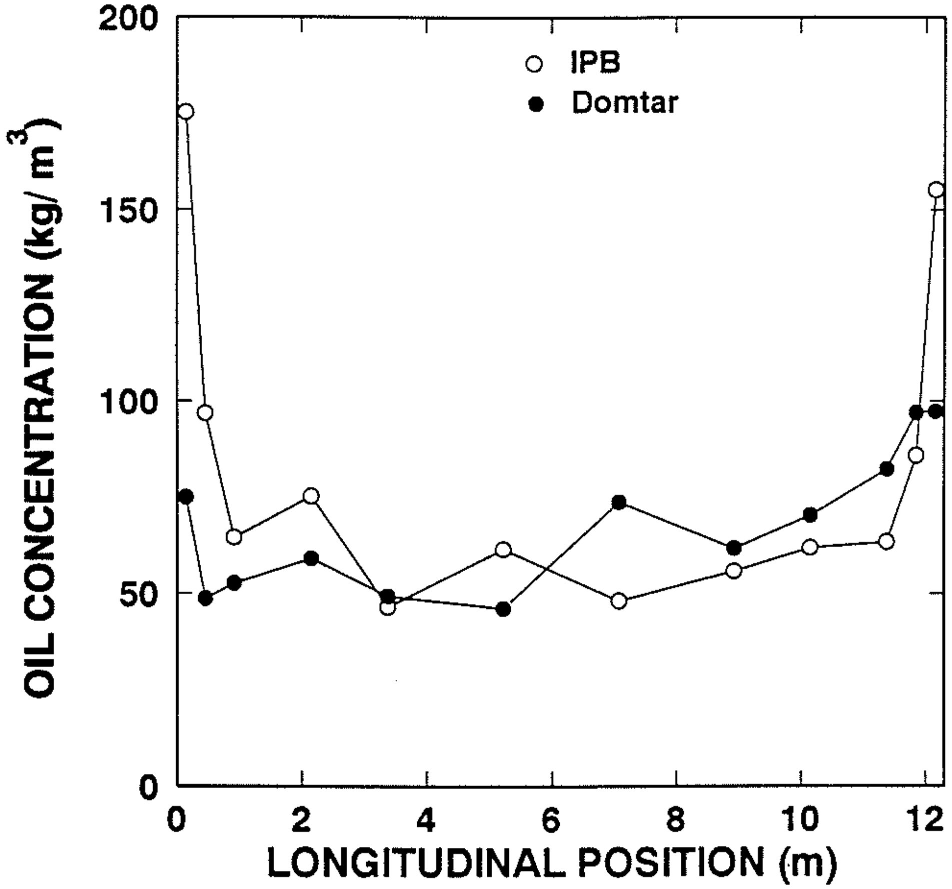


Figure 9. Treatment effect on oil longitudinal distribution

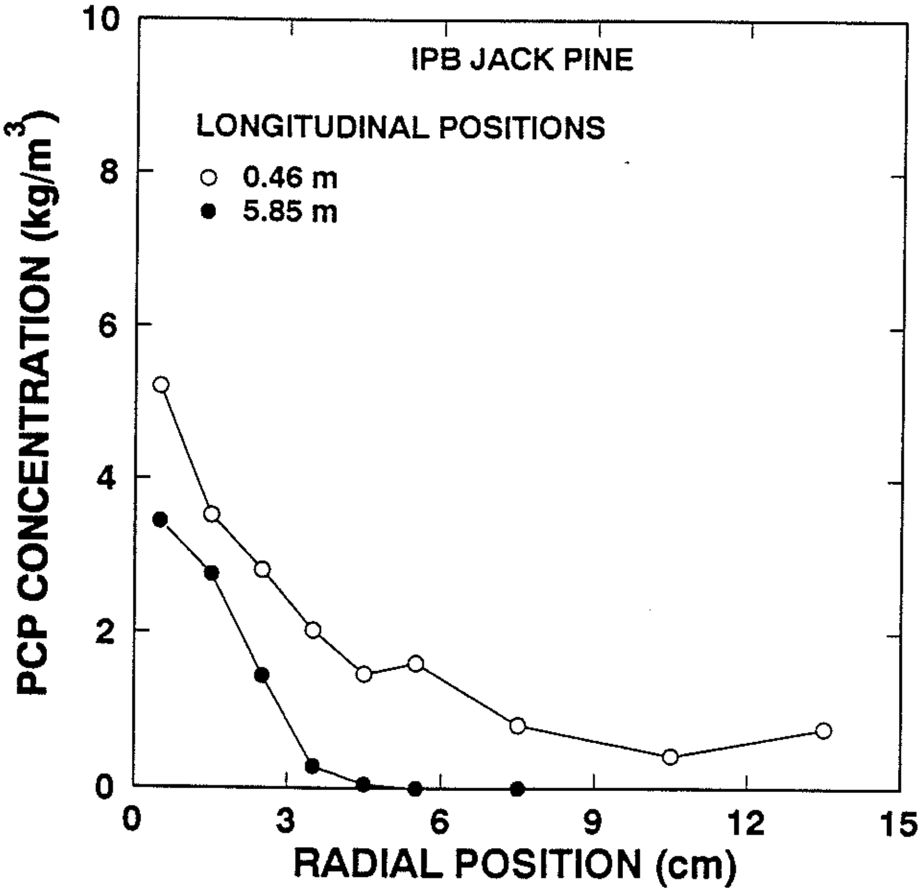


Figure 10. PCP radial distribution at two longitudinal positions

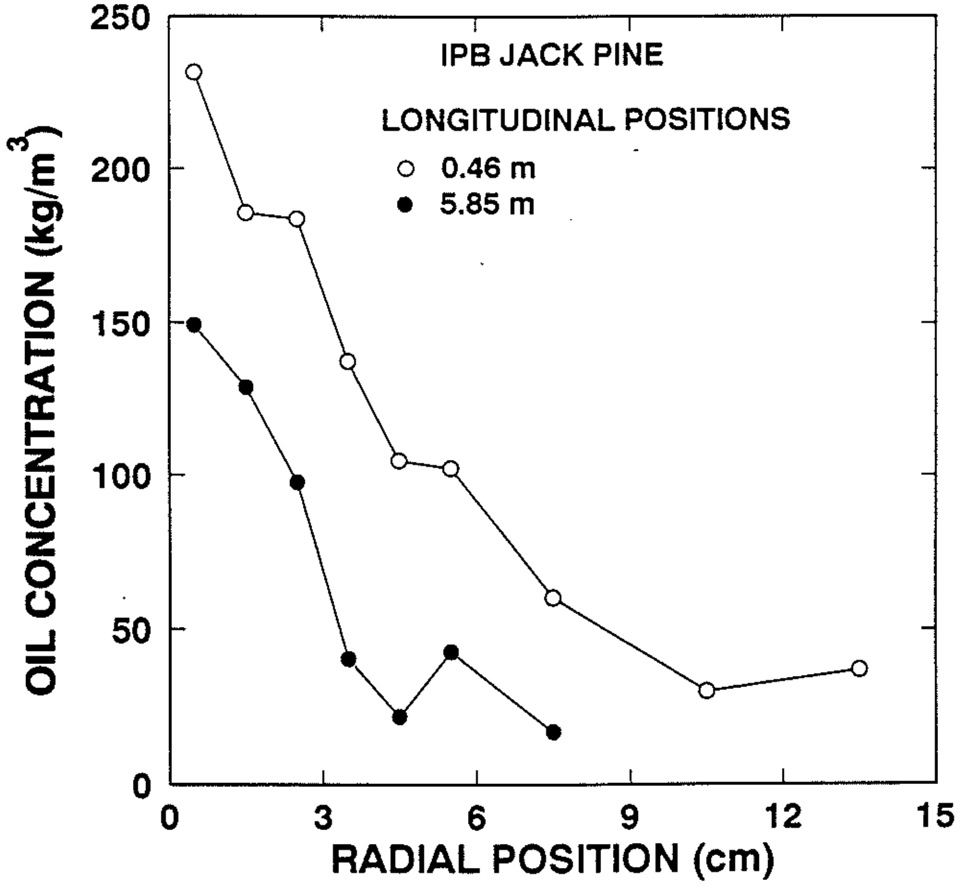


Figure 11. Oil radial distribution at two longitudinal positions

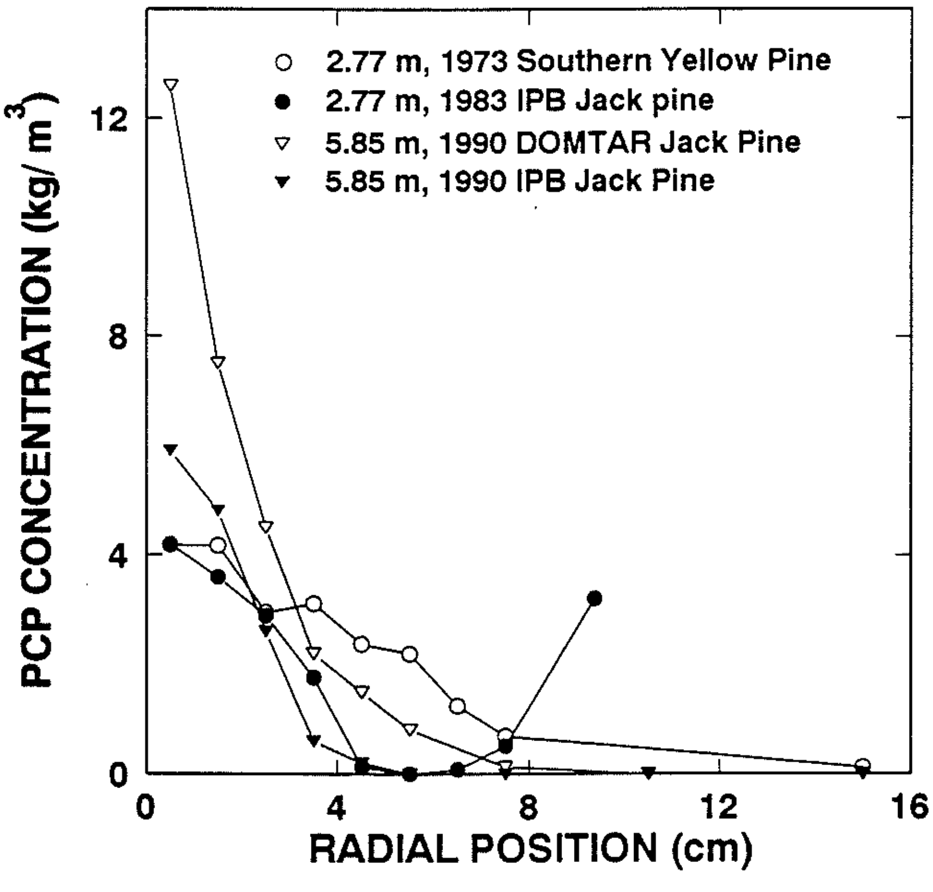


Figure 12. PCP radial distribution in various poles

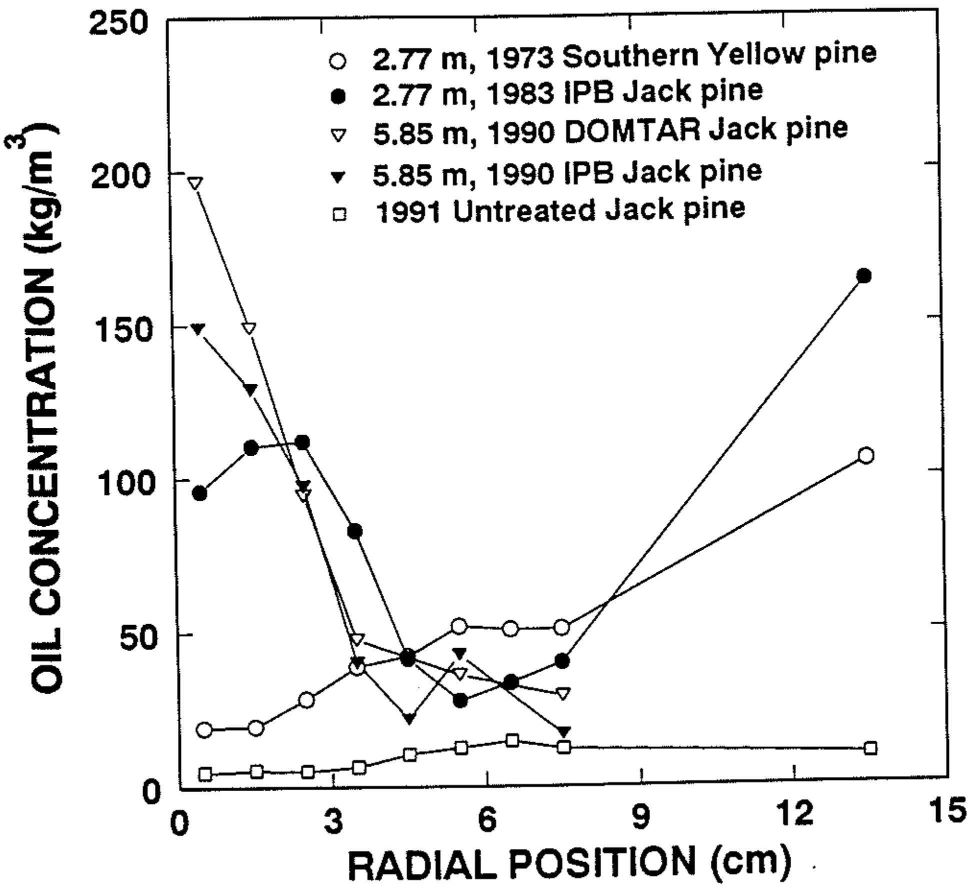


Figure 13. Oil radial distribution in various poles

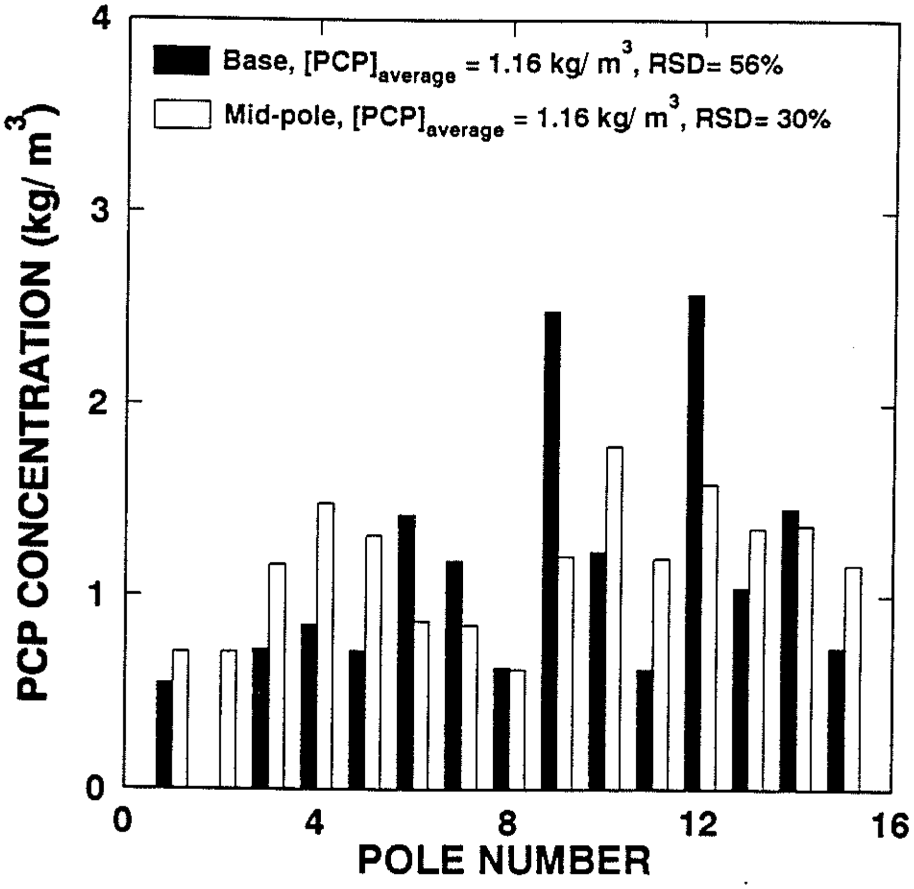


Figure 14. PCP concentration in fifteen 1983 in-service poles at two longitudinal positions

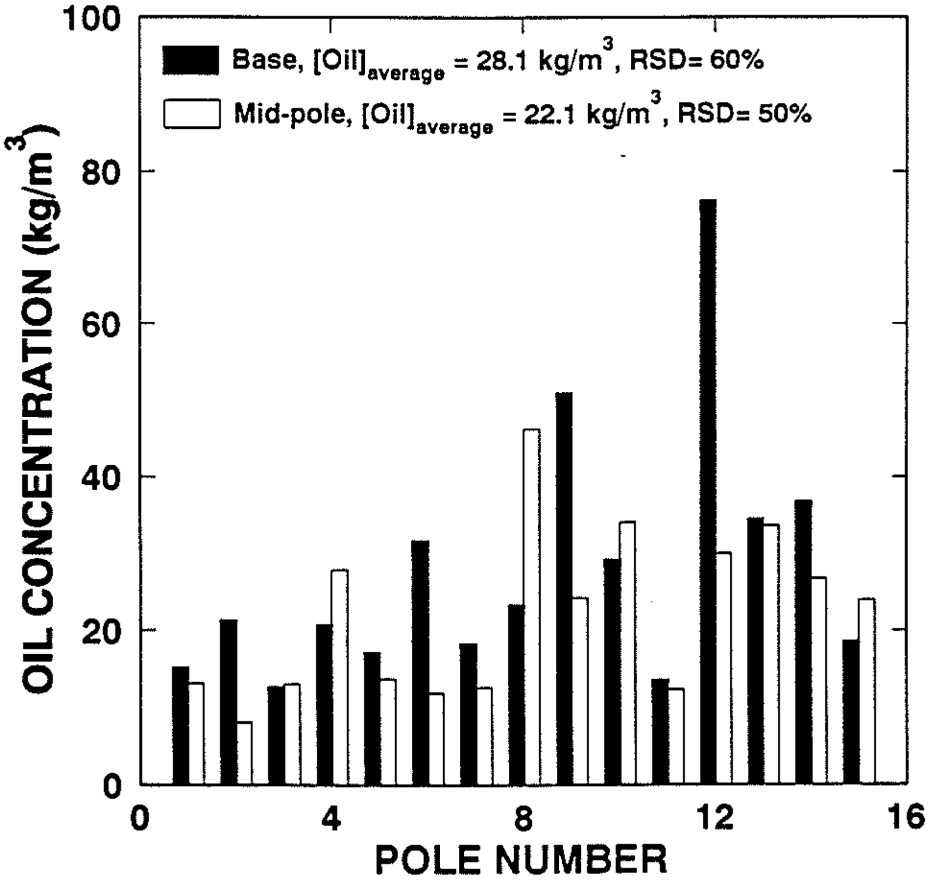


Figure 15. Oil concentration in fifteen 1983 in-service poles at two longitudinal positions

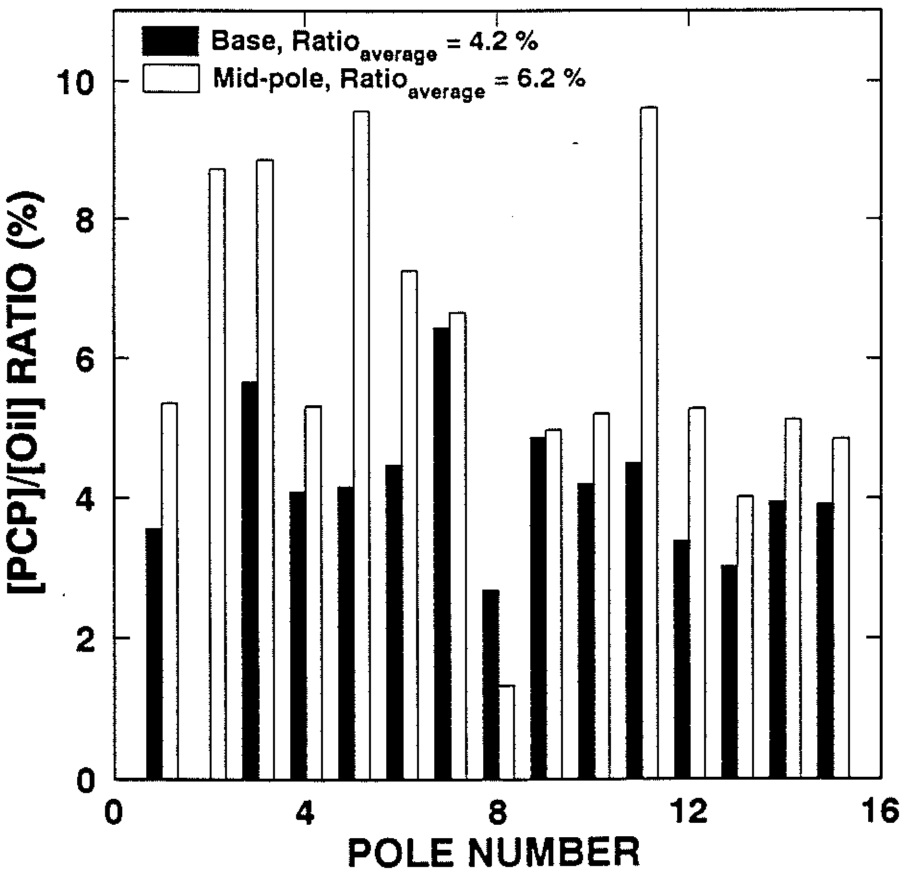


Figure 16. [PCP]/[Oil] ratio in fifteen 1983 in-service poles at two longitudinal positions

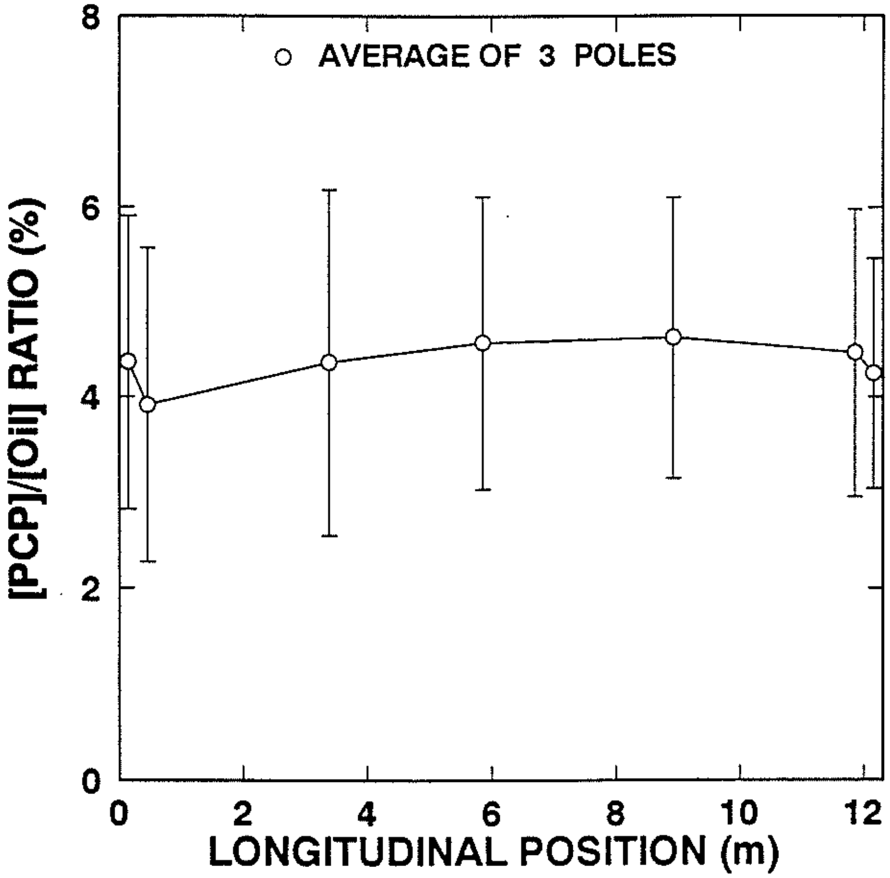


Figure 17. Longitudinal distribution of [PCP]/[Oil] ratio in 1990 freshly treated IPB poles