ABSTRACT

Pentachlorophenol (PCP) has been used as a preservative in wood industry over 40 years. If new regulations are passed, the disposal of used treated utility poles in landfills could be restricted because of the toxic properties of PCP. This study was undertaken to provide a better understanding of the rates and mechanisms of leaching of PCP from these poles.

Following the initial analytical method development for PCP determination, a study was done to apply and validate the method in a leaching characteristics study of PCP from Douglas Fir and Southern Pine.

The major factors which influence the leaching rate of PCP from wood were tested under laboratory conditions. The results show that pH is the most important among these factors. The leaching rate of PCP decreases linearly up to pH 5 then decreases in exponentially between pH 7 - pH 9. Increasing the temperature, volume or decreasing the ionic strength of leaching solution also increases the leaching rate of PCP from wood.

STUDY OF THE LEACHING OF PENTACHLOROPHENOL FROM TREATED UTILITY POLES

by
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APPROVAL PAGE

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CHAPTER 1

INTRODUCTION

1.1 Background of the Project

For the past forty years, pentachlorophenol (PCP) has been used extensively as a herbicide, fungicide and insecticide, mainly for the preservation of wood and wood products. This extensive use has caused concern among many in our pollution-conscious society mainly because of the toxic properties of this chemical(1-4). The purpose of this project is to study the leaching characteristics of PCP from discarded utility poles which are sometimes disposed of in landfills. The segment of this project which was undertaken at New Jersey Institute of Technology was designed to develop an analytical method for determination of pentachlorophenol in aqueous solutions and in wood, and to obtain experimental data on the distribution of pentachlorophenol in treated wood and to determine the rate of leaching in various solutions under at temperatures(5,6).

1.2 Scope of Study

In order to determine the leaching characteristics of PCP from utility poles disposed of in landfills, initial experiments on Southern Pine utility poles had been performed(7). These experiments include: development of analytical methods for determination of PCP in wood and in leachate solution; selection of factors that influence the leaching rate of PCP from wood and determination of the leaching rate of PCP from Southern Pine over a short period.

Based on these initial experiments, this further study includes:

1. Applications of the analytical method to Douglas Fir, another major type of wood used for utility poles.

2. Determination of leaching rate of PCP at various conditions, which included:

1) Selection of leaching solutions

2) Relatively long-term study of the leaching rate of PCP and the effect of factors including pH, temperature, volume of leaching solution and ionic strength for Douglas Fir and Southern Pine.

3. Estimation of leaching rate of PCP from utility poles during experimental periods ranging up to 92 days.

1.3 Properties of Pentachlorophenol

Pentachlorophenol (C_6Cl_5OH) is a fully chlorinated phenol, with a molecular weight of 266.36. The pure substance is a white solid needle-like crystal with melting point of 190-191°C and boiling point of 293°C. PCP is decomposed at 300°C or by strong oxidizing agents. It is a weak acid, with a pKa of 4.73. PCP is soluble in most organic solvents, oils and petroleum hydrocarbons(1,2,8). In aqueous solution, it has very limited solubility in its molecular form, but it can be converted to its salt form, with high solubility when it is in basic solution. According to the literature(1), the solubility of sodium pentachlorophenate is about 79 ppm at pH of 5.0, and is greater than 4,000 ppm at pH of 8.0.

1.4 Application and Potential Risk to Environment

Pentachlorophenol is widely used as a herbicide, fungicide and insecticide for preservation of wood and wood products throughout the world. Over 60% of wood utility poles are treated with PCP in the U.S.A. Southern Pine and Douglas Fir are the major types of wood used as utility poles(5), which are treated with PCP. A large number of treated poles are replaced each year after their 20-35 years of service(5). Because each utility pole contains several pounds of PCP, the potential exists for large amounts of PCP to be released into the environment, if the poles are not disposed of properly.

Pentachlorophenol, a pesticide which prevents wood from rotting and decaying, is a toxic agent not only to the wood destroying organisms, but also to human beings and other animals(4). PCP is not just poisonous in itself. During manufacture it unavoidably becomes contaminated with dioxins and dibenzofurans which are among the most carcinogenic chemicals known. Although PCP can be degraded to a certain extent in the environment by microbial degradation, the main metabolic pathways include not only the reductive dechlorination and eventual total degradation, but also conversion to pentachloroanisole, which again is a very stable molecule. These products break down slowly and remain toxic for a very long time in the environment(2). The disposal of used utility poles in landfills may cause the leaching of PCP from wood, PCP may migrate to ground water and contaminate PCP.

The Environmental Protection Agency(EPA) has promulgated a revised regulatory level for PCP in drinking water that may result in discarded PCP utility poles being declared as a hazardous waste. As a consequence, the estimated pole disposal costs could be increased greatly(5). Our research is designed to characterize the leaching process thus contributing to the design of methods to handle the used utility poles at a reasonable expense without causing a health or environmental problem.

1.5 Analytical Method

1. Determination of PCP

Many methods can be used for the determination of PCP. In the wood preserving industry, lime-ignition and copper-pyridine methods are used as standard methods for routine monitoring. Lime-ignition method is useful for determination of total chlorinated phenols by measuring the chloride ion produced during sample ignition, but this method is not applicable to samples containing halogens other than chlorine. The copper-pyridine method is intended as an alternate for the lime-ignition method because it is specific for determination of chlorinated phenols(9). These calorimetric methods are nonspecific for PCP because other chlorinated phenols also give the similar color reactions with PCP(4), They are only useful to determine total chlorinated phenols. Column and thin-layer chromatography techniques have also been developed for separating PCP. However, these methods are not suitable for low-level analysis of PCP. The best method for determination of PCP is conversion into the methyl ether followed by analyses using gas chromatography with an electron capture detector or GC coupled with mass spectrometry(4,10,11,12). But this method require an extensive amount of sample pre-treatment operation. For our study, high-performance liquid chromatography is the most suitable method because it has enough sensitivity for our study without complex sample pretreatment.

2. Extraction of PCP from Samples

a). Wood sample

In order to determine the PCP distribution in the pole, samples of wood powder were obtained by using a drill at specific points of utility pole, followed by extraction. Soxhlet extraction is recognized as the most complete method of extraction for solid samples(9). But it takes a very long time and uses a large volume of solvent for extraction.

Ultrasonic extraction is a simple and efficient method for extracting PCP from wood. Two successive extractions produce a satisfactory recovery. Therefore, we used this method for wood extraction.

b). Leaching solution sample

The use of a solid sorbent for the extraction and preconcentration of trace organic pollutants from water solutions has been widely investigated and the advantages of such a technique over a conventional liquid-liquid extraction have been well documented. One of the greatest advantages is the possibility of more efficient and reproducible recoveries(12). Therefore solid phase extraction(SPE) was chosen as suitable method for the leaching solution extraction.

CHAPTER 2

EXPERIMENTAL METHOD

2.1 Analysis of PCP in Wood

2.1.1 Sample Acquisition and Preparation

Two pieces of used utility poles were selected for this study. One was Douglas Fir, the other was Southern Pine. Both are cross-section slices and about 3 inch thick. They had been treated with pentachlorophenol in hydrocarbon solvent before they were placed in use. The poles had been exposed to normal weathering for 20 - 35 years.

Subsamples were obtained by drilling the wood poles at predetermined points from center to the surface of the pole in different directions at one inch intervals , and the wood powder was collected at each point. A sample of 0.500 g of wood powder was taken at each point for analysis.

2.1.2 Apparatus and Reagents

1. Apparatus

1) High performance liquid chromatography (HPLC)

A Waters LC system with 600E system controller, 715 ultra WISP autosampler, 994 programmable photodiode detector, 5200 printer plotter and computer system.

2) Ultrasonic bath (FS-28, Fisher Scientific)

3) Analytical balance.

4) Filter paper (Millipore Co. 0.45 micrometer, Type HV)

2. Reagents

1) Pentachlorophenol (Fluka, Cat No. 76470, Purity 99 %)

PCP stock standard solution: Prepare 200 ppm of PCP standard solution by dissolving 0.0200 grams of PCP in acetonitrile and diluting to volume in a 100 ml volumetric flask.

2) Acetonitrile (Fisher Scientific, HPLC grade)

3) Hydrochloric acid (Fluka, reagent grade)

2.1.3 Analytical Procedures

Take 0.500 g of wood powder, add 50.0 ml of acetonitrile and acidify with 6 N hydrochloric acid to make the pH of solution about 2-3, extract in ultrasonic bath for 30 min., then filter the extracts through a 0.45 micrometer HV filter paper and analyze the solution by HPLC. The wood residues and the used filter paper are again extracted ultrasonically with 50 ml acetonitrile, then filtered again and analyzed by HPLC. The content of PCP in wood is calculated by summing the amount of PCP found in each extraction. A external standard method is used for quantitation in our study. The standard solution is diluted from stock standard solution before use.

The HPLC operation conditions were as follows:

Waters LC systems(described in 2.1.1)

Column: C18 reversed phase column, 15 mm in length, 3.9 mm I.D. packed with 5 micrometer silica-based particles.

Mobile phase: 0.1% acetic acid in acetonitrile and 0.1% acetic acid in water.

The mobile phase gradient program was as follows:

Time = 0.0 min. 0.1%HAc/H_2O : 0.1%HAc/CH_3CN = 40 : 60

Time = 4.0 min. 0.1%HAc/H_2O : 0.1%HAc/CH_3CN = 40 : 60

Time = 14.0 min. 0.1%HAc/H_2O : 0.1%HAc/CH_3CN = 10 : 90

Time = 17.0 min. 0.1%HAc/H_2O : 0.1%HAc/CH_3CN = 40 : 60

Time = 25.0 min. 0.1%HAc/H_2O : 0.1%HAc/CH_3CN = 40 : 60

Flow rate: 1 ml/min.

Sparge rate: 10 ml/min.

Detector sensitivity: 0.2 absorbance units full scale

Analytical wavelength: 305 nm

Sample injection volume: 50 microliter

The chromatograms of a standard and sample extracts are shown in Figure 1, Figure 2 and Figure 3.

2.2 Leaching Rate Study

2.2.1 Apparatus and Reagents

1. Apparatus

1) HPLC system (described in 2.1.1)

2) Solid phase extraction system

Bakerbond 1 ml disposable SPE columns (J. T. Baker Inc. product No. 7095-03), packed with reversed phase phenylsilane (C_6H_5) bonded to silica gel (40 micrometer APD, 60A)

Supelco Inc. Visiprep solid phase extraction vacuum manifold.

3) Specific ion meter. (Orion Research Incorporation, Model 407A)

4) Environmental chamber. (30^oC+3^oC)

5) Filter paper (Millipore Co. 0.45 micrometer Type HA)

2. Reagent

1) Acetonitrile (Fisher Scientific. HPLC grade)

2) Hydrochloric acid. (Fluka. reagent grade)

3) Sodium chloride. (Fluka, reagent grade)

4) Acetic acid (reagent grade)

5) Sodium acetate (reagent grade)

6) Monopotassium phosphate (reagent grade)

7) Disodium phosphate (reagent grade)

8) Ammonia (reagent grade)

9) Ammonium chloride (reagent grade)

10) Sodium hydroxide (reagent grade)

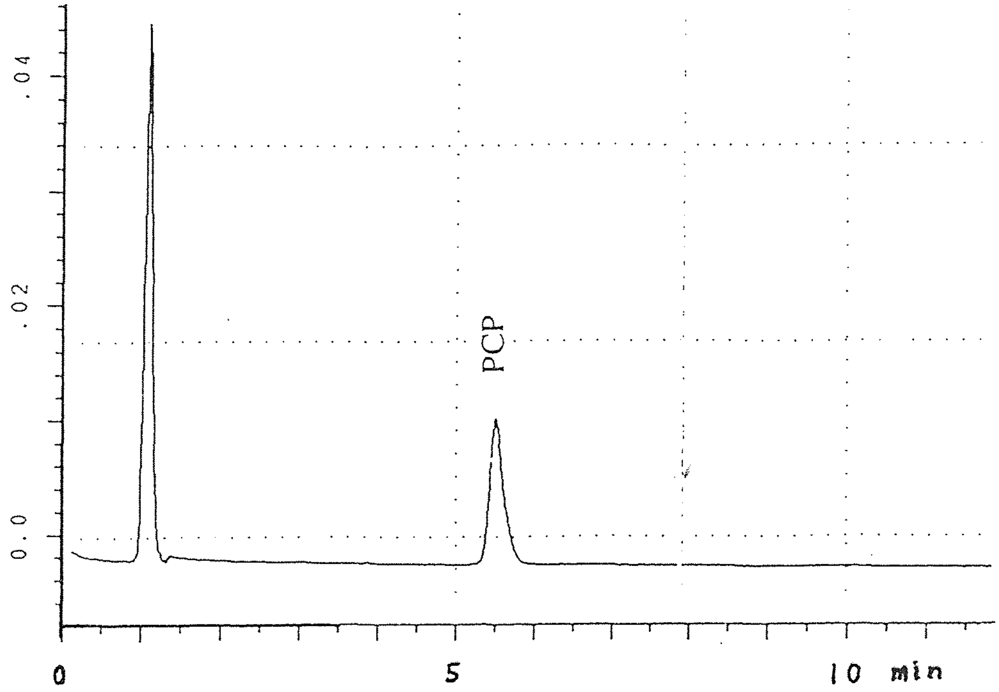

Figure 1 Chromatogram of PCP Standard

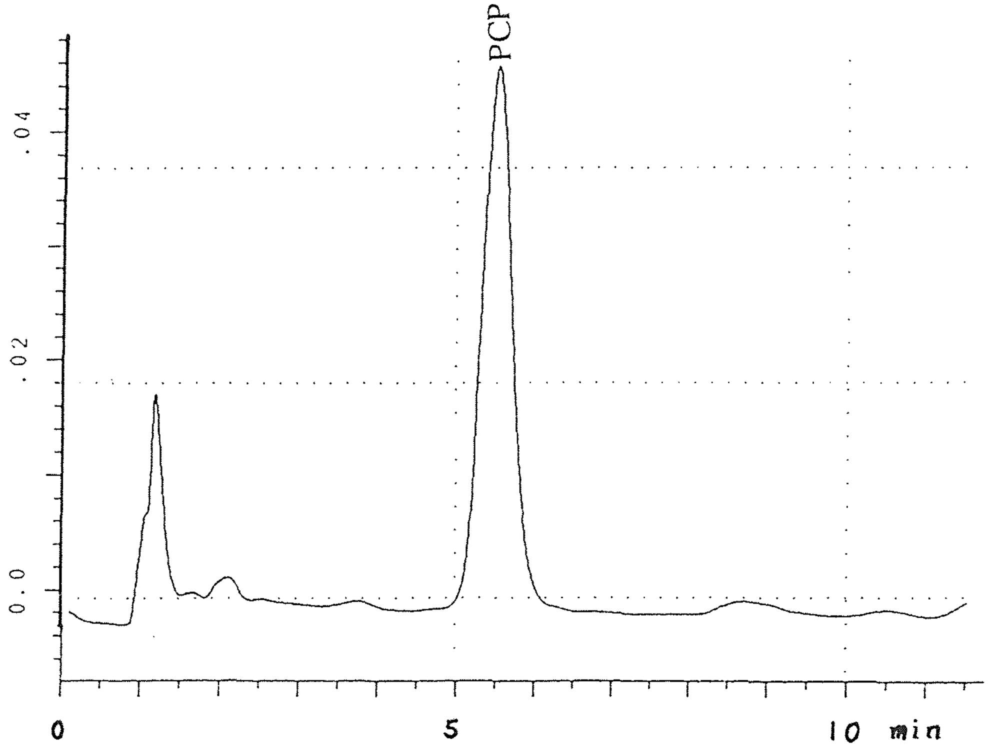

Figure 2 Chromatogram of PCP from Douglas Fir

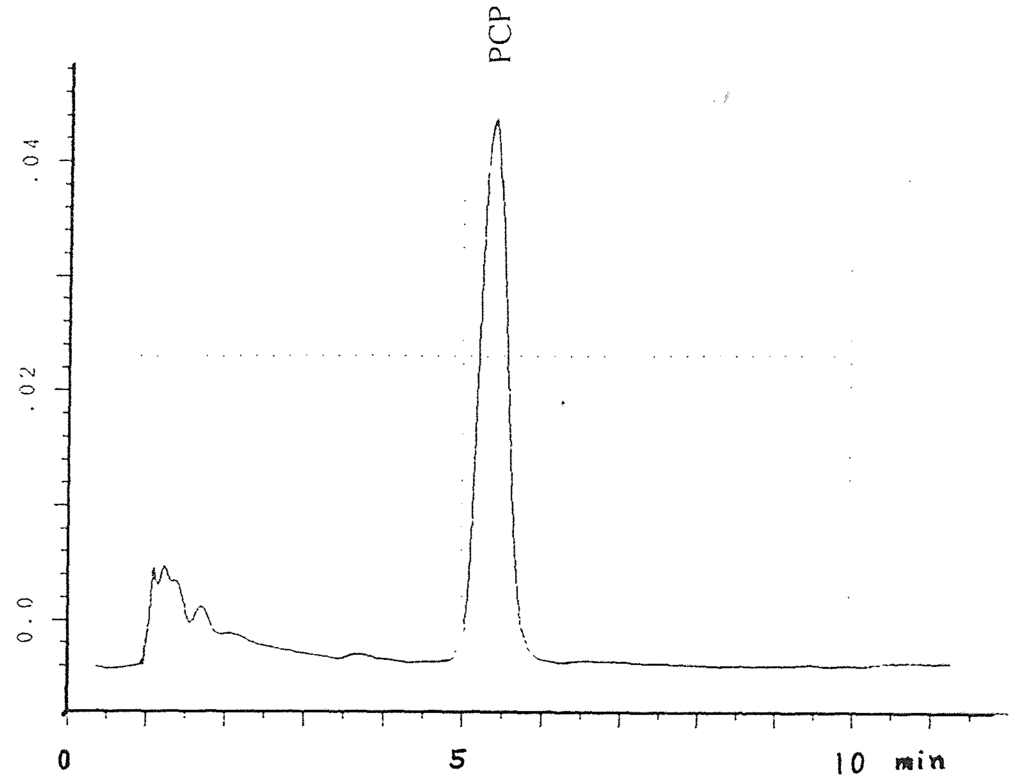

Figure 3 Chromatogram of PCP from Southern Pine

11) Boric acid (reagent grade)

12) Phosphoric acid (reagent grade)

13) Pentachlorophenol standard solution. (described in 2.1.1)

14) PCP standard solution for spike.

Dissolve 20.0 mg of PCP in 3-5 ml acetonitrile, add few drops of 6 N NaOH and dilute it to 100 ml with distilled water. This solution is used for spiking to prevent the loss of PCP during extraction. Spiking with standard diluted in acetonitrile might cause some PCP to pass through the SPE column, reducing the recovery.

2.2.2 Selection of Leaching Solutions

In the initial experiment, the buffer solutions of pH 3, 5, 7 were prepared using acetic acid and sodium acetate. Because of its weak buffer capability at pH values above 6, we used more suitable buffers for pH 7 and pH 9. In our study, we selected leaching solutions of pH 5, 7, 9 (from acidic to basic) to observe the effect of pH on leaching rate of PCP from wood. Table 1 is the preparation of buffer solutions that were used as leaching solutions. Since ionic strength of leaching solution may affect the leaching rate of PCP, this factor is taken into account during the preparation of leaching solutions. In addition, another sample was used to determine the effect of ionic strength. It was prepared by adding $CaCl_2$ to the leaching solution at pH 9 giving a concentration of 0.05 M $CaCl_2$ in this solution. The ionic strength of this solution was 0.225.

In order to directly observe the effect of pH on leaching rate of PCP from the wood, a series of leaching solution were prepared from pH 3 to pH 9 at 1 unit intervals. They were prepared by the mixture of three acid solutions (containing 0.04 M H_3BO_3, 0.04 M H_3PO_4 and 0.04 M HAc) and 0.2 M NaOH solution mixed in different ratios. Seven cubes of Douglas Fir were placed in 200 ml leaching solutions of different pH for 24 hours at 30^oC, then the leaching solutions were analyzed following the sample procedure. Table 2 shows the preparation of leaching solution for pH effect.

Table 1 Preparation of Buffer Solutions

pH	Combination	Ionic strength*
5.0	0.1 M HAc 1 part 0.1 M NaAc 3 parts	0.083
7.0	0.025 M KH_2PO_4 1 part 0.025 M Na_2HPO_4 5 parts	0.05
9.0	0.1 M NH_3 1 part 0.1 M NH_4Cl 3 parts	0.075

* Ionic strength is calculated by: $1/2\Sigma CiZi^2$
where C is the concentration of ion
Z is the number of charge

Table 2 Preparation of Leaching Solutions for pH Effect

pH	Volume of Mix. Acid (ml)	Volume of NaOH (ml)	Total Volume (ml)
3	170	30	200
4	161	39	200
5	148	52	200
6	141	59	200
7	131	69	200
8	125	75	200
9	117	83	200

2.2.3 Sample Preparations

Cubes of wood one inch on each side are used as subsamples for the leaching rate study. They are obtained by cutting the slice of pole from outer edge with a hand saw. Each subsample has 1 square inch of exposed outer surface and 5 square inches of fresh surfaces. It was necessary to polish the subsamples with sand paper to smooth the samples because rough samples will increase the sample surface areas and will affect the leaching rate of PCP.

2.2.4 Analytical Procedures

1. Leaching test conditions

Twelve pieces of cubes were tested in our leaching rate study. The leaching conditions for each sample are shown in Table 3. All samples were held at the specific condition for 2 days to reach equilibrium. At 2 day intervals, the leaching solutions were analyzed and replaced with fresh solutions.

2. Sample extraction

A 20 ml portion of leaching solution was taken for analysis. If the concentration was too high, a smaller amount of sample was measured out and was diluted to 20 ml. The solution was acidified to pH 2 - 3 with 6 N HCl in order to ensure that the PCP is present in its molecular form for extraction. Then 2 grams of NaCl in solution were added to aid PCP extraction by the salting out effect.

A 1 ml Bakerbond SPE column was preconditioned with 2 ml of acetonitrile, followed by 5 ml of 1N HCl. An adapter was used to attach a 50 ml reservoir to the top of the extraction column. The vacuum pump was adjusted to provide about 2 ml/min. of flow.

The sample solution was transferred carefully to the reservoir. The column was not allowed to dry during sample extraction.

After the entire sample solution had passed through, the column was washed with 5 ml 0.01 N HCl to eliminate interfering substances. The column was air dried for 2 min. Finally the sample was eluted with three successive 2.5 ml of acetonitrile, and the column was allowed to dry between each solvent elution. The elute was collected and diluted to a volume of 10.0 ml with acetonitrile. This solution was directly analyzed by HPLC.

3. HPLC operation conditions (described in 2.1.3)

Table 3 Leaching Conditions:

No.	Type	pH	T (^{o}C)	Ionic Strength	Volume (ml)
1	Fir	5	20	0.083	200
2	"	7	20	0.05	200
3	"	9	20	0.075	200
4	"	5	30	0.083	200
5	"	7	30	0.05	200
6*	"	7	30	0.05	200
7	"	9	30	0.075	200
8	"	9	30	0.225	200
9	Pine	5	30	0.083	200
10	"	7	30	0.05	200
11	"	9	30	0.075	200
12*	"	9	30	0.075	200

* Duplicate sample

2.3 Method Verification

In the initial study, it had been proved that good quantitative comparison could be made between HPLC with UV detection and GC/MS(7).

In our study, the sample spectrum of PCP by UV detection matches well with PCP standard, as well as in the initial study. The UV spectrums are shown in Figure 4, 5, 6.

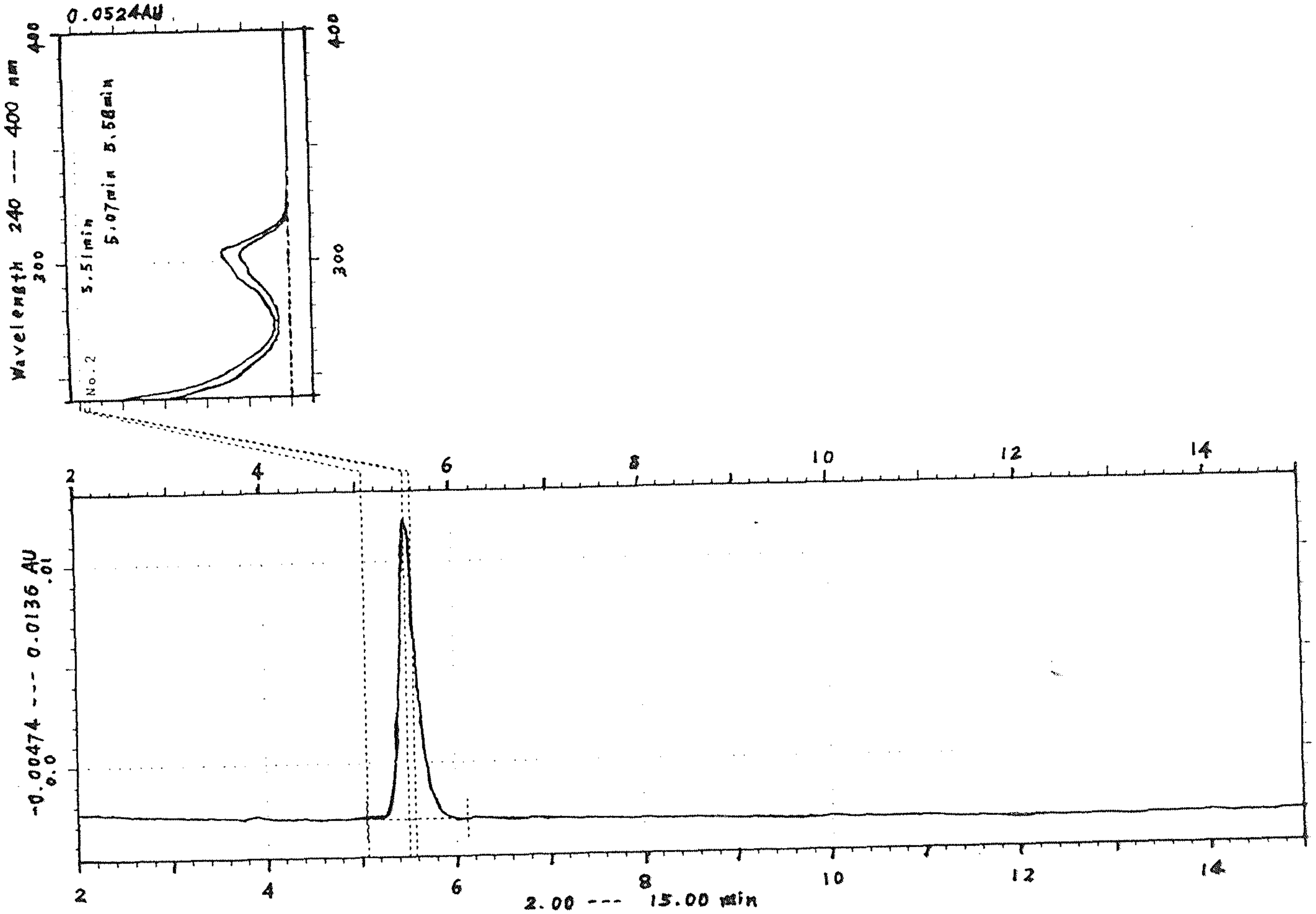

Figure 4 UV Spectrum of PCP Standard

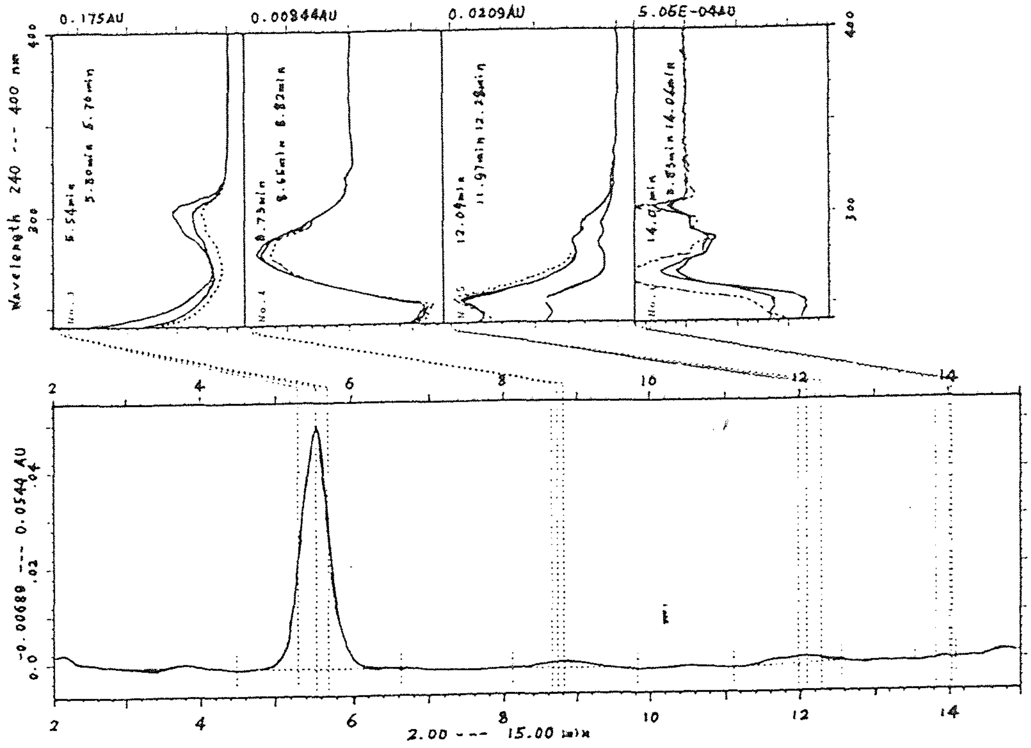

Figure 5 UV Spectrum of Extracts from Douglas Fir

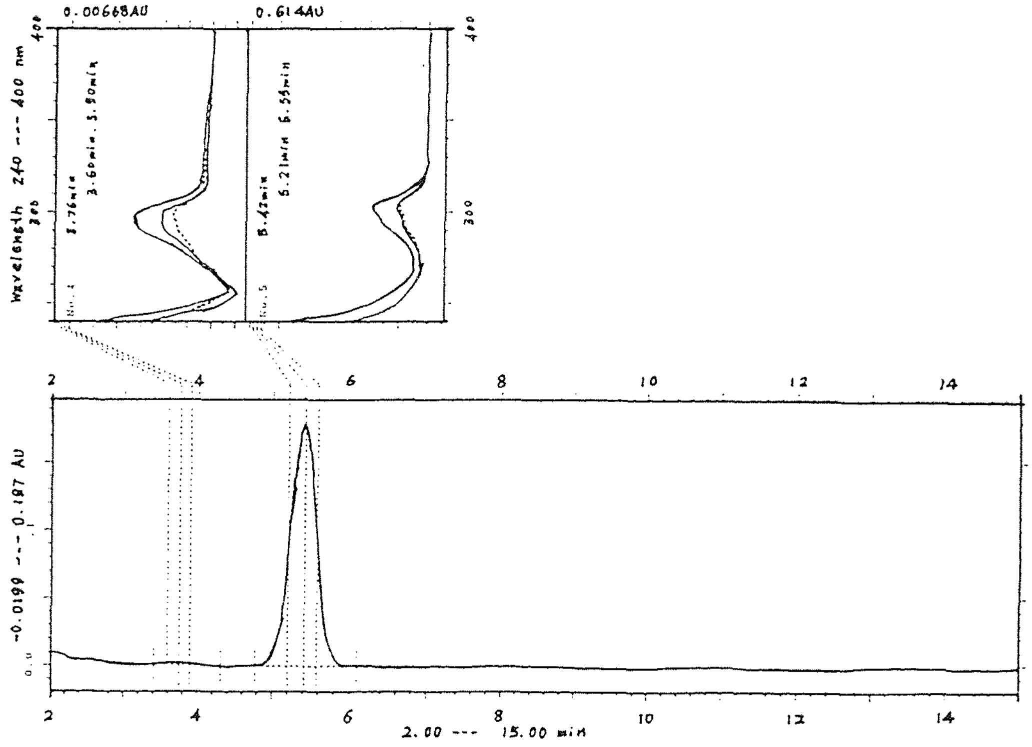

Figure 6 UV Spectrum of Extracts from Southern Pine

2.4 Quality Assurance in the Experiment

2.4.1 Representativeness of Samples

1. In order to determine the PCP distribution in the wood pole, the transverse slice of wood pole was drilled in two different directions from the center to the surface at about 1 inch intervals.

2. Wood cubes used for the leaching rate study were cut from same area of the wood pole because of the nonhomogeneous distribution of PCP in the pole. One of the surfaces of each cube was an original exposed outer surface, while the others were fresh surfaces. The weight of each cube was within a range of sample weights from 14.0098 to 15.3653 grams.

2.4.2 Accuracy of the Method

1. Efficiency of PCP extraction from wood

Wood samples were extracted twice. Two samples were extracted three times. The results show that each extraction received the almost same fraction of the PCP remaining in the wood. By applying these results to other samples, we calculated the extraction efficiency for each step. Table 4 shows that more than 85 % of PCP was extracted after the second extraction. The average extraction efficiency was 92.7%.

2. HPLC operation system

a) Mobile phase was freshly prepared every day.

b) The system was conditioned and cleaned before and after analysis for several hours with acidified 40% H_2O : 60% CH_3CN.

c) The calibration curve was checked and corrected every day.

3. Method blanks, duplicate samples, laboratory fortified blanks and matrix spikes were analyzed at the frequency of at least 10 % of all samples.

a) Method Detection limit (MDL) and Limit of Quantitation (LOQ)

MDL and LOQ were obtained by running method blanks. Samples of 20 ml of each leaching solution were placed in an environmental chamber at 30°C for two days, then analyzed following the sample procedures. The results are shown in Table 5.

Table 4 Extraction Efficiency of PCP from Wood

No. of Point	PCP(mg) in 1st. Ext.	PCP(mg) in 2nd. Ext.	PCP(mg) in 3rd. Ext.	Efficiency 1st. step	Efficiency 2nd. step
1	5.60	0.98	0.18	82.8%	97.3%
2	4.30	1.62	0.98*	62.3%	85.8%
3	2.55	0.96	0.58*	62.3%	85.8%
4	3.82	1.06	0.41*	72.2%	92.2%
5	1.91	0.70	0.40*	63.5%	86.8%
6	7.98	1.54	0.37*	80.7%	96.3%
7	4.70	1.53	0.74*	67.3%	89.2%
8	9.02	1.26	0.21*	86.0%	98.0%
9	10.25	1.32	0.20*	87.1%	98.3%
10	8.68	1.40	0.32	83.5%	97.0%

* Calculated results by assuming that the same fraction of PCP present in the wood was extracted at each step.

Table 5 Results of Method Blanks

pH	Number of Replicates	Method Blank Range (ppm)	Method Blank Average (ppm)	S.D.
5	7	0 - 0.33	0.077	0.136
7	6	0 - 0.16	0.090	0.072
9	6	0 - 0.21	0.087	0.098
Total	19	0 - 0.33	0.084	0.099

The MDL and LOQ were calculated by:

$$MDL = 3.14 \times S.D. = 0.30 \text{ ppm}$$

$$LOQ = 10 \times S.D. = 1.0 \text{ ppm}$$

b) Blank spikes

Determination of blank spikes is used for checking laboratory and method performance. Take 20 ml of leaching solution, add 1 ml of 200 ppm standard solution for spike and analyze it following the sample procedures. Table 6 shows the recovery of the spiked PCP from blanks.

Table 6 Recovery of PCP Standard in Blank Solutions

pH	Number of Replicates	Recovery Range	Average Recovery	S.D.	CV%
5	5	83 - 94%	88.5%	4.46	5.0
7	6	79 - 93%	86.4%	3.99	4.6
9	4	77 - 92%	84.8%	6.0	7.1
Total	15	77 - 94%	86.8%	4.92	5.7

c) Matrix spikes

One ml of 200 ppm standard solution was mixed into 20 ml of sample leaching solution and analyzed it following sample procedures. Table 7 shows the results.

Table 7 Recovery of Matrix Spikes

pH	Number of Replicates	Recovery Range	Average Recovery	S.D.	CV%
5	7	77 - 125%	91.6%	16.0	17.5
7	8	63 - 101%	77.5%	12.5	16.1
9	6	56 - 96%	80.0%	13.9	17.4
Total	21	56 - 125%	82.9%	14.5	17.8

d) Duplicate samples

Due to the inhomogenous distribution of PCP in wood poles, two kinds of duplicate samples were analyzed:

1. Duplicate cubes of samples, one from Douglas Fir at 30^{o}C, pH 7 and the other from Southern Pine at 30^{o}C, pH 9, were tested with other samples for leaching rate study during the experiment periods. The results are shown in Chapter 3 .

2. Duplicate leaching solutions of samples were also analyzed to assess the reproducibility of the analytical methodology. The relative standard deviations of all duplicate samples are within 10 %.

2.4.3 Interlaboratory Comparison

1. To insure the accuracy of laboratory prepared standard, our standard was compared with EPA supplied standard solution at three levels, as shown in Table 8

Table 8 Comparison of Our Standard with EPA Supplied Standard

Concentration (ppm)	EPA std. (area)	NJIT std. (area)	Bias
2.0	275377	264778	3.8 %
10.0	1342681	1248499	7.0 %
20.0	2656581	2581576	2.8 %

2. Some samples of leaching solution and standard solutions were sent to Stevens Institute of Technology who were also involved in this project. The comparison of results is shown in Table 9.

Table 9 Comparison of Std. & Samples with Stevens

Sample Name	NJIT Result	Stevens Result	RPD*
Std. 1	7.98 ppm	8.20 ppm	2.7 %
Std. 2	0.52 ppm	0.41 ppm	23.7 %
Std. 3	4.20 ppm	3.75 ppm	11.3 %
Sample 1	62.5 ppm	61.9 ppm	1.0 %
Sample 2	95.0 ppm	94.5 ppm	0.5 %

* RPD is relative percent difference

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Distribution of Pentachlorophenol in Wood Pole

Nine sample points were collected from the slice of Douglas Fir. Figure 7 shows the position of each sampling point. Table 10 shows the concentrations of PCP found at each point. These data show that same trend in PCP concentrations appears in each direction, and the highest concentration of PCP is near the outer surface, obviously because the PCP entered the wood pole from the outer surface during the treatment. The lowest concentration is between the center and the outer surface not at the center of the pole. It is probably because PCP entered the wood pole not only from the outer surface, but also from the two ends of wood pole. The center part of the wood pole may be more porous than other parts, so it may be easier to absorb the PCP there. Of course it also depends on the position of this slice in the wood pole. In addition, this wood pole had been in service for a period of time. The PCP concentration in the wood is expected to change under long period of exposure to the environment. Unfortunately, the history of this sample was not known. So we can not determine how much PCP had leached out to the environment and how the PCP migrated inside the wood.

Table 10 Distribution of PCP Content in the Douglas Fir

No. of Point	PCP Content %	No. of Point	PCP Content %	Average Content %
0	1.32			1.32
1	1.18	1'	0.70	0.94
2	0.98	2'	0.52	0.75
3	1.90	3'	1.25	1.58
4	2.06	4'	2.16	2.11
Total				1.35

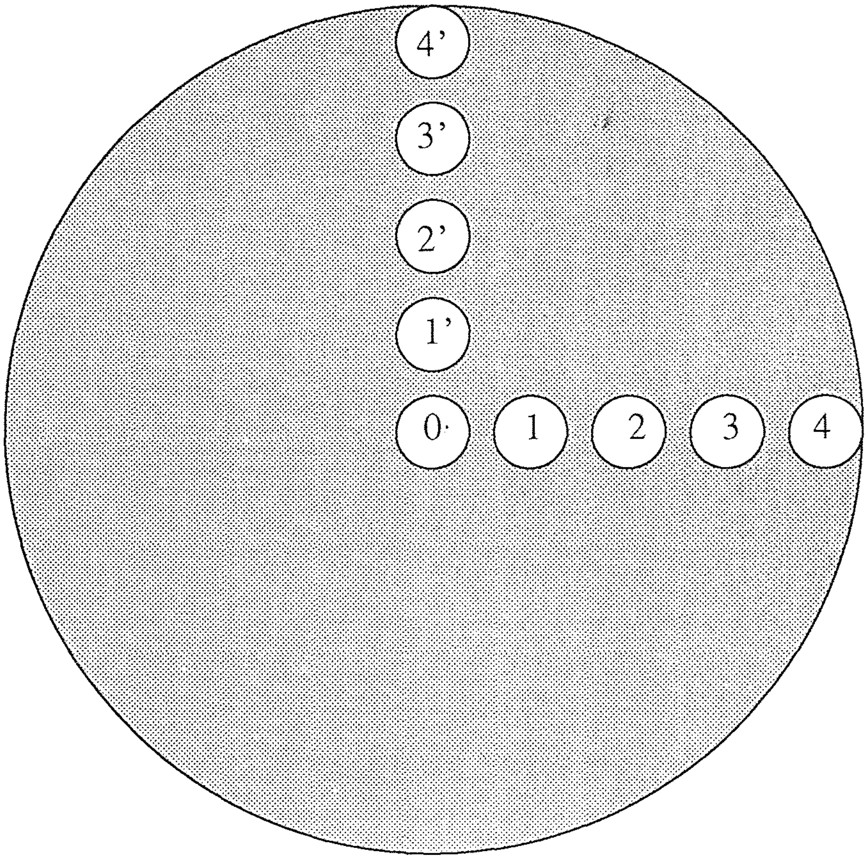

Figure 7 Pattern of Sample Collection from Pole Slice of Wood

3.2 Solubility of PCP and the Reason for Turbidity in Some Acidified Leaching Solutions

As mentioned in chapter 1, pentachlorophenol is soluble in most organic solvents with limited solubility in water. However PCP salts are highly water soluble in basic solution.

During the analysis of sample leaching solution, some samples become turbid when we acidified the leaching solutions of pH 7 and pH 9 with 6 N HCl. Some efforts were taken to determine whether or not the turbidity is caused by PCP. We placed 50 mg of pure PCP in three bottles with 100 ml leaching solution of pH 5, pH 7, pH 9, and shook them very vigorously. There same result occurred in all three bottles, and no turbidity was observed but the pure PCP is floating on the surface of solution or attached to the bottle wall. Another experiment was done by dissolving 50 mg of pure PCP in 5 ml of acetonitrile, then mixing with 100 ml leaching solutions at pH 5, pH 7 and pH 9. The solution at pH 5 became turbid and other two solutions were still clear. When we added 6 N HCl to adjust the solutions of pH 7 and pH 9 to pH 2 - 3, they also became turbid. When we added 6 N NaOH to the solution of pH 5, this solution became clear. These experiments show that pure pentachlorophenol is not soluble in water even in a basic water solution. The addition of a small amount of organic solvent will cause it to dissolve, be converted to PCP salt and than show high solubility in basic solution. These results well explain that the turbidity in acidified sample leaching solutions are caused by the leaching of more PCP from wood than can remain in solution. This amount of PCP exists as PCP salt in these solutions of pH 7 and pH 9 without turbidity. In addition, the treated wood pole contains remnants of the organic hydrocarbon solvent (diesel oil) which was used during the wood treatment. This solvent is leaching out along with PCP from the wood pole, which may increase the leaching of PCP and increases the solubility of PCP in water.

The turbidity of acidified sample leaching solutions may affect the PCP analysis because it may block the SPE column or decrease the flow rate of leaching solution passing through column. Therefore, this high concentration solutions should be diluted until there is no turbidity in acidified solution before analysis.

3.3 Factors Influencing the Leaching Rate of PCP from Wood

In order to determine the effects of pH, temperature and ionic strength on the leaching rate of PCP, 8 cubes of Douglas Fir and 4 cubes of Southern Pine were tested under the leaching conditions described in 2.2.4. Leaching solutions were changed every other day with fresh solutions and only alternate leaching solutions were analyzed. The experiment for Douglas Fir lasted 56 days with two samples at pH 5 (lowest leaching) and pH 9 (highest leaching) continued to 92 days. The Southern Pine test lasted 44 days. Table 11 and Table 12 shows the concentration of PCP found in each of the tested leaching solutions.

3.3.1 pH Effect on the Leaching Rate of PCP

The results in Table 10 and Table 11 show that the leaching rate of PCP is strongly dependent on the pH because of its greater solubility in basic solution and lower solubility in acidic solution. Figure 8 and Figure 9 show the plots of the leaching of Douglas Fir at temperatures of 20°C and 30°C respectively. Figure 10 shows the plot of the leaching of Southern Pine at 30°C. The curve of pH 5 is very different from that of pH 7 and pH 9. There is no significant change in the amount leached each day at pH 5 during experiment period, but the curves at pH 7 and pH 9 show significant decrease during that period, with the curve at pH 9 decreasing more rapidly than that at pH 7.

The effect of pH on leaching rate was also studied from pH 3 to pH 9 at 1 unit intervals (the leaching condition was described in section 2.2.2). Figure 11 is the plot of the result.

Table 11 Leaching Test for Douglas Fir (ppm)

Day	20°C pH 5	20°C pH 7	20°C pH 9	30°C pH 5	30°C pH 7	30°C pH 7*	30°C pH 9	30°C pH 9**
2	7.14	48.6	172	8.30	89.8		113	61.0
4	6.30	36.9	45.5	6.25	43.2	66.9	81.8	56.8
8	5.20	30.0	27.2	6.50	43.8	41.2	50.4	17.4
12	2.94	11.0	31.3	3.12	28.6	25.2	27.1	19.2
16	3.88	22.4	24.4	4.43	31.4	31.0	30.0	11.8
20	5.95	20.3	16.0	7.55	36.1	29.6	26.0	27.1
24	6.30	24.2	27.6	6.25	34.7	19.1	32.1	30.0
28	5.20	16.8	16.6	6.15	29.7	22.1	15.2	22.6
32	5.05	14.2	16.7	6.35	24.4	20.2	32.4	11.9
36	4.70	13.0	11.1	5.35	18.6		12.9	11.1
40	5.45	15.5	13.1	6.70	16.5	13.8	18.6	9.10
44	5.10	15.8	13.7	5.90	21.6	8.60	17.6	22.3
56	6.40	20.2	12.8	6.50	20.3	11.4	17.9	
64				5.20			24.7	
68				6.50			13.6	
80				5.00			7.60	
86				5.12			8.40	
92				4.93			7.10	

* Duplicate sample

** This solution also contained 0.05 M of $CaCl_2$

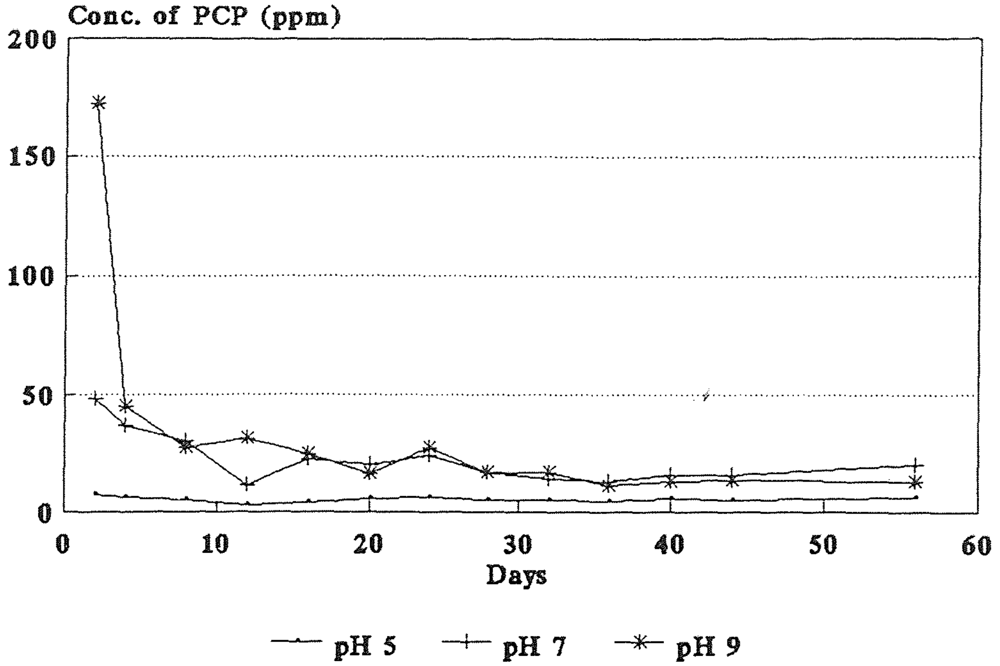

Figure 8 pH Effect on Leaching of PCP from Douglas Fir at 20C

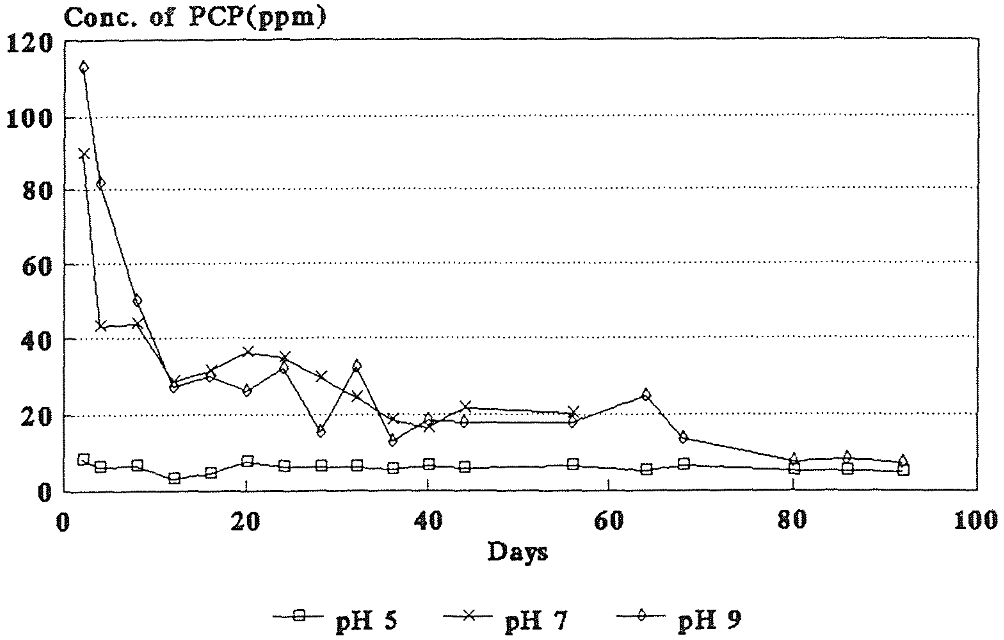

Figure 9 pH Effect on Leaching of PCP from Douglas Fir at 30C

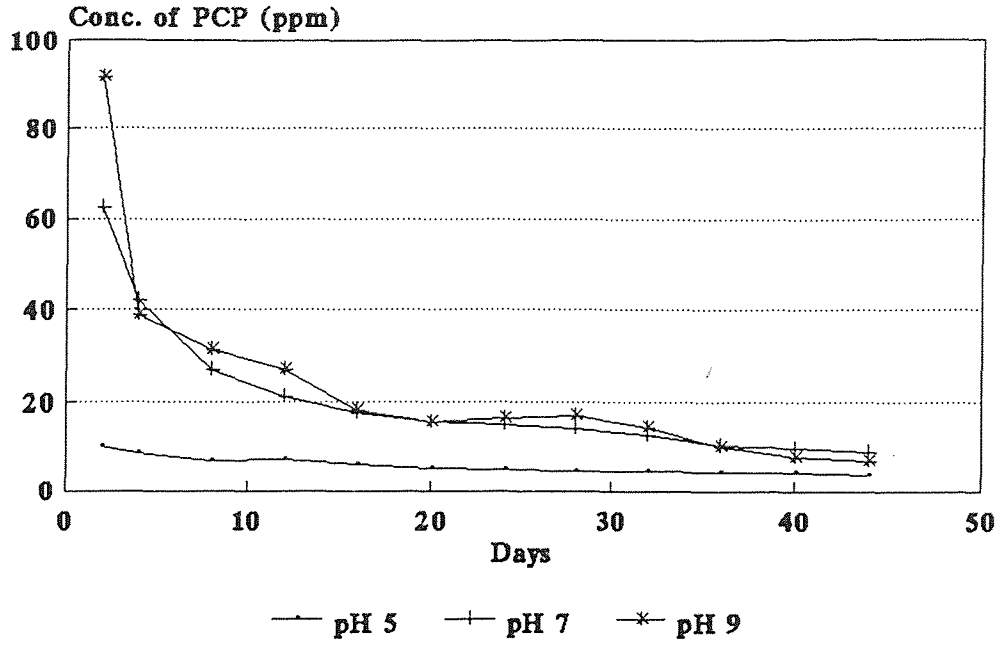

Figure 10 pH Effect on Leaching of PCP from Southern Pine at 30C

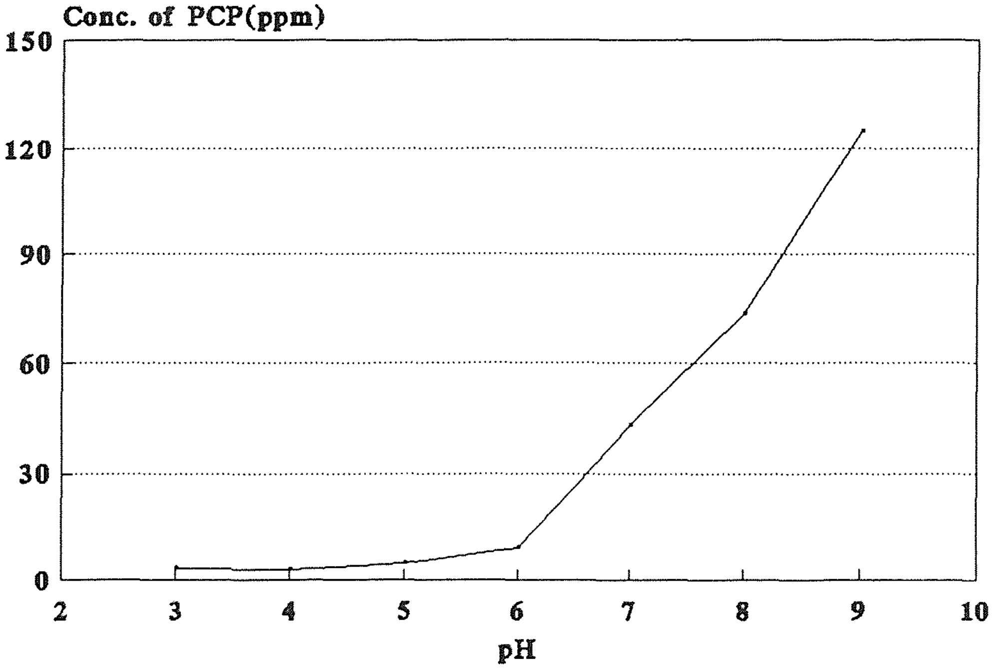

Figure 11 Leaching of PCP from Douglas Fir at Different pH Values

Table 12 Leaching Test for Southern Pine (ppm)

Day	30°C pH 5	30°C pH 7	30°C pH 9	30°C pH 9*
2	10.2	62.5	91.8	96.5
4	8.60	42.2	39.1	48.5
8	6.92	27.0	31.4	28.8
12	7.20	21.1	27.1	23.9
16	6.10	17.8	18.2	18.9
20	5.10	15.7	15.8	14.5
24	4.78	15.2	16.6	17.0
28	4.72	14.3	17.2	17.6
32	4.49	12.8	14.5	14.8
36	4.31	10.5	10.2	10.2
40	4.21	9.70	7.9	8.60
44	3.60	8.90	7.0	7.60

* Duplicate sample

3.3.2 Temperature Effect on the Leaching Rate of PCP

The temperature effect is as expected, with higher temperatures causing higher rates of leaching. Figure 12 shows the effect of temperature on leaching rate of PCP at pH 7.

3.3.3 Ionic Strength Effect on the Leaching Rate of PCP

The test of ionic strength effect was carried out by adding 0.05M $CaCl_2$ in the leaching solution of pH 9 at 30°C and compared with this solution that is free of $CaCl_2$. Figure 13 is the comparison of the results. It shows the increase of ionic strength of the leaching

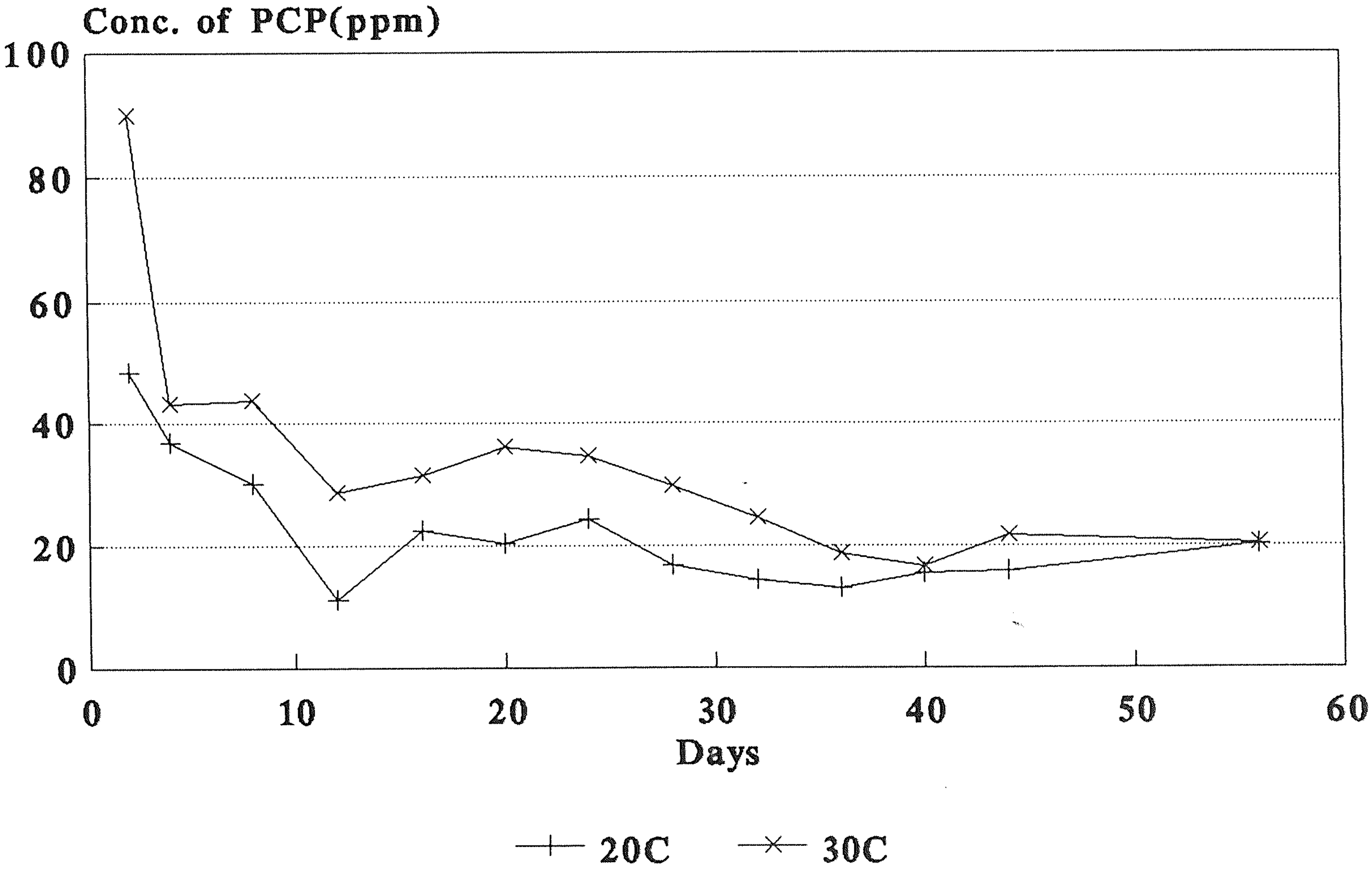

Figure 12 Temperature Effect on Leaching of PCP from Douglas Fir at pH 7

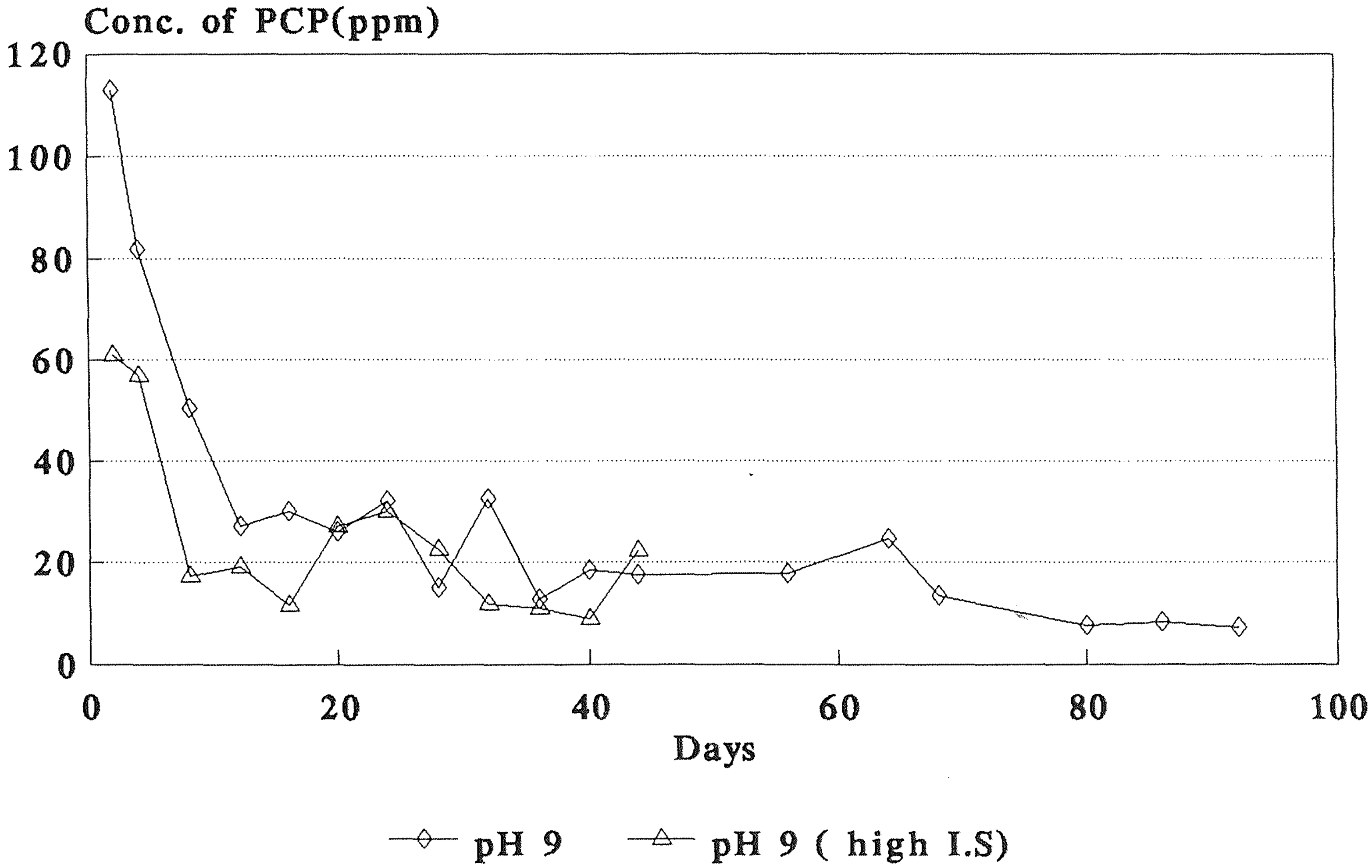

Figure 13 Ionic Strength Effect on Leaching of PCP from Douglas Fir at pH 9

solution will lower the rate of leaching of PCP, especially for higher concentration in the first few days. This result is expected because of the lower solubility of PCP in a solution containing added salt.

3.3.4 Volume of Leaching Solution Effect on Leaching Rate of PCP

The volume effect was tested with three cubes of Southern Pine by putting them in different volume of leaching solutions at room temperature. 100 ml, 200 ml and 400 ml of distilled water were used as leaching solutions. Each solution was changed every other day and only alternate samples were analyzed. Table 13 shows the results of each sample. Figure 14 is the plot of leaching amount of PCP at different volume of leaching solution. The results show that more PCP will leach out as the volume of leaching solution is increased. While the amount of PCP leached is different, the concentration of the solution does not vary significantly which leads to the conclusion that the saturation of the leaching solution is the eventual factor.

Table 13 Volume Effect on the Leaching of PCP

Day	100 ml		200 ml		400 ml	
	Conc. (ppm)	Amount (mg)	Conc. (ppm)	Amount (mg)	Conc. (ppm)	Amount (mg)
2	7.9	0.79	5.6	1.12	4.9	1.95
6	4.4	0.44	4.2	0.84	3.4	1.34
10	5.8	0.58	4.4	0.88	3.3	1.32
14	5.8	0.58	5.7	1.13	5.4	2.14
18	5.6	0.56	4.4	0.88	3.5	1.41
22	3.7	0.37	3.0	0.59	2.2	0.89

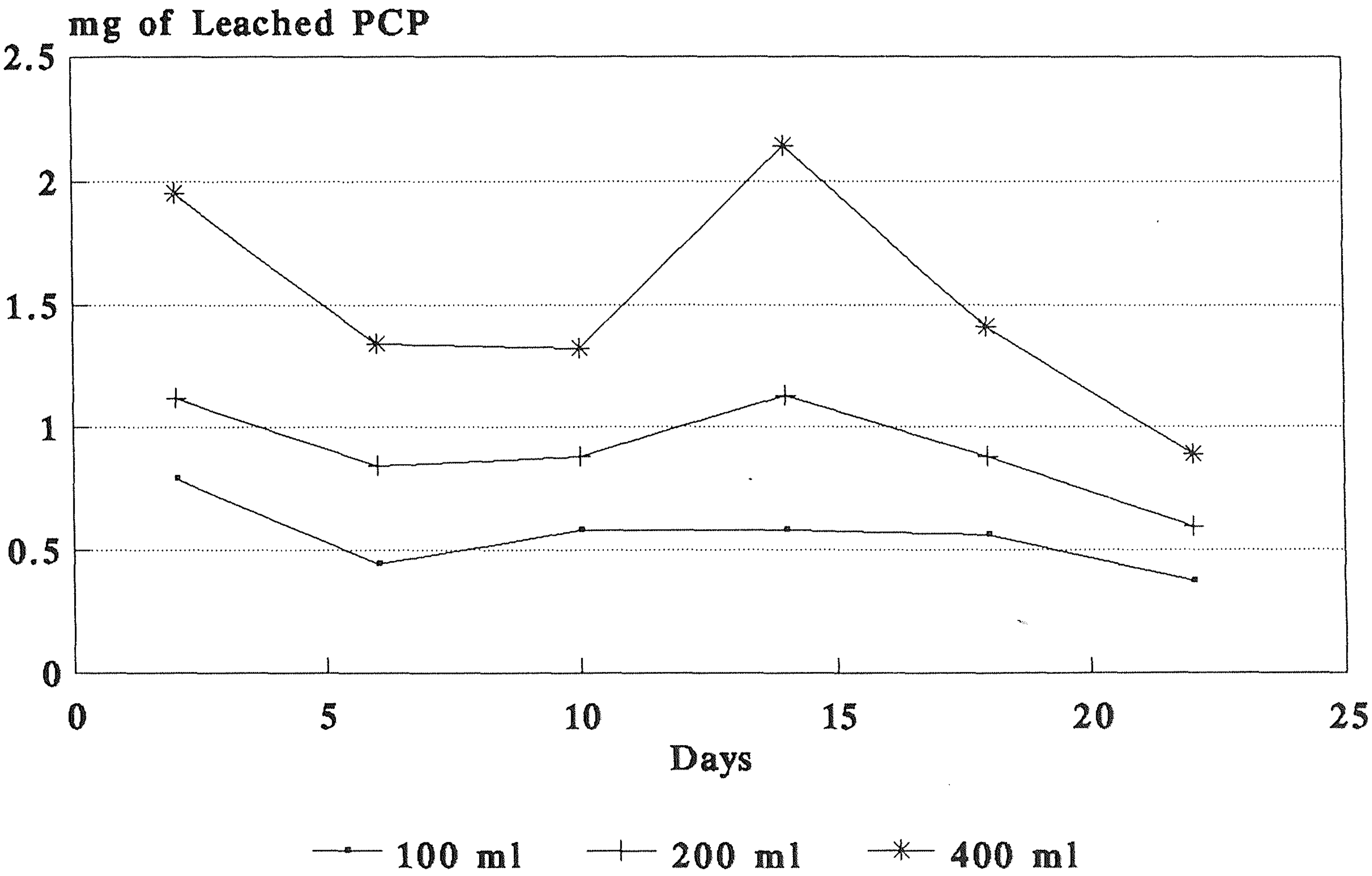

Figure 14 Volume of Leaching Solution Effect on Leaching of PCP

3.4 Estimation of the Amount of PCP Leached out from Wood During Experiment Period

Table 14 and Table 15 show the total amount of PCP leached out from each Douglas Fir and Southern Pine sample under various conditions in our experiments. The fastest leaching of PCP is at 30°C and pH 9. There is 75 % of PCP in wood leached out in 92 days, but it still has 25 % of PCP remaining in the wood.

Table 14 Total Amount of PCP Leached from the Douglas Fir

Temp (° C)	pH	Weight (g)	PCP* (mg)	Leached PCP in 58 Days		Leached PCP in 92 Day	
				mg	%	mg	%
20	5	14.1	298	30.6	10.3		
20	7	14.3	302	122	40.4		
20	9	14.0	296	154	52.0		
30	5	15.4	323	34.8	10.7	53	16.3
30	7	15.0	316	181	57.3		
30	9	14.8	312	192	61.5	234	75
30	9**	14.3	302	134	44.4		

* The PCP content in wood is 2.1 %

** For the effect of ionic strength

Table 15 Total Amount of PCP Leached from the Southern Pine

Temp. (°C)	pH	Weight (g)	PCP* (mg)	Leached PCP in 44 Days (mg)	Leaching % in 44 Days
30	5	15.5	264	24.9	9.4
30	7	16.7	284	82.6	29
30	9	16.2	275	96.5	35
30	9**	16.2	275	99.5	36

* The PCP content in wood is 1.7 %

** Duplicate sample

The calculation follows:

$$\text{Leached PCP \%} = \frac{\text{leached PCP}}{\text{amount of PCP in wood sample}} = \frac{A\ V\ D}{2\ C\ W} \times 10^{-4} \times 100\ \%$$

where: A is the average conc. of PCP in leaching solutions of leaching period (ppm)

V is the volume of leaching solution (ml)

D is the days of leaching

C is the content of PCP in wood pole (%)

W is the weight of wood sample (g)

3.5 Discussion and Prediction of Leaching Characteristics of PCP under Laboratory Conditions

From the results of leaching study, it seems that leaching rate of PCP at the condition of pH 5 declines very slowly in a linear-like decay during experiment period at both 20°C and 30°C. The accumulative amount of PCP leached out from wood increased linearly with time. By regressing the experimental data, we get the correlation equation and also can estimate how long the leaching of PCP will continue under laboratory condition for 1 inch cube of Douglas Fir and Southern Pine at pH 5. Table 16 shows the regression results.

Table 16 Regression Results at pH 5

Wood Type	pH	Temp. (°C)	Correlation Equation	Correlation Coefficient	Days of Leaching
Fir	5	20	$Y = 0.515\ X + 0.35$	0.999	577
Fir	5	30	$Y = 0.59\ X + 0.23$	0.999	547
Pine	5	30	$Y = 0.548\ X + 2.5$	0.993	478

Y Accumulative amount of PCP leached from the cube
X Days of leaching

The leaching study also shows that the leaching of PCP at pH 7 and pH 9 at 20°C or 30°C has a significant decrease during the first 12 days, then decreases slowly. The accumulative amount of PCP leached out from wood increased nonlinearly with time. It well matched the correlation equation of exponential association. Table 17 shows the regression results under each condition. Figure 15 is the regression curve with experiment data at pH 9, 30^{o}C during 92 days. The fastest leaching is estimated to last 209 days for 1 inch cube of wood.

These regression models for estimating the complete leaching were based on the study for 1 inch cube under laboratory conditions, it will be much longer for a whole pole under natural conditions. So if the poles are not disposed of properly, they could cause long-term potential risk to the environment, assuming no other means of retardation, stabilization or destruction take place.

Table 17 Regression Results at pH 7 and pH 9

Wood Type	pH	Temp. (^{o}C)	Correlation Equation	Correlation Coefficient	Days of Leaching
Fir	7	20	$Y = 350 (1 - e^{-0.00655X}) + 10.9$	0.997	272
Fir	9	20	$Y = 300 (1 - e^{-0.0087X}) + 37.4$	0.991	228
Fir	7	30	$Y = 320 (1 - e^{-0.0126X}) + 12.6$	0.998	269
Fir	9	30	$Y = 300 (1 - e^{-0.0124X}) + 34.4$	0.993	209
Fir*	9	30	$Y = 315 (1 - e^{-0.008X}) + 14.1$	0.993	307
Pine	7	30	$Y = 315 (1 - e^{-0.0065X}) + 16.6$	0.985	291
Pine	9	30	$Y = 330 (1 - e^{-0.0067X}) + 21.8$	0.985	217

* For ionic strength test
Y Accumulative amount of PCP leached out from the cube
X Days of leaching

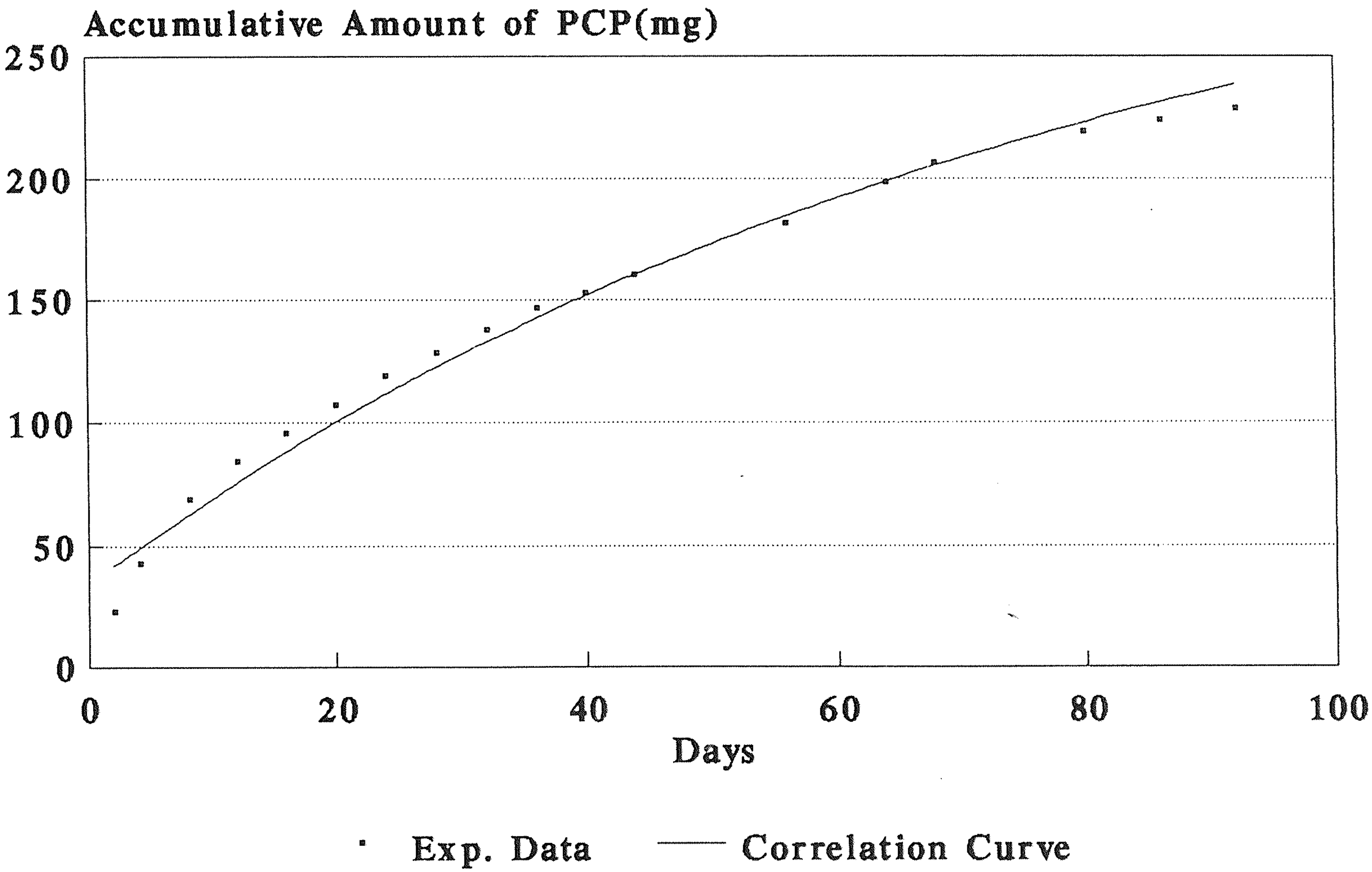

Figure 15 Correlation Curve of Leached PCP from Douglas Fir at 30C, pH9

CHAPTER 4

CONCLUSIONS

To study the leaching characteristics of PCP from treated utility poles under laboratory conditions, ultrasonic extraction with acetonitrile followed by HPLC was employed for the wood analysis and solid phase extraction followed by HPLC was employed for leaching solution analysis. The method detection limit is 0.3 ppm and the limit of quatitation is 1.0 ppm. The recoveries of blank spikes are > 85% with coefficient variation < 7.1 %, the recoveries of matrix spikes are > 77.5 % with C.V. % < 18 %. The results of samples and standards agreed well with those analyzed by Stevens Institute of Technology.

The study of the PCP distribution in wood pole shows that the highest content of PCP is at the outer surface of pole, the lowest content is between the center and the outer surface not at the center of the pole. A probable explanation is that the PCP entered the wood poles from both the outer surface and the two ends of pole, and that the center part of poles is more absorbent toward the PCP.

In the leaching rate study, the following results were obtained:

1. pH of leaching solution is the most significant factor influencing the leaching rate of PCP. The leaching rate increases as the pH rises and it increases greatly when pH > 6.
2. An increase in temperature will cause higher leaching rate.
3. An increase in ionic strength will lower the leaching rate of PCP.
4. An increase in volume of leaching solution will increase the leaching rate of PCP.
5. The fastest leaching of PCP from Douglas Fir in our study is at 30°C, pH 9. The percentage of PCP that leached out in 92 days is about 75% while the leaching of PCP at pH 5, 30°C for 92 days is only 16.3 %.
6. The leaching characteristics of PCP under laboratory conditions are modeled as follows:

a) At pH 5 the accumulative amount of PCP leached out from the wood cube increased linearly with time that can be expressed as: $Y = AX + B$

where: Y is the accumulative amount of PCP leached out from the cube

X is the days of leaching

A and B are constant under constant leaching conditions

b) At pH > 7, the accumulative amount of PCP leached out from wood cube increased nonlinearly with time that can be expressed as: $Y = Ae^{-BX} + C$

where: Y is the accumulative amount of PCP leached out from the cube

X is the days of leaching

A,B and C are constants under constant conditions

By using these models, we may predict how long the leaching will last. At the condition of pH 9, 30°C, the leaching is estimated to last 209 days, and at pH 5, 20°C, the leaching will last 577 days for a 1 inch cube under laboratory conditions. It will be much longer for a whole pole.

According to the results of our study, we may provide some useful recommendations for the wood disposal. The used utility poles should be kept under acidic conditions to minimize the leaching of PCP, or be treated with basic solution to remove PCP before they are discarded.

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