Effect of physical properties of pentachlorophenol and creosote components on vaporization from treated wood: Review of prior data

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Abstract

This paper contains a review of the literature related to vaporization of organic wood preservatives, pentachlorophenol and creosote from treated samples of lumber. These studies are related to the effects of temperature, carrier solvents, coatings, and other experimental parameters. A re-examination of the results from experiments related to temperature effects on the vaporization of organic wood preservatives from treated wood is also included. A semi-empirical equation that correlates the boiling point of creosote components and pentachlorophenol with air concentrations of test specimens at different temperatures is described.

The purpose of this paper is to review previous studies relative to the vaporization of organic wood preservatives from treated wood and to describe how vaporization rates are affected by concentration, heat of vaporization, and surrounding temperature. In October of 1978 the United States Environmental Protection Agency issued notices of Rebuttable Presumptions Against Registration (RPAR) on creosote, inorganic arsenicals, and pentachlorophenol (PCP). As a result of what became known as the RPAR process, existing information was compiled and new information generated through laboratory tests in meeting the re-registration requirements of these products as wood preservatives (Anonymous 1980). One of the earliest reports of airborne levels of PCP in an enclosed area listed concentrations as high as 160 $\mu g/m^3$ (Gebefugi 1979). Later investigations during the time period 1978 to 1985 include laboratory studies of samples of southern pine lumber treated with PCP in three different carrier solvents: methylene chloride, liquefied petroleum gas, and P9-Type A oil (Ingram et al. 1981a). Samples of southern pine (1.9 cm by 7.6 cm by 30 cm) were treated with a solution of PCP in the selected solvent to a retention of approximately 0.4 pcf of active ingredient. Each sample was evaluated in a test chamber with experimental variables of temperature, air flow rate, relative humidity, and sampling times. Glass impingers containing dilute NaOH in water were used to trap airborne PCP from air flowing through the test chamber over the treated sample. The amount of PCP in each impinger was determined using gas chromatography/mass spectrometry isotope dilute analysis with 18_0 labeled PCP (Ingram et al. 1979).

One of the important observations from this study was that vaporization of PCP was lower for samples where P9-Type A oil was the carrier solvent. The other important observation in this study was that a 20° to 30°C increase in temperature resulted in a three- to fourfold increase in airborne PCP concentrations. This observation indicated that PCP evaporated from the surface of the treated wood into the surrounding atmosphere at a rate related to the partial vapor pressure of PCP. The measured concentrations of PCP in air followed the pressure-temperature relation as predicted by

the Clausius-Clapeyron relation in Equation [1]:

$$d(\ln P)/d(1/Tex) = -Hvap/R \quad [1]$$

where:

P = vapor pressure

Tex = temperature kelvin (K)

$Hvap$ = heat of vaporization

R = universal gas constant expressed in the appropriate units of measurement (Ingram et al. 1981a, 1981b)

It was reported that relative humidity had little or no effect on the measured levels of PCP.

Equation [2] can be used to determine the heat of vaporization of pure compounds from experimental data (Moore 1962).

$$-\ln(P) = Hvap/R \; (1/Tex) + c \quad [2]$$

If vapor pressure measurements are made at different temperatures with pure compounds, and the data are presented graphically as $\ln(p)$ versus $(1/Tex)$, the slope is equal to $Hvap/R$ and c is the y-intercept (Moore 1962).

The concentration of PCP in air did not change over the range of flow rates studied (0.2 to 1.0 L/min). This observation indicates that "airborne concentrations" remained constant and "rates of vaporization" at the surface of the sample changed with airflow rate. At a temperature of 43°C, the highest examined, concentration of PCP in air was 310 µg/m³ with methylene chloride as the carrier solvent (Ingram et. al. 1981a). With an airflow rate of 1.0 L/min. this value corresponds to a rate of vaporization of 0.31 µg/min. Under the same conditions, samples of lumber treated with PCP in P9-type A oil gave airborne concentrations of 170 µg/m³, or a rate of vaporization of 0.17 µg/min.

Subsequent experiments with a wide variety of solvents and co-solvents indicated that heavy oils and nonvolatile polar solvents gave the lowest PCP vaporization rates, while southern pine lumber treated with methylene chloride or mineral spirits without a nonvolatile co-solvent gave the highest rates of PCP vaporization (Ingram et al. 1981b). Higher rates of PCP vaporization were observed in the second study due to a change in size of the test cylinder. A 4.2-liter glass test chamber, which was about 10 percent of the volume of the first test cylin-

der, was used in this study. Also, a number of paints and coating systems were evaluated to determine their capacity to reduce PCP vaporization from treated southern pine (Ingram et al. 1983). Similar results with quanternary ammonium salts that prevented the vaporization of PCP by complex formation were also reported (Warren et al. 1982). A summary of the results from studies on the vaporization of PCP from treated wood was previously published (Ingram et al. 1986).

While the studies of vaporization of PCP from wood were focused on a single compound of relatively low concentration, measurements of the rates of vaporization of creosote from treated wood presented different problems. Creosote is made up of about 16 major components and over 250 minor components. The components vary in degree of volatility as well as concentration. Samples of creosote-treated lumber were evaluated in the same test chamber (4.2 L) as used for the PCP vaporization experiments. Airflow rates were in the range of 0.25 to 1.0 L/min. and the temperature range was from 20° to 38°C. Air was passed through tubes packed with approximately 0.6 g Amberlite XAD-2 resin for the duration of each experiment. The adsorbed volatile compounds were eluted with pentane and the amounts of each compound were determined using an internal standard and capillary gas chromatography with flame ionization detection (Ingram et al. 1984).

The airborne concentrations of compounds commonly present in creosote (indene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthene, dibenzofuran, and fluorine) were determined for all air samples tested. Concentrations of creosote components in air ranged from 0.5 mg/m³ for fluorene to 198 mg/m³ for naphthalene. Naphthalene made up approximately 75 percent of the total amount of volatile compounds in air samples but was only 10.5 percent of the liquid creosote used to treat the samples. Other, more nonvolatile, components of creosote such as phenanthrene, carbazole, fluoranthene, pyrene, 1,2-benzanthracene, and chrysene were not observed as components of the volatile material. The concentrations of creosote components in air were higher than the concentration of PCP under similar test conditions. The effect of an increase in temperature on the rates of vaporization of creosote components

was similar to that observed for PCP. Airflow rate also affected the rate of creosote vaporization. The concentration of the more volatile components increased slightly when the airflow rate was decreased from 1.0 to 0.20 L/min. (Ingram et al. 1984).

Although results from these experiments were reported as the weight of compound per unit volume of air, the treatment of this amount of compound as a gas relative to the partial pressure is useful. For example, 100 µg/m³ of PCP corresponds to 3.75×10^{-7} moles/m³ on a mole/volume basis. Using the relation $V = nRTex/P$, the actual volume of PCP vapor in 1 m³ of air is 9.16×10^{-3} cm³ at 25°C and 1 atm pressure. For gases, 1 part per million by volume (PPMv) equals 1 cm³ in a cubic meter, so that 9.16×10^{-3} cm³ of PCP in a cubic meter equals 9.16×10^{-3} PPMv. Because the total pressure of a gas mixture is equal to the sum of the partial pressures of the individual components, then 100 µg/m³ of PCP vapor corresponds to a partial vapor pressure of 9.2×10^{-9} atm (7.0×10^{-6} mm) at 25°C. This value is approximately 6.4 percent of the reported vapor pressure of 1.1×10^{-4} mm at the same temperature. The value of 6.4 percent is derived in a manner that corresponds to the calculation of relative humidity where water vapor is the gas of interest.

Impact of boiling point on vaporization of PCP and creosote components

The concentration of individual creosote components in wood was related to the amount of that component found in air samples. Graphical plots of $\ln(Ca/Cw)$ versus the boiling point at 1 atm of the respective compound were linear for the range of experimental variables (Ingram et al. 1984). In the 1984 paper, Ca equals the concentration of the specific creosote component in air and Cw equals the concentration of the same component in wood. Graphical presentation of these data in the 1984 publication gave four separate and almost parallel lines for each temperature.

A slightly different approach to viewing these results is to set Tex in Equation [2] equal to the boiling point of the compound which by definition sets P equal to 1 atm. Hence, for a vapor pressure of 1 atm $c = Hvap/RTb$. Substituting c into Equation [1] gives Equation [3], which is the same basic equation as described for pure compounds (Atkins 1999):
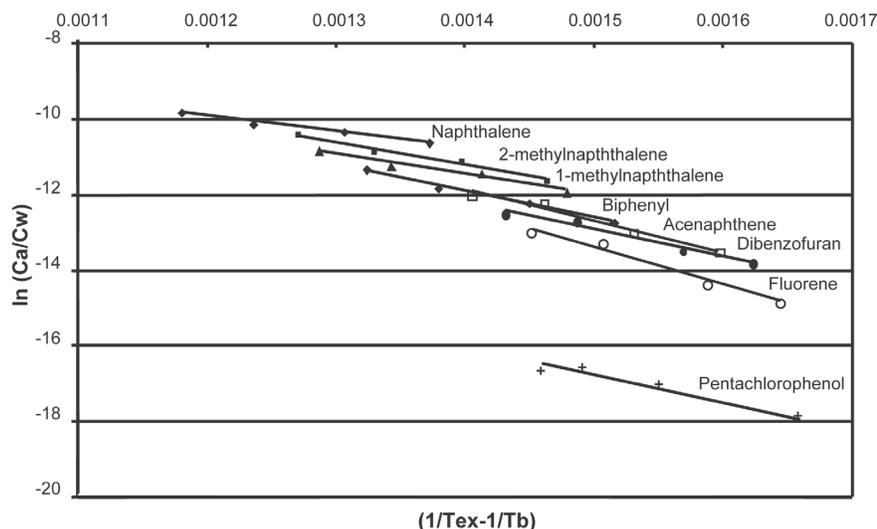
Figure 1. — Plots of creosote and PCP vaporization data showing combined effects of concentration of each component in wood, temperature of experiment, and boiling point of each compound. Ca = concentration of compound in air, CW = concentration of compound in wood, Tex = temperature of experiment (K), and tb = boiling point of each compound (K).

Table 1. — List of creosote compounds, slopes, and r^2 values from the data presented in **Figure 1**.

Compound	Slope × 0.001	r^2
Naphthalene	-4.01	0.99
2-methylnaphthalene	-5.85	0.97
1-methylnaphthalene	-5.40	0.97
Biphenyl	-7.10	0.99
Acenaphthene	-8.27	0.97
Dibenzofuran	-7.02	0.98
Fluorene	-9.82	0.98
PCP	-7.35	0.96

Table 2. — List of compounds, calculated heats of vaporization, reported heats of vaporization, and boiling points for volatile creosote components.

Compound	$Hvap$ CA database[a]	$Hvap$ calculated	Boiling point[a]
	- - - - - - - - - - - - - (kJ/mole) - - - - - - - - - - - -		(°C)
Naphthalene	43.85	32.6	218
2-Methylnaphthalene	45.75	48.6	239
1-Methylnaphthalene	46.03	44.9	240
Biphenyl	47.55	59.1	255
Acenaphthene	49.68	68.8	279
Dibenzofuran	50.5	58.3	287
Fluorene	51.18	59.8	294
PCP	57.2	61.1	310

[a]Heats of vaporization and boiling points for each compound were taken from the online American Chemical Society Chemical Abstract Data Base using SciFinder.

$$-\ln(Pa) = Hvap/R \, (1/Tex - 1/Tb) \quad [3]$$

Assuming for solutions, or solutions in solids, that the partial pressure of the compound is linearly related to the concentration of the individual compound, $\ln(Pa)$ can be replaced by [$\ln Ca - \ln Cw + \ln c'$]. This approximation gives the semi-empirical formula of Equation [**4**].

$$-\ln(Ca/Cw) = Hvap/R \, (1/Tex - 1/Tb) + \ln(c') \quad [4]$$

Ca and Cw are the same as described in previous equations and $\ln(c')$ is a proportionality constant that corresponds to the y intercept in the graphical presentation of the data. There is an underlying

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[1] Values were taken from the online American Chemical Society Chemical Abstract Database Using Sci Finder.

assumption that Ca and Cw are constant during the course of the experiment. It is important to note that these experiments were conducted with freshly treated samples and the amount of organic material at the surface was at the maximum for the life of the sample.

Using this equation as a model, data for creosote components from Figure 6 in the 1984 publication were re-plotted as shown in **Figure 1**. Measurements for PCP concentrations were taken from a previous publication (Ingram 1981b). The r^2 values for each line ranged from 0.96 to 0.99, which indicated that the results from these measurements were essentially linear over the range of values and conditions used in these experiments (**Table 1**).

The heat of vaporization (*Hvap*) for each compound was calculated from the respective slopes. A comparison of the experimental *Hvap* to the *Hvap* from the literature[1] indicated that the heats of vaporizations were comparable (**Table 2**). The experimental values for biphenyl, acenaphathene, dibenzofuran, and fluorene were higher than the values reported in the literature.

The calculated heat of vaporization for naphthalene was lower than the literature value. The boiling points for the compounds listed in **Table 2** ranged from 218° to 294°C. Melting points and solubility of each compound in the mixture may also be a factor. Phenanthrene, anthracene, fluoranthene, and pyrene were not observed in measurable concentrations in air samples during these studies. These four compounds occur at concentrations comparable to those compounds in **Table 2**, but have higher boiling points.

The slope of the PCP data followed the same trend as the data for creosote components (**Fig. 1** and **Table 2**). The line for PCP was displaced to a different point along the x-y axis of the graph. The different location on the graph is due to the lower concentration of PCP observed in these experiments. The polarity, degree of fixation, and tendency of PCP to behave as a moderately strong acid may be factors related to the lower concentrations of PCP in air samples.

Discussion

Vaporization of organic wood preservatives from treated wood may account for a significant route of depletion for compounds with adequate vapor pressure at ambient temperature. Compounds with high boiling points, and thus low vapor pressures, will have a decreased tendency to evaporate. Diffusion and the rate of movement of chem-

icals to the surface of the wood of individual molecules is likely an important factor as samples are aged or weathered. The non-polar compounds in creosote appear to follow a general trend over the range of boiling points. However, samples treated with PCP (boiling point = 310°C) gave lower concentrations in air when tested under the same conditions as the creosote-treated samples. The lower vaporization tendency of PCP may be due to polarity H-bonding.

The heat of vaporization of each individual compound is approximately related to the boiling point by an empirical value called Trouton's constant. These values are available both in text and on-line databases and can be used with Equation [**4**] to estimate the relative volatility of potential wood preservatives. This model may serve as a good approximation to volatility, however, due to differences in polarity, solubility, and effect of solvents, each compound should be evaluated under the conditions of intended use.

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