Potential groundwater pollution from chemically treated wood

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Abstract

This paper presents results of recent studies conducted to assess the groundwater pollution potential of pentachlorophenol (PCP) treated wood. Specifically, studies on leaching rates, adsorption desorption and anaerobic biodegradability under different conditions have been conducted on soils and groundwater collected from wood treating facilities and telephone pole sites in six locations throughout the United States. The results of the laboratory measurements provided the necessary parameters to conduct modeling studies using the United States Environmental Protection Agency Composite Model for Landfills (USEPA CML) which assesses the extend of adverse impact of PCP on aquifers. The modeling results can be used to provide regulatory guidelines with respect to alternative disposal practices in solid waste landfills as well as performing risk assessments for site specific scenarios.

1 Introduction

Chemical preservation of wood has been practiced in the United States for over 100 years. The wood is usually treated under pressure with PCP in petroleum or other solvents, creosote, water solutions of heavy metals (copper, chromium, arsenic and zinc), copper and zinc aqueous solutions in ammonia, and fire retardants (combinations of phosphates, borates, boric acid, and/or zinc compounds). The wood is impregnated with a solution containing the preservatives by application of pressure (50 to 200 psi) or by immersion in the preserving solution.

Older processes used oil-based preservatives which produced significant quantities of sludge wastes and wastewater. Modern facilities have turned to water soluble preservatives which generate little or no wastewater, and small quantities of metal-containing sludges. Sources of contamination at wood preserving sites include: 1) process wastewater from conditioning, treated wood washing, preservative formulation recovery, and rinsing of drums and storage tanks, and 2) surface runoff water from process areas, drip pads, and treated wood storage areas [11].

Process sludges and residuals have been historically dumped in unlined, earthen pits which have become major sources of groundwater contamination as these wastes can migrate through the soils into the aquifers. Moreover, excess preservatives from the treated wood surfaces can be carried by rain into the subsurface. In addition, the fate of PCP eluted from treated products in contact with the soil has been a rising concern. Leaching tests performed on PCP-treated Douglas Fir showed that the rate of release of PCP is initially controlled by the pH of the extracting solution and temperature. However, once the surface concentration is depleted the rate of release is controlled by diffusion of the substance from the inner wood layers to the surface [1]. This paper focuses on the potential contamination resulting from PCP treated wood. More specifically, soil sorption and microbially mediated transformation, under anaerobic conditions, are examined in order to assess the fate and transport of PCP in the subsurface environment.

Approximately 48,000,000 ft^3 of wood was treated with PCP in the United States in 1988 [11]. Most of the PCP-treated wood is used for utility poles, crossarms, and fence posts. Aged treated wood products are usually landfilled and PCP often appears in the leachate of landfills that received such wastes. Technical grade PCP contains 85% to 90% PCP, 4% to 8% 2,3,4,6-tetrachlorophenol, 2% to 4% higher chlorophenols, and 0.1% dioxins and furans. PCP is denser than water but the commonly used solution contains petroleum solvents forming a mixture less dense than water which floats on top of the groundwater as a light nonaqueous phase liquid (LNAPL).

The objective of this paper is to investigate the effects of anaerobic biodegradation and sorption on the Dilution/Attenuation Factor (DAF) in partially and fully saturated soils. The DAF is the inverse of the normalized concentration at a compliance point in the underlying aquifer with respect to a given source in the unsaturated zone. The DAF of a specific compound can be obtained by computer simulations using a model proposed by USEPA CML [9]. The DAFs are in turn used to compute the regulatory levels of a hazardous substance in a landfill or surface impoundment.

In order to produce realistic DAF values for PCP, under various environmental scenarios, CML requires data on sorption and degradation of the compound in groundwater-soil matrices. The organic carbon partition coefficient, K_{oc}, an adsorption partition coefficient normalized with respect to the organic carbon content, was obtained from batch adsorption experiments with natural soils. Anaerobic biodegradation rates were established by conducting experiments in serum vials, which were incubated at 10°C and 20°C for 64 weeks, using soil and groundwater collected from various locations in the United States.

2 PCP Adsorption by Natural Soils

The mobility of PCP in the subsurface is influenced by its solubility in the groundwater-soil matrix, precipitation and complexation reactions, and the chemical and physical properties of the soil. PCP is a weak organic acid ($pK_a = 4.75$) and its aqueous solubility is 14 mg/L at 20°C but it is a function of both pH and temperature. Sorption of PCP by soils is strongly affected by the presence of co-solvents such as diesel oil [3] and solution pH. [4,8]. At low pH the neutral form of the PCP predominates and adsorption by soils is favored. However, at elevated pH the pentachorophenate ion is the predominant species and soil adsorption is weak. This implies that the mobility of PCP in the subsurface is higher in alkaline environments due to the low affinity of the anionic form of the acid for the soil surface. The organic carbon partition coefficient is defined as:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad (1)$$

where f_{oc} is the percent organic carbon content of the soil and K_d is the linear partition coefficient of adsorption given by:

$$K_d = \frac{q_e}{C_e} \qquad (2)$$

where q_e and C_e are the equilibrium concentration of PCP in the solid and liquid phases respectively.

The batch adsorption studies were conducted in accordance with the EPA protocol for determination of sorption of chemicals by soils [10]. Natural soils of varying organic carbon content, grain size distribution, cation exchange capacity (CEC), and clay and silt content were used and the experiments were carried out in three pH domains. From the sorption data isotherms were constructed and the normalized organic carbon partition coefficients were calculated. The average K_{oc} values at pH of 4, 7, and 10 were 25015, 973 and 477 respectively. These values were supplied to the CML simulator for the estimation of the DAFs.

3 PCP anaerobic biodegradation

Numerous fungal and bacterial species, capable of using PCP as a sole carbon source have been reported in the literature. A wide variety of pathways for the degradation of PCP, contingent upon the microbial communities involved, are reviewed by the World Health Organization [12]. Possible mechanisms include methylation, acylation, dechlorination and hydroxylation. Among the most important metabolic intermediates are tetra-, tri-, and di- chlorophenols and anisole. These metabolites may be subject to further transformations leading to complete mineralization as evidenced by CO_2 and Cl^- production reported by Murthy *et al.* [6] and Suzuki [7]. Microbial degradation of PCP has been documented for various environments including aqueous suspensions and soil samples under aerobic as well as anaerobic conditions. Reducing environments, such as those observed under anaerobic conditions, tend to favor reductive dechlorination. In addition to various chlorinated intermediates, phenol and complete mineralization products (CH_4 and CO_2) have been reported in the literature [2]. It is also noteworthy that a number of aromatic compounds that may co-exist with PCP in contaminated sites can be biodegraded via the chlorophenol route. [5].

Since in most contaminated sites aerobic conditions may be present only in top soil formations, the present study focused in anaerobic biotransformation of PCP by indigenous microbial species acclimated to the specific contaminant. The objective of this part of the study was to establish anaerobic biodegradability of PCP, determine the first-order kinetic constant and estimate the half-life. These data are then used as input to CML model for the determination of the DAF for PCP. The biodegradability study followed the EPA protocol titled *Anaerobic Microbiological Transformation Rate Data for Chemicals in Subsurface Environment* (40 CFR, Part 795.54). A total of 2268 serum bottles were prepared; 189 bottles for each of the 12 samples. Amended (with added sulfate) and unamended microcosms, were incubated at two temperatures representative of average site conditions (10 and 20 °C). Analysis included HPLC, GC/MS for PCP and transformation intermediates, ion chromatography for sulfate and chloride, dissolved oxygen and pH. Active, negative and positive controls were maintained to provide a good background for the experiments.

The results of the microcosm analysis over a 64 week period were evaluated and first order degradation constants were derived by curve fitting.

Subsequently, anaerobic degradation half lives were determined and were found to vary in the range of 23 to 64 weeks with an average value of 52.32 weeks (366 days). A typical PCP concentration history of a microcosm under anaerobic conditions is shown in Figure 1.

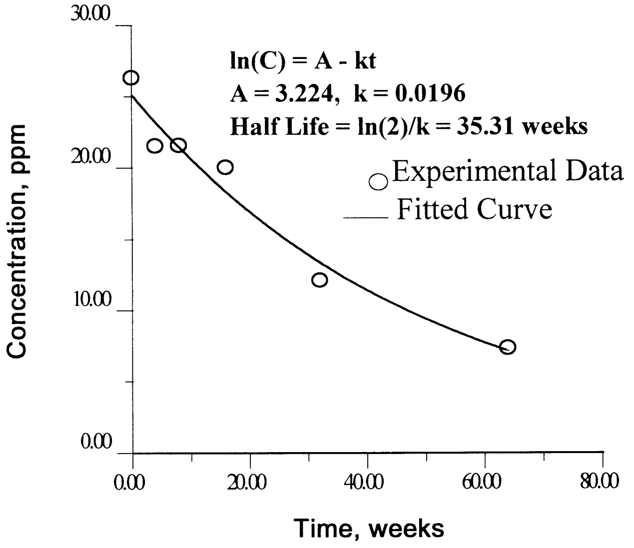

Figure 1. Typical PCP concentration history in a microcosm bottle under anaerobic conditions

4 Modeling studies

Modeling studies were performed using the EPA CML. The EPACML simulates the movement and fate of contaminants originating from a landfill, through the unsaturated and saturated zones. The model consists of one dimensional flow and mass transport modules in the unsaturated zone and a three dimensional mass transport module, under one dimensional uniform flow, in the saturated zone. The model is used to back-calculate the allowable concentration of a chemical constituent at the source (below a landfill or a disposal area) such that the concentration at a receptor location does not exceed a maximum health based threshold level. The code uses a Monte Carlo scheme to quantify uncertainties in the input parameters by randomly generating parameter values. The model computes concentration values at various locations downgradient of a disposal facility. If C_w represents the normalized concentration of a constituent at a receptor location, and C_t represents the health based maximum concentration of the same constituent at the same location, the maximum allowable concentration at the landfill location C_l is computed as:

$$C_l = \frac{C_t}{C_w} \tag{3}$$

The inverse of the normalized concentration at the receptor location is defined as the DAF.

The allowable health based concentration at a receptor location, also called the Maximum Contaminant Level (MCL) for PCP is 0.001 mg/l. This level has been set on the basis of PCP's classification as a B2 carcinogen. The regulatory level which if exceeded would classify a PCP treated matrix such as wood, as a hazardous waste, on the basis of the Toxicity Characteristics Leaching Procedure (TCLP test), is related to the MCL and DAF as follows:

$$\textbf{Regulatory Hazardous Waste Level} = \textbf{DAF} \times \textbf{MCL} \tag{4}$$

From TCLP tests conducted in various sections of PCP treated telephone poles it has been found that the PCP concentration in the TCLP leachate ranges from not detected to over 20 mg/l with an average value of approximately 10 mg/l. In order for PCP treated wood not to be classified as a hazardous waste, DAF values in excess of 10,000 must be computed in EPACML simulations.

The CML computes DAF values on the basis of statistically distributed, nationally averaged input parameters, derived from actual landfill sites in the United States. The model produces nationwide DAFs on the basis of leachate concentrations necessary to have various percentiles of landfill sites in compliance. For regulatory purposes, the USEPA has been using the 85th percentile (i.e., the maximum allowable leachate concentration is chosen such that at least 85% of the sites are in compliance) for DAF computations. However the USEPA has recently proposed that the confidence interval be increased to the 95 th percentile. Both percentiles are reported in the model runs presented herein.

The importance of the DAF values computed by the CML in setting a regulatory value for PCP is obvious from the above explanation. The model output is influenced greatly by three parameters namely, the sorption coefficient, the biodegradation rate constant and the total time of simulation (source duration). Results of selected computer simulations are shown in Table 1. The first six rows of Table 1 show the DAF values obtained from a sensitivity analysis of CML for arbitrary values of K_{oc} and biodegradation half lives. The last row shows the resulting DAF from a simulation using the average values of K_{oc} and anaerobic biodegradation half life obtained from the laboratory experiments conducted for this study. It is observed that very high DAFs are obtained for both the 85th and 95th percentiles, much higher than it is required to classify PCP treated wood as hazardous waste. It must be noted that a simulation time of 100 years was used, which assumes that PCP is leaching at the landfill for the entire duration at the maximum concentration. This is a quite conservative assumption. Lower DAFs are expected for longer simulation times. A new version of CML recently released by the USEPA accounts for a finite contaminant mass at the source.

Table 1. Variation of Nationwide DAF as Computed by CML

Simulation Time(years)	K_{oc} (ml/g)	Half Life (days)	DAF (85th Percentl.)	DAF (95th Percentl.)
100	0	∞	26.2	4.5
100	500	∞	2.3×10^{4}	35.3
100	2500	∞	1.0×10^{36}	9.3×10^{3}
∞	0	1000	5.6×10^{3}	117.6
∞	0	500	1.5×10^{5}	640.2
∞	0	366	2.5×10^{6}	7.5×10^{3}
100	973	366	1.0×10^{36}	8.6×10^{13}

5 Conclusions

The results of the study reported in this paper show that neglecting adsorption and biodegradation mechanisms in the derivation of regulatory limits for PCP treated wood, yields excessively conservative values. It has been shown by applying laboratory derived values of adsorption coefficients and biodegradation half lives, that the EPACML model yields DAF values which under certain conditions may not warrant the classification of PCP treated wood as hazardous waste.

6 Acknowledgments

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7 References

1. Bellcore. *Pentachlorophenol leaching characteristics study*, Special Report SR-NWT-002742, 1, Morristown NJ, 1993.
2. Bryant, F. O. et al. Regiospecific dechlorination of pentachlorophenol by dichlorophenol-adapted microorganism in fresh water, anaerobic sediment slurries, *Appl. Environ. Microbiol.*, 1991, **57**, 2293-2301.
3. Cristodoulatos, C. et al. Adsorption of pentachlorophenol by natural soils, *J. Environ. Sci. Health,* 1994, **A29(5)**, 883-898.
4. Lee, S. L. et al. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems, *Environ. Sci. Technol.*, 1990, **24**, 654-661.
5. Mueller, J. E. et al. Bench scale evaluation of alternative biological treatment processes for the remediation of pentachlorophenol- and creosote-contaminated materials: slurry phase bioremediation, *Environ. Sci. Techol.*, 1991, **25**, 213.
6. Murthy, N. B. K. et al. Degradation of pentachlorophenol (PCP) in aerobic and anaerobic soil, *J. Environ. Sci. Health,* 1979, **B14**, 1-14.
7. Suzuki, T. Metabolism of pentachlorophenol by a soil microbe, *J. Envron. Sci. Health,* 1977, **B12**, 113-127.
8. Talimcioglu, N. M. et al. Adsorption effects on the transport of pentachlorophenol in soils, in Joint CSCE-ASCE National Conference on Environmental Engineering (eds. R. N. Yong, H. Hadjinicolaou, A. M. O. Mohamed), pp. 1257-1264, *Conference Proceedings,* Montreal, Canada, 1993.
9. USEPA. *Background document for EPA's Composite Model for Landfills (EPACML)*, Office of Solid Waste, Washington DC, 1990.
10. USEPA. *Batch-type procedures for estimating soil adsorption of chemicals*, EPA/530-SW-87-006-F, Washington DC, 1992.
11. USEPA. *Contaminants and Remedial Options at Wood Preserving Sites,* EPA/600/R-92/182, Office of Research and Development, Washington DC, 1992.
12. World Health Organization (WHO). Environmental Health Criteria 71, *Pentachlorophenol,* United Nations Environmental Programme, International Labour Organization, World Health Organization, Geneva, 1987.