

**Literature Review, Computer Model and Assessment
of the Potential Environmental Risks Associated With
Pentachlorophenol Treated Wood Products
Used in Aquatic Environments**

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Introduction

Pentachlorophenol or “Penta” was described in the scientific literature as early as 1841 and has been commercially produced since 1936. Products using pentachlorophenol as an active ingredient have been used as herbicides, insecticides, fungicides, molluscicides and bactericides (EPA, 1980). In 1994, the total industry production of wood treated with oil-borne preservatives (primarily pentachlorophenol with some copper naphthenate) was 41,297,000 cubic feet representing 6.5% of the total volume of treated wood produced in the United States. Utility pole preservation accounted for 71% of the total U.S. oilborne production (AWPI, 1994). The U.S. EPA approved Consumer Information Sheet (CIS) for pentachlorophenol contains the following permitted and restricted uses:

Permitted uses for penta:

1. *Ground contact areas of farm buildings where domestic animals or livestock are unlikely to crib (bite) or lick the wood.*
2. *Penta treated wood can be incidentally used in the construction of bridges and docks in direct or indirect contact with either human or livestock drinking water.*
3. *Penta treated wood can be used in building interiors (including farm buildings) where the wood is in ground contact providing that two coats of an appropriate sealer are applied.*
4. *Penta is typically used for the preservation of utility poles, crossarms, bridges, fenceposts and other uses requiring that the strength of the wood be retained.*

Restricted uses of penta

1. *Penta treated logs should not be used in constructing homes.*
2. *Penta treated wood should not be used in applications where prolonged contact with the skin may occur such as outdoor furniture unless a sealer is applied.*
3. *Penta should not be used in areas where domestic animals are likely to crib (bite) or lick the wood. In addition, Penta should not be used for farrowing or brooding facilities.*
4. *For animal or human food storage.*
5. *For cutting-boards or countertops.*

Because wood that has been preserved with penta does not become brittle and retains its strength, it can be the material of choice in bridge construction. In addition, aquatic environments can be exposed to pentachlorophenol when preserved utility poles are used to cross streams and wetlands. The purpose of this risk assessment model is to provide project proponents and regulators with a quantitative risk assessment to judge the potential risks associated with the use of pentachlorophenol where it may come into contact with aquatic environments.

Sources of pentachlorophenol and observed environmental concentrations

The U.S. Department of Agriculture (USDA, 1980) notes that pentachlorophenol is, “ubiquitous in aquatic environments and its sources are unclear.” Observable levels may result from direct contamination, from degradation of other organic compounds, or from chlorination of water. The report notes that circumstantial evidence, including the detection of penta in rain water, indicates that penta may occasionally be present in ambient air.

Historically, pentachlorophenol has been used extensively in agriculture and industry as an insecticide, fungicide, herbicide, algicide and disinfectant. However, the major commercial application of technical grade pentachlorophenol is in the wood preservation industry. Eisler (1989) reported that 80 percent of the 23 million kg of technical penta produced annually was used for wood preservation. He noted that pentachlorophenol is found at levels from < 1 to up to 7.3 µg/L in some British Columbia waters. In general, Eisler’s (1989) data infer a correlation between industrial – urban centers and increasing pentachlorophenol concentrations in the water column.

Matsumoto (1982) noted that many phenolic acids are naturally produced by vascular plants and their detritus. However, he stipulated that he found no evidence of naturally occurring pentachlorophenol in his study of polluted Tokyo river water and pristine river, reservoir and pond waters on the Bonin Islands. No information was obtained suggesting that penta is biosynthesized and there are no known significant natural sources of pentachlorophenol. However, Lampi *et al.* (1992) observed up to 30 to 70 µg pentachlorophenol/kg dry sediment in cores dated back to the 17th century. They concluded this may have been due to wood burning and aerial transport, because the lake is five miles from the nearest settlement and tens of kilometers from the nearest industries.

Environmental chemistry of pentachlorophenol

Pentachlorophenol (C₆Cl₅OH) has a relative molecular mass of 266.34, a melting point of 190 °C, a boiling point of 310 °C and a density of 1.98 g/cm³ at 22 °C. The vapor pressure is 0.00415 Pa at 20°C. Pentachlorophenol has a pH dependent octanol-water partition coefficient (log K_{ow}) of 3.3 at neutral pH, 5.1 at pH = 4 and 1.9 at pH = 8 and readily dissolves in most organic solvents. Its solubility in water is also pH dependent and varies between 10 mg/L at pH 6 to 20 mg/L at pH 8 (Mackay *et al.*, 1995).

In the 1970’s and 1980’s science’s recognition of the toxicity of some dioxins led to increased public concern. The dioxin 2,3,7,8 tetrachlorodibenzo commonly called 2,3,7,8-TCDD

was recognized as an exceptionally toxic compound – at least to some test organisms. This fact, coupled with the knowledge that this compound was present in Agent Orange, the defoliant used in Vietnam, heightened concern. Eisler (1989) noted that many commercial samples of technical grade penta were heavily contaminated with a large number of potentially toxic compounds including dibenzofurans, dioxins and hexachlorobenzenes. The relative toxicity and accumulation potential of some of these contaminants exceeded that associated with the parent pentachlorophenol by several orders of magnitude (Huckins and Petty, 1981). For example, Eisler (1986) reported that some isomers of hexachlorodibenzodioxin, present in technical grade penta at concentrations of 1,000 to 17,300 µg/kg during the 1970's, were lethal to guinea pigs at doses of 60 to 100 µg/kg body weight. The dioxins in pentachlorophenol of greatest concern are the hexachlorodibenzo-p-dioxins (HxCDD). The U.S. EPA has limited the concentration of this compound to 2 mg/kg in commercial pentachlorophenol sold in the United States. A maximum concentration in any one batch of 4 mg/kg is allowed.

Penta is not dissociated from its hydroxyl ion in aqueous solutions with pH lower than 5.0. However, as the pH increases, the bioavailability and toxicity of pentachlorophenol decreases because less of the compound is found in the undissociated form. The solubility of penta and potential for adsorption to suspended inorganic particulate matter (particularly clay) is positively correlated with the dissociated fraction which increases significantly at pH above 6.5.

Fate of pentachlorophenol in aquatic environments

Introduction. Pentachlorophenol may be dissolved in water or sorbed to suspended matter or bottom sediments. In addition, penta is taken up by fauna and flora that metabolize the compound at varying rates. Penta readily degrades in the environment by chemical, microbiological, and photochemical processes (USDA, 1980; Eisler, 1989). Photochemical degradation is a function of the spectrum and intensity of incident light and appears to proceed rapidly in natural environments with half-lives of 0.15 to 15 days (Smith *et al.*, 1987). The degradation of penta in sediments is dependent on a number of environmental factors discussed below. Half-life in sediments can range from days to years depending on environmental conditions. The ultimate fate of penta appears to be burial in anaerobic sediments under infrequently encountered conditions or mineralization to carbon dioxide and water.

Fate of dissolved penta. Penta that is dissolved in water may be removed by volatilization, photodegradation, absorption, or biodegradation. Penta is subject to rapid photodegradation under laboratory conditions. Boyle *et al.* (1980) examined the degradation of pentachlorophenol in a two by two array of microcosms that did and did not contain natural lake sediments held under aerobic and anaerobic conditions. At the end of the 131 day experiment, the authors determined the pentachlorophenol half-life under each of the four conditions. Their results are summarized in Table (1). Fisher (1990) concluded that in aerobic and organically rich environments, the half-life of dissolved and sedimented pentachlorophenol would be on the order of one week. Middaugh *et al.* (1993) determined that the gram-negative bacterium, *Pseudomonas sp.* (strain SR3) was able to degrade pentachlorophenol and that penta provided an adequate sole

carbon source sustaining growth. Nearly complete degradation of 39,000 to 40,000 µg penta/L was accomplished by acclimated *Pseudomonas sp.*. Pentachlorophenol half-lives in freshwater streams reported in McAllister *et al.* (1996) varied between 40 and 120 hours.

Table 1. Pentachlorophenol remaining in water and sediments at the end of 131 days in each of four aquaria. Residues are in milligrams of pentachlorophenol for each compartment at the end of 131 days. One hundred milligrams of pentachlorophenol were originally added to the aquaria. The water column half-life is given for penta as determined in this experiment.

Test Conditions	Total Penta in Water	Water half-life	Penta in sediments	Total Penta
Aerobic without Mud (lighted)	0.95	18.6 days		0.950
Aerobic with Mud (lighted)	0.21	13.9 days	0.03	0.240
Anaerobic without Mud (dark)	16.00	79.8 days		16.000
Anaerobic with Mud (dark)	0.005	12.8 days	0.04	0.045

Boyle *et al.* (1980) also partitioned the ¹⁴C at the end of the experiment. The bulk (99%) of the sedimented ¹⁴C was observed in the non-biogenic clay fraction. They also found ¹⁴C in algae, floating flocculent material and other biogenic material in the water column. Minimal ¹⁴C was observed elsewhere in the microcosms (including the aquarium sides and cover). The authors concluded that pentachlorophenol degradation was positively correlated with incident light levels, pH, oxygen and the presence of sediment. They concluded that pentachlorophenol is likely most persistent in the deoxygenated hypolimnion water of lakes. A number of environmental factors affect the rate at which pentachlorophenol is degraded in natural aquatic environments. The following paragraphs discuss these factors.

Effects of pH and water temperature on the degradation of pentachlorophenol.

Valo *et al.* (1985) found that the metabolism of pentachlorophenol was inhibited at temperatures less than 8 °C or greater than 50 °C. Optimum degradation occurred at 28 °C. Jarvinen and Puhakka (1994) and Jarvinen *et al.* (1994) found that 99% of the penta present in contaminated groundwater was degraded at temperatures of 5 to 10 °C. Trevors (1982) documented no penta degradation by acclimated *Pseudomonas* at 0 °C. Pentachlorophenol degradation rates at 4 °C were dependent of the specific *Pseudomonas* strain used. However, an average of 28.2 percent of the initial 50,000 µg penta/L substrate was metabolized in 80 days at 4 °C while 50.2% of the same concentration was metabolized in 8 days at 20 °C.

Valo *et al.* (1985) observed pentachlorophenol degradation at pH values between 5.6 and 8.0. A neutral or slightly acidic pH was found to be optimum. Wong and Crosby (1981) observed pentachlorophenol half-lives of approximately 100 hours at pH 3.3 and 3.5 hours at pH 7.3 in sterile solutions containing 100,000 µg penta/L. No pentachlorophenol degradation was observed in flasks maintained in the dark.

It appears that pentachlorophenol degradation is optimum at pH values between ca. 6.5 and 8.0 and at temperatures between 10 and 30 °C. These are conditions expected in much of North America during all seasons excepting winter when low temperatures at northern latitudes

can be expected to decrease pentachlorophenol degradation rates. In addition, pentachlorophenol is expected to degrade more slowly in areas subjected to low pH.

Adaptation to pentachlorophenol by microbial communities. Larsson *et al.* (1988) and Larsson and Lemkemeier (1989) observed significantly higher pentachlorophenol degradation by unacclimated microbial communities inhabiting brown water lakes containing high levels of humic acid when compared with clear water lakes. These authors concluded that the microbe communities inhabiting brown water lakes had adapted to the higher phenol levels naturally present in the water and therefore were pre-acclimated to metabolize pentachlorophenol.

McAllister *et al.* (1996) reviewed the literature pertaining to the microbial degradation of pentachlorophenol. They confirmed that sediment pentachlorophenol levels exceeding 300 µg/kg inhibit microbial degradation until a period of acclimation has passed. Once acclimation had begun, it appears that the higher the initial concentration of PCP, the longer the maximum number of viable cells, capable of degrading PCP, was maintained. Gonzalez and Hu (1991) observed that lag phases of 10 hours occurred at 10 mg/L, 30 hours at 20 mg/L, 55 hours at 44 mg/L, 80 hours at 80 mg/L and 200 hours at 200 mg/L.

In summary it appeared that microbial communities were not generally preadapted to metabolize pentachlorophenol. Initial exposure of naïve communities to penta concentrations as low as 300 µg penta/L can reduce growth. An adaptation period of several hours to perhaps two weeks is necessary for community adaptation to pentachlorophenol. Following this time, adapted communities can tolerate much higher concentrations of pentachlorophenol and rapidly metabolize penta.

Effects of additional sources of carbon on pentachlorophenol metabolism. Topp *et al.* (1988) studied the response of pentachlorophenol-degrading *Flavobacterium sp.* to high levels of penta with and without the addition of sodium glutamate as a cometabolite. They found that the specific activity of penta-degrading cells in the absence of supplementary carbon was 1.51×10^{-13} g penta/cell-hr. They showed that the form and amount of alternate substrates was important in determining the metabolism of pentachlorophenol. For instance, optimal stimulation of pentachlorophenol removal required the addition of 3.0 g sodium glutamate/L. However, glutamate in combination with glucose or cellobiose partially repressed penta metabolism. *Flavobacterium* removed 2.5% of the penta from a 25,000 µg /L initial concentration. The addition of 4 g sodium glutamate/L increased metabolism resulting in the removal of 61.9% of the penta in three hours. However, when the mixture was amended with 4 g sodium glutamate and 5 g/L glucose, penta metabolism was reduced to 15.5% in three hours. It was the combination of the two substrates that reduced penta metabolism because in a separate experiment the authors found that the addition of 0.5 g of glucose to the medium in the absence of sodium glutamate resulted in the complete degradation of an initial 61,000 µg penta /L solution by *Flavobacterium sp.* The amount of penta removed decreased when incremental amounts of sodium glutamate were added to the glucose. Topp *et al.* (1988) did not discuss the possibility that *Flavobacterium sp.* acclimated to and degraded pentachlorophenol when it represented a sole carbon source – but preferentially shifted to alternate substrates when available. Perhaps rather

than acting antagonistically, the combination of sodium glutamate and glucose acted synergistically reducing the dependence of the bacteria on pentachlorophenol. Yu and Ward (1995) observed maximum pentachlorophenol degradation in medium supplemented with glucose and peptone.

Topp *et al.* (1988) found that amendment with supplementary source of carbon reduced the lag time required before significant penta metabolism commenced. These authors noted that penta concentrations greater than 20,000 µg/L inhibit *Escherichia coli* and that *Pseudomonas* was inhibited at concentrations above 500,000 µg/L. They also reported that 50,000 µg penta/L was degraded as a sole source of carbon after a lag phase of 90 hours.

Pentachlorophenol half-lives in freshwater streams reported in McAllister *et al.* (1996) varied between 40 and 120 hours. Consistent with Liu *et al.* (1981) McAllister *et al.* (1996) that additional substrates tends to reduce penta degradation rates and hypothesized that adsorbed penta is less bioavailable. McAllister *et al.* (1996) also noted that the most widely studied pentachlorophenol degrading microorganisms are the pure-culture bacterial strains, *Flavobacterium* and *Rhodococcus chlorophenolicus*. The enzymes responsible for initiating the catabolism of pentachlorophenol by *Flavobacterium sp.* have been isolated and characterized. Furthermore the genes encoding these enzymes have been characterized and cloned into *E. coli*, which then demonstrated the ability to degrade pentachlorophenol.

These reports suggest that pentachlorophenol will be degraded more rapidly in organically rich environments. However, some caution is necessary because there is evidence that some combinations of organic substrates appear to result in slightly reduced degradation rates.

Effects of water hardness on the fate of dissolved pentachlorophenol. Brockway *et al.* (1984) studied the fate of pentachlorophenol in static and continuous-flow hard and soft water mesocosms they observed no significant effect on the fate or effects of penta associated with water hardness.

Fate of pentachlorophenol in sediments. Pentachlorophenol is moderately persistent in soil. Published data indicate that pentachlorophenol can persist in soils for variable times ranging from weeks (21 days) to five years. Under most conditions, penta will seldom persist in the soil for periods exceeding nine months and its half-life will frequently be far less. Numerous studies have identified soil microorganisms capable of penta degradation. In most studies of penta biodegradation, acclimated populations of microorganisms have been utilized. Since the current major use of penta is for wood preservation, the likeliest source of soil contamination is leaching or bleeding of the preservative from treated wood. Such phenomena may result in low levels of penta contamination within several feet of the pole.

Sedimentation of pentachlorophenol. Fisher (1990) constructed microcosms with water at pH 4, 6 and 8 and sediments with 0.0 and 3.0 percent total organic carbon. She found that more penta was partitioned to the sediments at lower pH than at higher pH. In addition, she reported a positive correlation between sediment TOC and penta concentration. The organisms in the high TOC microcosms accumulated significantly less penta than did those in the 0.0%

TOC systems. This work is consistent with Eisler's (1989) observation that at low pH, pentachlorophenol is fully protonated and lipophilic whereas at high pH where it is ionized and unlikely to adsorb to organic ligands.

Shimizu *et al.* (1992) determined the adsorption coefficients of pentachlorophenol in aquatic environments with varying organic carbon (0.72 to 2.38 percent) and varying clay content (10.1 to 60.8 percent). They concluded that at pH values between 6 and 8, the adsorption coefficient was not influenced significantly by organic carbon content (Correlation coefficient = 0.12) but was positively correlated with clay content (Correlation coefficient = 0.94). This work suggests that clay particles (which frequently carry an electrical charge), rather than particulate or dissolved organic carbon form a more likely adsorption nucleus in aquatic environments.

In summary, it appears that the potential for sedimentation of pentachlorophenol is a complex problem driven by at least the following parameters:

- Water column pH. At reduced pH values, pentachlorophenol tends to be in the fully protonated and more lipophilic. It would therefore, be expected to adsorb to dissolved or particulate organic matter. On the other hand, at higher values of pH, more of the pentachlorophenol is expected to be ionized with a higher potential for binding to polar adsorption nuclei represented by particulate inorganic matter (silt and clay).
- It appears that more pentachlorophenol will be partitioned from the water column to sediments having increased organic carbon content. This can have a significant effect in removing pentachlorophenol from the water column.

Degradation of sedimented pentachlorophenol. Bryand and Rogers (1990) describe the degradation of pentachlorophenol in anaerobic sediments from diverse locations around the world. They observed that dechlorination did not occur for at least the first 15 days of exposure in unadapted sediments. However, following that adaptation period, pentachlorophenol was completely degraded by 33 days. A second addition of 70 mg pentachlorophenol/kg sediment on day 33 was rapidly dechlorinated to about 25 mg/kg in two days. In contrast, they observed no biotransformation within a 40-day period of penta added to unadapted Cherokee Pond sediments. The point made in this study is that not all microbes have the ability to dechlorinate penta as a first degradative step. Their study is consistent with other reports indicating that unacclimated, but biological rich sediments, require a period of approximately two weeks for development of suitable microbial communities before aerobic or anaerobic degradation of pentachlorophenol begins. However, when established, these communities rapidly catabolize penta. Interestingly, these authors found no degradation of pentachlorophenol in autoclaved sediments – further emphasizing the microbial nature of the observed degradation.

Van Gestel and Ma (1988) determined pentachlorophenol half-lives in low pH and organically rich Holten (pH = 5.6; 6.1% organic matter) and Kooyenburg (pH ~ 5.0; 3.7% organic matter) soils of 23.2 to 47.9 days respectively. There was no significant difference in the half-lives of pentachlorophenol in these two sediments.

Smith and Novak (1987) found that pentachlorophenol concentrations as high as 25,000 $\mu\text{g/L}$ in saturated soils were degraded to non-detectable levels in less than three months. They found that chlorophenol degradation rates were linearly related to the initial concentration and varied between 100 $\mu\text{g/L-day}$ at 200 $\mu\text{g/L}$ initial concentration to $>10,000$ $\mu\text{g/L-day}$ at an initial concentration of ca 800,000 $\mu\text{g/L}$.

Effects of sediment oxidation-reduction potential. Delaune *et al.* (1983) examined the degradation of pentachlorophenol in estuarine sediments following a major accidental spill in a Louisiana Gulf Coast estuary. They completed a series of laboratory experiments in which pH was manipulated between 5.0 and 9.0 and sediment redox between -250 mV and $+500$ mV. The authors found maximum degradation at pH = 8.0 with declines at either lower or higher values. Pentachlorophenol was observed to degrade at all values of redox. However, significantly higher degradation rates were observed under aerobic ($+250$ and $+500$ mV) than with reducing (0.0 and -250 mV) conditions. A half-life of ca. 24 days was apparent at pH 6.5 and a redox potential of $+500$ mV. However, at this pH, minimal degradation was observed at any other value of redox. At a pH of 8.0, significant degradation was observed at $+250$ and $+500$ mV redox potentials and a half-life of 26.5 days was apparent at $+500$ mV. The authors found that pentachlorophenol was more tightly bound to oxidized sediment solids than to reduced sediments. Therefore, they concluded that there was a tendency for pentachlorophenol to become preferentially associated with the thin oxidized surface sediment horizon, as well as with suspended colloidal particulates, which would also tend to be oxidized. Under either condition, the penta would be retained in the photic zone of shallow estuaries where the potential for photodegradation would be enhanced. The authors concluded that although tidal transport and photodegradation in the water column could play a role in the removal of residual pentachlorophenol from a spill area, their laboratory studies suggested that degradation under either aerobic or anaerobic conditions could account for the disappearance of residual penta left in the immediate vicinity of the spill or that which was transported from the spill site and deposited onto the bottom in adjacent waterbodies.

Anaerobic degradation of pentachlorophenol. Guthrie *et al.* (1984) studied the anaerobic degradation of pentachlorophenol as a component of sewage sludge during treatment. They found methanogenic bacteria were unaffected by pentachlorophenol concentrations <200 $\mu\text{g/L}$. Acclimation of the bacterial flora to penta raised the inhibition threshold to ca. 600 $\mu\text{g/L}$. They found that pentachlorophenol is biodegradable anaerobically and that removal was so complete that the soluble concentrations in the Phase II reactors were below detection limits of 5 $\mu\text{g/L}$. Sorption appeared a minor mechanism of penta removal and volatilization was considered insignificant. The authors concluded that pentachlorophenol undergoes extensive anaerobic biodegradation – especially by acclimated microbial communities. Anaerobic degradation of pentachlorophenol has been confirmed by Kudo (1989).

Liu *et al.* (1981) observed similar results in their comparison of aerobic and anaerobic degradation of sedimented pentachlorophenol at pH = 7.0. They observed an increase in the aerobic half-life of 0.36 days to 190 days in anaerobic conditions. They also found that the

inclusion of either sodium chlorophenolate or glucose as a second substrate inhibited, rather than enhanced the anaerobic degradation of pentachlorophenol. In contrast, Valo *et al.* (1985) found that pentachlorophenol degradation was enhanced by the addition of 0.4 or 40 mM NH₄Cl.

Bryant and Rogers (1990) examined the degradation of pentachlorophenol in anaerobic sediments from Georgia, Florida, New York and the Soviet Union. They observed an adaptation period of ca. 15 to 20 days during which little penta degradation occurred. Degradation in anaerobic sediments was rapid with an unstated half-life of two to seven days.

Table 2. Summary of pentachlorophenol half-lives, principle reasons for degradation and the effects of various environmental parameters on degradation rates.

a. Reported pentachlorophenol half-life in water

Author	Half-life (days)	Conditions
Boyle <i>et al.</i> (1980)	18.6	Aerobic in the laboratory
Boyle <i>et al.</i> (1980)	79.8	Anaerobic in the laboratory
Crossland and Wolff (1985)	2.0 to 4.7	Outdoor mesocosms
Liu <i>et al.</i> (1981)	0.36	Aerobic in the laboratory
Liu <i>et al.</i> (1981)	190.0	Anaerobic in laboratory
Wong and Crosby (1981)	2.0	PH 7.3 (natural sun-light)
Yu and Ward (1995)	~1.5	Mixed bacterial cultures

a. Effects of pH on pentachlorophenol half-life

Author	pH	Half-life (hours)	Conditions
Wong and Crosby (1981)	7.3	3.5	Laboratory F40BL lamps
Wong and Crosby (1981)	3.3	100.0	Laboratory F40 BL lamps
Wong and Crosby (1981)	7.3	48.0	Natural sunlight

a. Effects of Ambient temperature on pentachlorophenol half-life

Author	T °C	Half-life (days)	Conditions
Topp <i>et al.</i> (1988)	4	>80	<i>Pseudomonas</i> cultures
Topp <i>et al.</i> (1988)	20	<12	<i>Pseudomonas</i> cultures

a. Anticipated half-life of pentachlorophenol in soils or sediments

Author	Half-life (days)	Conditions
DeLaune <i>et al.</i> (1983)	24 to 26	Natural estuarine sediments
McAllister <i>et al.</i> (1996)	10 to 70	Flooded soils
McAllister <i>et al.</i> (1996)	< 2 to >5	Freshwater streams
Neary <i>et al.</i> (1990)	Average 30	Southern ecosystems
Smith and Novak (1987)	<5	9 to 13 mg PCP/L unsaturated soil
Smith and Novak (1987)	~15	Average 3 mg PCP/L unsaturated soil

e. Effects of sediment reduction – oxidation potential

Author	Half-life Aerobic (days)	Half-life Anaerobic (days)
Boyle <i>et al.</i> (1980)	13.9	12.8
Bryant and Rogers (1990)		2 to 5

McAllister <i>et al.</i> (1996)		144
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a. Pentachlorophenol half life in plants and animals.

Author (hours)	Species	Penta Half-life
Benner and Tjeerdema (1993)	<i>Atherinops affinis</i>	52.7 hours
Glickman <i>et al.</i> (1977)	<i>Onchorhynchus mykiss</i>	6.2 to 6.9 hours

Data provided in Baker *et al.* (1980), DeLaune *et al.* (1983) and Boyle *et al.* (1980) was interpreted to produce half-lives as a function of initial pentachlorophenol concentration, reduction oxidation potential, pH and temperature. Sedimented half-life was estimated assuming that microbes require 15 days to adapt to pentachlorophenol and that degradation rates remain linear at all times. This is a small database and the methodology is not precise. However, the results are consistent with the remainder of the literature and appear to reasonably predict sedimented pentachlorophenol half-lives that are important in understanding the accumulation in sediments.

Table (3). Estimated sedimented pentachlorophenol half-lives as a function of the initial pentachlorophenol concentration, reduction-oxidation potential, pH and temperature. Sedimented penta half-lives were estimated from data in Baker *et al.* (1980), DeLaune *et al.* (1983) and Boyle *et al.* (1980).

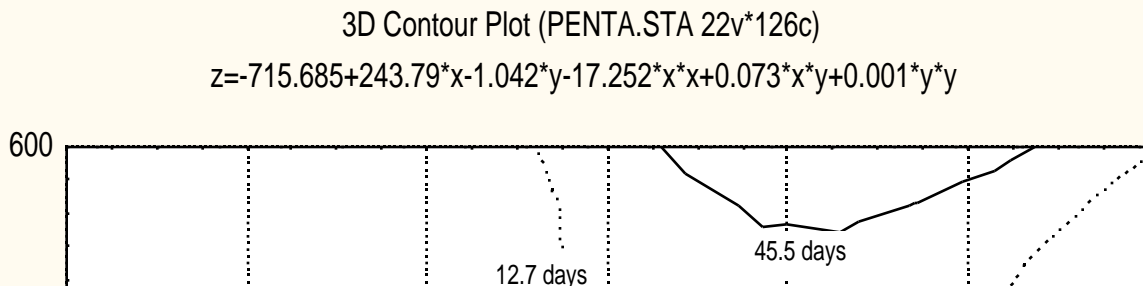
Source	Initial Penta Concentration (µg/kg)	Redox Potential (mV)	pH	Temp (°C)	Half-life (days)
Baker	100.0	250	7.1	0.0	47.5
Baker	100.0	250	6.9	20.0	36.7
Boyle	1400.0	0	4.5	15.0	13.0
Boyle	1400.0	250	6.8	15.0	7.5
DeLaune	20.0	500	6.5	33.1	6.0
DeLaune	20.0	250	6.5	33.1	103.5
DeLaune	20.0	0	6.5	33.1	178.8
DeLaune	20.0	500	8.0	33.1	12.0
DeLaune	20.0	250	8.0	33.1	32.5
DeLaune	20.0	0	8.0	33.1	81.0
DeLaune	20.0	-250.0	8.0	33.1	290.0
DeLaune	20.0	500.0	9.0	33.1	50.0
DeLaune	20.0	250.0	9.0	33.1	50.0

These data were analyzed using linear and non-linear regression analysis. Within the ranges of the data at hand, sedimented pentachlorophenol half-life was not a function of the initial concentration ($p = 0.10$) or temperature ($p = 0.40$). In addition, the constant term was not significant ($p = 0.42$). Redox potential and pH were significant factors ($p = 0.001$ and $p < 0.000$ respectively). The final regression was highly significant ($P < 0.00015$) and it explained 76

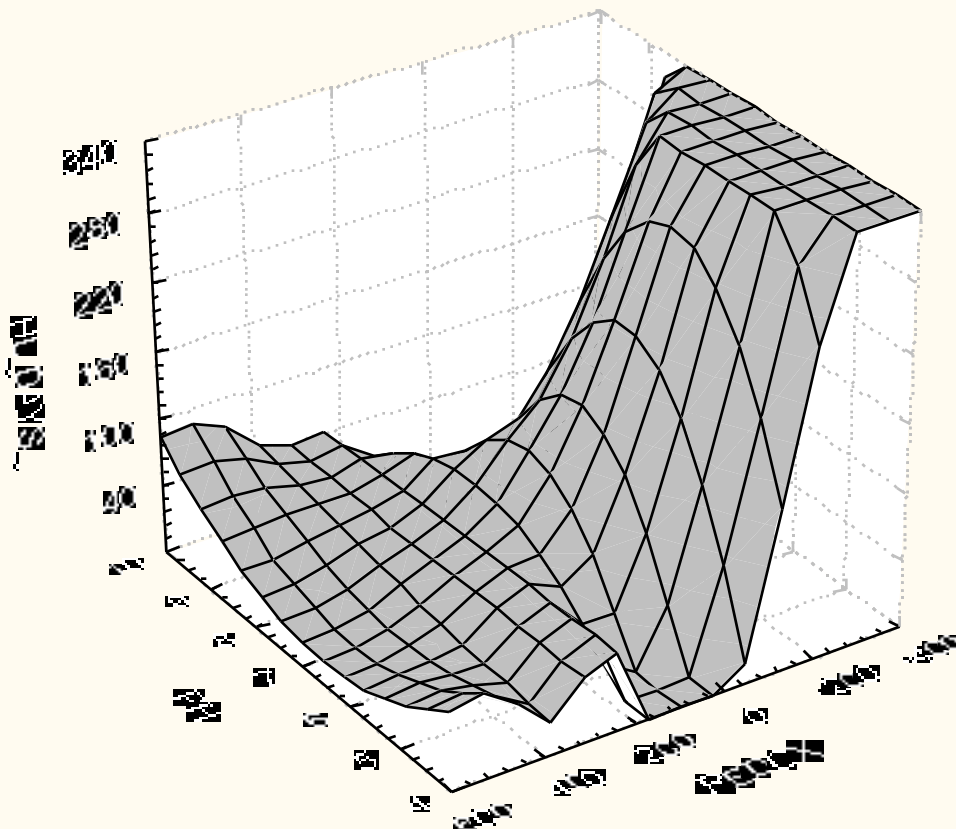
percent of the variation in the database. The underlying assumptions requiring normally distributed residuals and homoscedasticity were met. The resulting predictive equation is:

$$\text{Equation (1) Sedimented Penta Half-life} = 18.19448 * \text{pH} - 0.29284 * \text{Redox (mV)}$$

At a pH of 7.5, this equation predicts a pentachlorophenol half-life of 63 days in reasonably well oxygenated (+250 mV) sediments. In reducing sediments (-100 mV), the half-life is significantly increased to 165.7 days. Figure (1) provides a more detailed graphical representation constructed using a quadratic smoothing routine in the Statistica™ software package. Under normal environmental conditions, the redox potential in surface sediments will vary between -100 and +400 mV and the pH is expected to vary between perhaps 6 and 8.5. Figure (1) suggests that under these conditions, sedimented pentachlorophenol half-lives will vary significantly between 12.7 days and 176.4 days. The linear equation used to make predictions in this model predicts a half-life of 24.8 days at pH = 7.8 and +400 mV and 156.6 days at pH = 7.0 and -100 mV.



3D Surface Plot (PENTA.STA 22v*126c)



maximum of ca. 18 $\mu\text{g}/\text{kg}$. The authors concluded that their results suggest that a chronic influx of pentachlorophenol at a concentration of 10 $\mu\text{g}/\text{L}$, to an estuarine environment, resulted in elevated concentrations in the water, sediment, and shrimp. Penta concentrations in the shrimp (maximum of ca. 18 $\mu\text{g}/\text{g}$ on day 20) were positively correlated with water column concentrations rather than with sediment concentrations. This suggests direct uptake from the water rather than biomagnification from infaunal and epifaunal prey. Once the source of pentachlorophenol was removed, the compound rapidly disappeared from the water, shrimp and sediments – apparently in a matter of hours or days.

Crossland and Wolff (1985) determined the half-life of pentachlorophenol in outdoor ponds repeatedly dosed to maintain a concentration of 50 to 100 μg penta/L. The authors hypothesized that evaporation, sorption, hydrolysis, biodegradation and indirect phototransformation of penta would be of minor importance under the environmental conditions at the ponds. The partition coefficient for penta between water and sediments was predicted to be near unity. The authors used the SOLAR mathematical model to calculate a direct photodegradation rate constant for the transformation of penta in the ponds whose pH varied between 7.3 and 10.3 with a mean of 8.3. A series of bioassays were conducted and pond invertebrates were enumerated at levels of taxonomy exceeding Order. The results appeared consistent with the general body of literature describing the toxicity of pentachlorophenol. The observed half-lives of pentachlorophenol in the three treatment ponds varied between 2.0 and 4.7 days and was in good agreement with the predicted half-lives based on results of the SOLAR analysis. The authors concluded that direct phototransformation was responsible for nearly all of the pentachlorophenol degradation observed in this study. In addition, they noted that at the end of the study, sediment concentrations of pentachlorophenol were very similar to water column concentrations. They hypothesized that an insufficient period of time had elapsed for development of a microbial community capable of efficiently metabolizing penta in the sediments.

Robinson *et al.* (1983) examined the degradation of pentachlorophenol in a series of experimental ponds contaminated by a single high dose of pentachlorophenol (1,000 $\mu\text{g}/\text{L}$) followed by a series of small doses (0.2, 0.2, 0.4, and 0.4 mg/L) at monthly intervals. Two of the replicated sets of ponds held only phytoplankton whereas the third set of ponds contained rooted macrophytes. The authors found higher metabolism of pentachlorophenol in the ponds containing rooted macrophytes. The increased degradation of penta in the macrophyte ponds resulted in lower body burdens in channel catfish, bluegill and largemouth bass. These fish species survived the highest dose of penta (1,000 $\mu\text{g}/\text{L}$) in the pond containing macrophytes but succumbed in the ponds containing only phytoplankton. The authors suggested three hypotheses as possible explanations for these results. However, only two of those hypotheses appear different from each other: (1) the presence of the macrophytes resulted in a different chemical or physical environment in the ponds that increased penta degradation and; (2) the macrophytes or aufwuchs community associated with the macrophytes were incorporating penta as a conjugate or within the cell structure.

Fisher (1990) observed that the concentration of dissolved pentachlorophenol increased with increasing pH but that the uptake by both organisms and sediments was decreased. She also observed that increasing sediment organic carbon was associated with higher sediment levels of penta and reduced concentrations in the water column.

Delaune *et al.* (1983) studied the fate of pentachlorophenol following a major spill in a Louisiana Gulf coast estuary. They found that the degradation of pentachlorophenol was strongly influenced by sediment pH and redox potential. Degradation rates decreased with decreasing sediment redox and were maximized at pH = 8.0 with reduced degradation at either higher or lower pH values. In addition, these authors found that penta was more tightly bound to oxidized sediment than to reduced sediment. They observed that essentially all of the pentachlorophenol had disappeared from the spill area within 18 months and hypothesized that observed microbial degradation could account for the degradation. Sediments in the study area contained three to five percent carbon and the sediment pH was essentially neutral at 6.8.

It is apparent that a variety of micro-organisms are able to degrade pentachlorophenol. In general, it appears that aerobic degradation is more efficient than anaerobic degradation and that increased degradation occurs at moderate temperatures (between 10 °C and 35 °C). In most instances, it appears that penta degradation by microbial communities is enhanced by the presence of alternate carbon substrates.

Metabolism of pentachlorophenol in aquatic environments.

Fisher (1990) noted that algae, invertebrates and vertebrates rapidly metabolized pentachlorophenol. Biotransformation rates (BTI) were significantly higher in algae, especially at higher pH levels and in association with high TOC sediments. Biotransformation rates in snails and fish varied between 0.52 and 3.88 with no significantly different rates between the two phyla.

Kukkonen and Oikari (1988) examined the metabolism of pentachlorophenol in the cladoceran *Daphnia magna*. The authors found that neonate (<24 hours old) and adult daphnia were able to equally metabolize pentachlorophenol and that humic content in the aquaria (DOC up to 23.5 mg/L) had no effect on the metabolic rate. The concentration of pentachlorophenol in these experiments was 20 µg penta/L and the pH was low at 5.5. The authors did not determine a metabolic half-life. However, their data indicated that the concentration of free penta in the water column declined to 50% of the initial value in ca. 10 hours and that 50% of the penta taken up by *Daphnia magna* was metabolized in approximately 24 hours. They concluded that the principle metabolic pathway in *D. magna* involved sulfate conjugation.

Trujillo *et al.* (1982) found the half-life of pentachlorophenol in midges to be 4.7 days. However, data in Lydy *et al.* (1993) suggests that midge tissue concentrations of pentachlorophenol peaked at ca. 24 to 14 hours and then declined rapidly to 50% of the maximum in ca. 24 hours. The authors' calculated a half-life of 15 hours for pentachlorophenol in the midge.

Glickman *et al.* (1977) determined pentachlorophenol half-lives in a variety of rainbow trout (*Oncorhynchus mykiss*) tissues. The values varied from 6.2 hours in blood to 23.7 hours in

fat. Pentachlorophenol is lipophilic and these results suggest that there is short-term sequestration in body lipids. The authors found high penta levels in the bile of these fish and concluded that the pentachlorophenol was being conjugated with bile and excreted.

Stehly and Hayton (1989) examined the metabolism of pentachlorophenol in rainbow trout, fathead minnows, sheepshead minnow, firemouth and goldfish exposed to penta for 64 hours. They found that penta metabolism was species specific. Consistent with other studies, these authors found that biliary excretion accounted for less than 30% of the total pentachlorophenol metabolites and that 76% of the penta metabolites in bile consisted of pentachlorophenol-sulfate or pentachlorophenol-glucuronide. All of the metabolites excreted into the water were sulfate conjugates while bile was enriched in glucuronide conjugates.

Similar results were demonstrated by Cravedi *et al.* (1995) in Arctic char (*Salvelinus alpinus*) eleutheroembryos (end of yolk sac resorption or 50 to 100 mg wet weight). Test pH was 7.9 and duration was 48 hours. They observed that pentachlorophenol-glucuronide accounted for 24.2% of the ^{14}C found in water at the end of 48 hours. The parent pentachlorophenol accounted for 29.5% and pentachlorophenylsulfate represented 49.4% of the ^{14}C present in the water column.

Benner and Tjeerdema (1993) studied the toxicokinetics and biotransformation of pentachlorophenol in a marine species of fish (*Atherinops affinis*). The fish were exposed to 50 μg penta/L for 24 hours to determine the bioconcentration factor, elimination rate constant and the elimination rate half-life. The absorption rate constant was 0.012/hr leading to a bioconcentration factor of 278. The elimination rate constant was higher at 0.014/h and an elimination half-life of 52.7 hours was determined. During 24 hours of exposure to clean seawater, topsmelt depurated 32.9% of the retained pentachlorophenol and residues. Most (64.9%) of the penta was excreted unaltered. However, pentachlorophenol metabolites pentachlorophenylsulfate (18.9%) and pentachloro-D-glucuronide (16.2%) were also observed. The authors note that these same compounds have been identified as intermediates in the metabolism of pentachlorophenol by goldfish, fathead minnows, rainbow trout, firemouths (*Cichlasoma meeki*), sheepshead minnows and striped bass. The authors conclude that topsmelt rapidly absorb and more slowly depurate pentachlorophenol after short-term exposure through excretion and/or detoxification by sulfation and glucuronidation.

Bioconcentration and bioaccumulation of pentachlorophenol

Introduction. Bioconcentration and bioaccumulation of contaminants is of special importance because some aquatic species, most notably bivalves, have demonstrated an ability to rapidly bioconcentrate contaminants in water to high tissue levels. The concern is that persistent contaminants may move up the food chain, biomagnifying to higher concentrations in each trophic level, until contaminants found at non-toxic levels in the ambient environment reach concentrations where they do cause stress and disease. For effective biomagnification and movement of contaminants through the food chain, several conditions must be met.

First, organisms must have the ability to bioconcentrate low levels of contaminants from the water column or their food. Second, these contaminants, or their toxic metabolic

intermediates, must be retained, unaltered, in the tissues of the organism until it falls prey to an animal at a higher trophic level.

There are a number of factors that mitigate against biomagnification. If contaminants are not absorbed, they cannot accumulate. Numerous organisms, particularly vertebrates, have the ability to either metabolize or to excrete organic contaminants. The gut, liver, kidney and gall bladder are common sites of pentachlorophenol concentration, metabolism and excretion in vertebrates. If the contaminants are either rapidly excreted, or they are metabolized to non toxic compounds, then the chain is broken and biomagnification is not effective in passing contaminants upward through the food chain.

DDT is an excellent example of a persistent compound that was bioconcentrated from low levels in the water to higher levels; first in plankton, then in fish, and finally in bird populations with devastating consequences.

Bioconcentration of pentachlorophenol from the water column. The uptake of pentachlorophenol is a function pH (Fisher, 1990; Fisher and Wadleigh, 1986) and not so much of water concentration. At pH 4.0, for example, penta is fully protonated and therefore highly lipophilic resulting in higher bioconcentration potential. Conversely, penta is completely ionized at pH 9.0 with lower bioconcentration potential and significantly reduced toxicity. In general, Fisher (1990) observed a negative correlation between the uptake of pentachlorophenol by algae, snails and fish with pH. Highest bioconcentration factors were found at pH 4 (BCF = 117.2 to 681.9). Bioconcentration factors at environmentally realistic pH values of 6.0 and 8.0 ranged from 3.8 (algae at pH = 8.0) to 271.1 (fish at pH = 6.0).

Makela and Oikari (1990) determined pentachlorophenol BCFs in adult (55 mm valve length) freshwater mussels (*Anadonta anatina*) of 145 to 342. Tests were conducted at a pH of 6.5 in penta concentrations of 7 and 14 µg/L. However, an equilibrium penta concentration of only 1.8 ± 0.1 µg/L in four and 16 hours in the two experiments. They found higher penta concentrations in the digestive gland and kidney when compared with whole body soft tissues. In a more recent experiment using (¹⁴C)-pentachlorophenol, these same authors (Makela and Oikari, 1995) found steady state bioconcentration factors averaging 100 in *Anadonta anatina* and 73 in *Pseudanodonta complanata*. The pH in these experiments was 6.5 and the pentachlorophenol concentration 9.7 µg/L. The bioconcentration factors were determined as the body burden of penta (measured in a number of ways) divided by the **final** concentration of pentachlorophenol. It must be recognized that when determining bioconcentration factors for labile chemicals, such as pentachlorophenol, the average exposure affecting uptake is likely much higher than the final concentration, which tends to inflate the BCF. It would appear that the development of biologically meaningful bioconcentration factors should use some intermediate concentration of the contaminant. An appropriate protocol would necessarily require consideration of the dynamics of degradation in the ambient water integrated over time compared with the depuration and metabolism of the contaminant in the organism at question.

Niimi and Cho (1983) suggest that pentachlorophenol is rapidly accumulated and eliminated by trout in the natural environment. Uptake from water appeared to be the most important pathway, and any accumulation through food was thought to represent only a minor

contribution. Consistent with Glickman *et al.* (1977) and Rogers *et al.* (1990), these authors observed highest penta levels in the liver and bile of fish fed penta contaminated feed to satiation for 40 days. Biliary excretion appeared to be a major route of depuration. They noted that the residence time of pentachlorophenol in water was short and suggested that its impact on fish would be most evident in localized areas that receive a continuous input of pentachlorophenol from a point source. Furthermore, Niimi and Cho (1983) concluded that bioaccumulation (biomagnification) of pentachlorophenol through the food chain is minimal based on the results of their study and the observation that penta levels in smelt and alewife, the primary forage species for many Lake Ontario salmonids, were similar to concentrations found in the predators.

Bioconcentration of pentachlorophenol from sediments. The ultimate fate of pentachlorophenol deposited in aquatic environments is either decomposition in the water column or sedimentation. Fisher (1990) concluded that, “Thus, for the organic sediment system, bioaccumulation will be determined by interactions between pH, available sorption sites, degree of ionization of PCP and levels of sediment ingestion.”

Midges are deposit feeders and are known to rework sediments by feeding and burrowing. Therefore, midges are not only exposed to pentachlorophenol in interstitial water, but they also ingest contaminated particles. Fry and Fisher (1990) compared the bioaccumulation of pentachlorophenol by *Chironomus riparius* allowed to burrow in pentachlorophenol contaminated sediments with similar midges held in suspension directly above the sediments. A third experiment exposed dead midge larvae to contaminated sediments to evaluate the passive uptake of penta. The authors documented bioconcentration factors of 229 from water and 7.3 from sediment in which the midges were burrowing.

The bodies of dead midges exposed to contaminated sediment yielded a BCF of 13.3. Fry and Fisher (1990) noted that Trujillo *et al.* (1982) found the half life of pentachlorophenol in midges to be 4.7 days and hypothesized that lack of metabolic degradation in the passive uptake experiment contributed to the higher ultimate pentachlorophenol body burden in the dead chironomids. However, they noted that ionized pentachlorophenol appeared to have a significant affinity for the body wall of the dead larvae and concluded that passive uptake from pore water appeared to be important to the accumulation of pentachlorophenol from sediments.

Fry and Fisher (1990) noted that pentachlorophenol has a log K_{ow} of 5.01. They concluded that penta does not behave like a neutral lipophilic compound and therefore its activity and fate were not predictable from its octanol-water partition coefficient. In contrast, Lydy *et al.* (1994), found that bioconcentration factors in the midge *Chironomus riparius* (BCF = 458) were reasonably well predicted by a much lower octanol-water partition coefficient ($K_{ow} = 758$) when the water concentration was 9 μg penta/L.

Fisher (1990) found that the sorption of penta to organic sediment significantly reduced its concentration in the water column at all pH levels, thereby reducing accumulation of pentachlorophenol in the microcosm's organisms. At environmentally realistic pH values of 6 to 8, bioconcentration factors were lower in microcosms with 3 percent TOC sediments when compared with sediments lacking any TOC.

Haque and Ebing (1988) examined the bioconcentration of pentachlorophenol from water and soil. They determined bioconcentration factors from soil of 6.3 for *Allolobophora caliginosa* and 22.2 for *Lumbricus terrestris*. They found that penta was rapidly bound to the soil and concluded that ingestion of contaminated particles was a significant pathway.

Van-Gestel and Ma (1988) investigated the toxicity and bioaccumulation of pentachlorophenol in the earthworms *Eisenia fetida andrei* and *Lumbricus rubellus* in organically rich sandy soils (3.7 to 6.1% organic matter) of low pH (5.0 to 5.6). The LC₅₀ values for *Lumbricus rubellus* were 883 mg penta/ kg dry soil in Holten soil (pH = 5.6 and 6.1% organic matter) and 1,094 mg penta/kg dry soil in Kooyenburg soil (pH ~ 5.0 and 3.7% organic matter). The differences in these LC₅₀ values were not significant. Bioconcentration factors were based on the average of the sediment values on day 0 and day 14 – this appears a more reasonable approach than using the values on the last day as done by Makela and Oikari (1990). The bioconcentration factor based on bulk sediment penta concentration varied between 3.4 and 8.0. In contrast, the bioconcentration factors varied between 426 and 996 when based on porewater penta concentrations. The authors suggest that the porewater BCF is consistent with bioconcentration factors of 475 observed in fish.

Biomagnification of pentachlorophenol from food. Schuytema *et al.* (1993) fed mealworms contaminated with between 64.8 and 2,604 µg penta/g to African clawed frogs (*Xenopus laevis*) for 27 days. They observed no mortality in the frogs and no significant bioaccumulation of pentachlorophenol. Highest concentrations of penta were found in the liver of frogs. However, these levels were inversely proportional to the level of penta in the mealworms. Penta was found in frog liver at <4.6 µg/g in frogs fed mealworms contaminated to 64.8 µg penta/g, whereas, the liver of frogs fed mealworms with 2,604.6 µg penta/g contained penta at < 0.6 µg/g.

Niimi and Cho (1983) determined the uptake from food and half-life of pentachlorophenol in rainbow trout (*Oncorhynchus mykiss*). Trout fed diets containing 40 µg penta/kg food attained whole body levels of 2 µg/kg over the three month study. Trout fed with penta contaminated feeds that were 75 times higher (3,000 µg/kg) accumulated 40 µg penta/kg by the end of 40 days. This level then declined to 20 µg/kg by the end of the study. The biological half life of penta in trout was estimated to be approximately 7 days.

This observation is consistent with the literature describing the depuration and metabolism of pentachlorophenol in vertebrates and invertebrates. It appears that penta clearance in all tested organisms is fast enough to minimize any potential for the compounds biomagnification in food chains.

Pentachlorophenol toxicity in aquatic environments

Introduction. Pentachlorophenol is known to uncouple oxidative phosphorylation, inhibiting ATP pathways important to respiration in both animal and plant cells. In addition, Moreland and Hilton ((1976) described penta as a more general inhibitory uncoupler, suggesting that it has several sites of action, including photophosphorylation, protein synthesis and lipid biosynthesis

(Morrod, 1976). All of the mechanisms of penta's toxicity have not been precisely defined, but may generally involve the disruption of cellular membranes (Jayaweera, *et al.*, 1982; Senger and Ruhl, 1980; and Smejtek *et al.*, 1983).

Acute toxicity causes observable physiological lesions and is usually measured by mortality. Penta interferes with the oxidative phosphorylation by uncoupling the production of adenosine triphosphate from adenosine diphosphate. Because this process provides the energy source for cellular metabolism in most organisms, pentachlorophenol is a broad-spectrum biocide.

A common measure of acute toxicity is the concentration of a toxicant that causes 50% mortality in a test population within some specified period of time (often 96 hours). This parameter is referred to as the 96-hr LC₅₀. Eisler (1989) summarized 96-hr LC₅₀ concentrations for aquatic organisms. For most freshwater species, the 96-h LC₅₀ varied between 100 and 2,000 µg penta/L. In general, Eisler's (1989) data suggest that freshwater vertebrates (fish) are more sensitive than invertebrates. Table (4) summarizes the lower LC₅₀ values provided by Eisler (1989) for salmonids and centrarchids. Salmonids of the genus *Oncorhynchus* appear most sensitive. In contrast, invertebrate LC₅₀ values are typically above 100 µg/L.

Table 4. Acute toxicity of freshwater fish to pentachlorophenol (96-h LC₅₀) reported in Eisler (1989).

Species	Concentration (µg penta/L)
<i>Oncorhynchus mykiss</i> (rainbow trout)	34 to 121
<i>Oncorhynchus nerka</i> (sockeye salmon)	63 to 68
<i>Oncorhynchus tshawytscha</i> (chinook salmon)	68 to 78
<i>Salmo salar</i> (Atlantic salmon)	500
<i>Salvelinus fontinalis</i> (brook trout)	128
<i>Lepomis macrochirus</i> (bluegill)	120 to 350
<i>Micropterus salmoides</i> (largemouth bass)	136 to 287

Chronic toxicity of pentachlorophenol in aquatic organisms. Toxicants can have more subtle effects that are important to the competitiveness of individuals in natural environments and to the sustainability of populations of organisms. Numerous endpoints are evaluated in assessing chronic effects. Most commonly, these endpoints involve reproduction and/or growth. The lowest contaminant concentration in a bioassay that does not produce an observable effect is referred to as the No Observed Effect Concentration (NOEC). The lowest concentration at which the effect being evaluated was observed is referred to as the Lowest Observed Effect Concentration or LOEC. If an effect is observed at 200 µg/L but not at 100 µg/L, the first value would be reported as the LOEC and the second as the NOEC. The actual effects threshold would lie somewhere between the two values. ENVIRON (1996) summarized a number of chronic endpoints for aquatic fauna and flora exposed to pentachlorophenol. Their data is further

summarized to include only those data that included test pH in Table (5). The U.S. EPA freshwater chronic standard for pentachlorophenol is included for comparison in Table (5).

Roszell and Anderson (1994) examined the effect of pentachlorophenol on non-specific immune function in two phagocytic cell populations isolated from the estuarine fish, *Fundulus heteroclitus*. They found that phagocytosis of yeast particles was significantly inhibited at penta concentrations greater than 5,000 µg/L. A comparison of phagocytic response between controls and a pentachlorophenol level of 1,000 µg/L did not reveal significant differences.

Brown *et al.* (1987) observed a reduced number of feeding acts in the young of largemouth bass exposed to pentachlorophenol concentrations of 67 and 88 µg/L but not at concentrations less than 67 µg/L. Endpoints measured included the number of feeding attempts, and the numbers of misses and mistakes. The No Observed Effect Level was 45 µg penta/L. Hardness (65 mg/L as CaCO₃) and pH (7.7) were not measured directly in this experiment but were assumed equal to that observed in a 1985 study using the same water supply.

Table 5. No Observed Effects Level (NOEL) and Lowest Observed Effects Level (LOEL) associated with pentachlorophenol in freshwater environments. All pentachlorophenol values are in µg penta/L.

Endpoint	Duration	Species	NOEL	LOEL	pH	Temp.	EPA Chronic Standard
Reproduction; number viable eggs	16	<i>Lymnaea stagnalis</i> (snail)	50	NR	8.0	18.3	46.5
Larval Survival and reproduction	10 – 28	American Flagfish	55	102	6.9 5	25	5.4
Biomass & mortality, eggs @ 10°C alevins @ 15 °C; fry @ 20 °C	>28	<i>Oncorhynchus mykiss</i>	10.9	25	8.0	10-20	15.6
Hatchability, survival & growth	32	<i>Pimephales promelas</i>	16.5	34.6	6.5	25	3.5
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	6	13	7.4	25	8.6
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	36	85	7.4	25	8.6
Survival & growth (fry & juveniles)	90	<i>Pimephales promelas</i>	>130	>130	9.4	25	63.9
Early life stage hatchability, survival & growth	32	<i>Pimephales promelas</i>	44.9	73	7.5 5	25	10.0
Hatchability survival & growth	32	<i>Pimephales promelas</i>	63.7	125	8.5	25	25.9
Hatchability survival & growth	32	<i>Pimephales promelas</i>	27.6	58.2	7.5		9.5
Hatchability survival & growth	32	<i>Pimephales promelas</i>	32	75	8.0		15.6
Growth	56	<i>Chaetogammarus marinus</i>	100	NR	8.0	NR	15.6
Number of viable oocytes	18	<i>Oncorhynchus mykiss</i>	11	19	7.4	12	8.6
Number of viable oocytes	18	<i>Oncorhynchus mykiss</i>	12	22	7.5	12.5	9.5
Reproduction	21	<i>Daphnia magna</i>	180	320	8.0	20	15.6
Survival and reproduction	7	<i>Daphnia magna</i>	100	500	8	20	15.6
Inhibition of cell growth	5	<i>Skeletonema costatum</i>	11	20	8.1	19-22	17.3
Inhibition of cell growth	5	<i>Selenastrum capricornutum</i>	12	17	7.5	24-25	9.5
Inhibited cell growth	5	<i>Anabaena flos-aquae</i>	7.8	18	7.5	24-25	9.5
Growth, reduction; biomass	21	<i>Elodea canadensis</i>	230	380	7.9 5	22	14.9
Inhibited cell growth	5	<i>Inavricula pelliculosa</i>	40	77	7.5	25	9.5
Inhibited cell growth	5	<i>Anabaena flos-aquae</i>	7.8	18	7.5	24-25	9.5

					0		
FronD density & biomass	14	<i>Lemna gibba</i>	32	72	5.0	23-27	0.8

Keller (1993) notes that in 1993 there were over 40 species of freshwater unionid mussels listed as endangered or threatened under the Endangered Species Act (PL 100-707). Keller determined a 48-h LC₅₀ value in juvenile *Anadonta imbecilis* at pH 7.0 and compared the results with concurrent bioassays on *Daphnia magna* and *Lepomis macrochirus*. Here results indicated that the 48-h LC₅₀ for the juvenile mussels (610 µg penta/L) was greater than the 48-h LC₅₀ for the daphnid (330 µg/L) or the 96-h LC₅₀ for bluegills (240 µg/L). At pH = 7.0, the U.S. EPA chronic pentachlorophenol water quality standard is 5.73 giving a safety factor of 106.

Effects of temperature on the toxicity of pentachlorophenol. Fisher (1986) examined the toxicity of pentachlorophenol to the midge *Chironomus riparius* at 15, 25 and 35 °C. The endpoint she examined was a flight response following stimulation with a pair of forceps during exposure to PCP in soft water at pH 7.0. Fisher observed that EC₅₀ values increased from 1,176 µg/L at 15°C to 1,556 at 25 °C and then declined to 631 µg PCP/L at 35 °C. She concluded that midge metabolism was increased at the higher temperatures and that penta's interference with respiration (phosphorylation of ADP to ATP) at the higher metabolic rate was responsible for the increased EC₅₀ at 35 °C. Similar results were reported by Fisher (1991) in an experiment conducted at pH values of 4, 6 and 8. The EC₅₀ values for penta in this study varied between 253 µg/L at a pH of 4 and temperature of 35 °C to 2,052 µg penta/L at pH 8 and 25 °C. Eisler (1989) cites similar results from Hedtke *et al.* (1986) and Hedtke and Arthur 1985) who reported positive correlations between EC₅₀ and temperature for fathead minnows (*Pimephales promelas*), the isopod *Asellus racovitzai* and the snail *Physa gyrina*.

In summary, it appears that the toxicity of pentachlorophenol to aquatic species increases with increasing temperature. Similar increases in the toxicity of pentachlorophenol to *Notopterus notopterus* with increasing temperature (16, 23 and 36 °C) were observed by Gupta *et al.* (1983).

Effects of pH on the toxicity of pentachlorophenol. Fisher (1991) demonstrated that the toxicity of pentachlorophenol is inversely related to pH. The effective concentration (EC₅₀) of pentachlorophenol resulting in failure of *Chironomus riparius* to execute an appropriate flight response increased from 384 µg/L at 25 °C and pH = 4 to 2,052 µg penta/L at the same temperature and pH = 8.0.

Smith *et al.* (1987) examined the toxicity of pentachlorophenol to *Selenastrum capricornutum* and found that culture media equilibrium pH and 96-h EC₅₀ were very strongly correlated (r = 1.00) between pH values of 7.3 and 8.5. The authors' concluded that the toxicity of pentachlorophenol is due primarily to the concentration of the undissociated compound.

The dependence of pentachlorophenol toxicity on pH was further elucidated by Spehar *et al.* (1985) in fish and amphipods. They found that acute exposures in all three species showed that pentachlorophenol toxicity was decreased with increasing pH. Kaila and Saarikoski (1977) observed a similar response in the crayfish (*Astacus fluviatilis*). The 8-day LC₅₀ decreased from 53 mg/L at pH 7.5 to 9 mg penta/L at pH 6.5.

Stehly and Hayton (1990) described the uptake and clearance of pentachlorophenol in goldfish (*Carassius auratus*) as a function of environmental pH (7.0, 8.0 and 9.0). The authors found reduced uptake and clearance at increasing pH. They concluded that pH-related changes in the pharmacokinetics of penta resulted in a decrease in its bioconcentration factor with increasing pH and suggested that this could account for both the decreased capacity of the fish to accumulate penta and its reduced toxicity at higher pH values.

Early life stage exposures of fathead minnows showed that chronic penta toxicity and bioaccumulation were similarly decreased when pH values were increased. They developed a relationship describing bioconcentration as a function of pH given below. Reported bioconcentration values ranged from 1,066 at pH 6.5 to 281 at pH 8.5.

$$\text{Fathead minnow bioconcentration factor} = 10^{(4.80 - 0.28 \cdot \text{pH})} \quad (R^2 = 0.94)$$

The authors concluded that the decrease in chronic pentachlorophenol toxicity appeared to be due to reduced bioaccumulation and toxicity as a direct result of the increased dissociation at higher pH values.

Effects of water hardness on the toxicity of pentachlorophenol. Inglis and Davis (1972) examined the effects of water hardness (13.0, 52.2, 208.7 and 365.2 mg CaCO₃/L) on six species of fish, including rainbow trout. Reported values of pH ranged from 7.8 at a hardness of 13.0 mg/L to pH = 8.0 at all other values of hardness. The authors concluded that water hardness had no significant effect on the toxicity of pentachlorophenol to any of the tested species.

Effects of dissolved organic carbon on the toxicity of pentachlorophenol. Lee *et al.* (1993) examined the acute toxicity of pentachlorophenol to zebrafish (*Brachydanio rerio*) and the cladoceran, *Daphnia magna*, at total organic carbon concentrations varying between 0.0 and 50 mg/L. They observed no significant difference in the 96-h EC₅₀ (zebrafish bioassay) or 48-h EC₅₀ (*Daphnia magna*) as a function of TOC at any of the tested values.

Pentachlorophenol toxicity to aquatic plants. Smith *et al.* (1987) investigated the toxicity of pentachlorophenol to *Selenastrum capricornutum* as a function of pH and found that the 96-h EC₅₀ was given by the relationship:

$$96\text{-h EC}_{50} (\textit{Selenastrum capricornutum}) = \exp^{(0.847 \cdot \text{pH} - 4.28)}$$

The regression coefficients in this relationship are similar to the current U.S. EPA pentachlorophenol standard and demonstrates reduced toxicity at elevated levels of pH where more pentachlorophenol is in the dissociated form (i.e. having lost the OH radical). The authors suggest that the toxicity of pentachlorophenol is primarily associated with the undissociated species of the compound.

Potential for contamination of groundwater by pentachlorophenol. Goerlitz *et al.* (1985) examined the potential for pentachlorophenol contamination of groundwater at a wood preserving facility near Pensacola, Florida. They did not find pentachlorophenol in groundwater and concluded that the low solubility of PCP at the groundwater pH of 6.0 was responsible.

LaFrance *et al.* (1994) examined the adsorption and mobility of pentachlorophenol as a function of dissolved organic carbon and pH and concluded that dissolved organic matter does not promote nor diminish pentachlorophenol adsorption and transport in soil column under conditions representative of an environmentally relevant groundwater-soil system exposed to penta concentrations less than 100 µg/L. At high penta concentrations ~ 800 µg/L, dissolved organic matter may increase the adsorption of penta.

Warith *et al.* (1993) examined the mobility of pentachlorophenol in soils containing high levels of total organic carbon ($f_{oc} = 16\%$). Similar soils might be found in a wetland or in an organically rich estuarine environment. Based on their data, the authors concluded that the migration potential of pentachlorophenol in the environment is considered minimal. In summary, it appears that penta is strongly sorbed to soil; hence, leaching through the soil profile and contamination of groundwater is considered unlikely.

The physicochemical properties of pentachlorophenol and these reports indicated that there is little potential for the contamination of groundwater associated with the use of pentachlorophenol treated wood.

Regulatory criteria for the protection of aquatic resources. Section 304 (a) (1) of the Clean Water Act (33 U.S.C. 1314 (a) (1)) required the U.S. Environmental Protection Agency to publish and update ambient water quality criteria. These criteria reflect the latest scientific knowledge of the identifiable effects on the health and welfare of aquatic resources including fauna, flora and human uses.

The brief review provided in this document is consistent with EPA (1986) in predicting that pentachlorophenol acute and chronic toxicity are inversely correlated with water pH and dissolved oxygen concentration and directly correlated with temperature. At pH = 6.5, the EPA found that acute values ranged from 4.4 to > 43,920 µg penta/L. Chronic values ranged from <1.835 to 79.66 µg penta/L. The mean acute-chronic ratios ranged from 0.89 to 15.79 µg/L. Freshwater algae were affected by concentrations as low as 7.5 µg/L, whereas vascular plants were adversely affected at 189 µg/L and above. Bioconcentration factors ranged from 7.3 to 1,066 in three species of fish.

Procedures described in the “Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses” indicate that excepting where a locally important species is highly sensitive to pentachlorophenol, freshwater aquatic organisms and their uses should not be affected unacceptably if the average short term concentrations (µg penta/L) do not exceed the numerical values given by:

Acute criterion: One-hour average concentration $< \exp^{(1.005 \cdot \text{pH} - 4.830)}$ (µg/L)

Chronic criterion: Four day average (once every three years) $< \exp^{(1.005 \cdot \text{pH} - 5.290)}$ ($\mu\text{g/L}$)

It should be noted that these are not appropriate concentrations for continuous exposure and they are not No Observed Effect Levels or Threshold Effects Levels. For instance, at a pH of 6.8, the chronic criterion for penta is 4.68 $\mu\text{g/L}$. At this pH, the EPA (1986) notes that a pentachlorophenol concentration of 1.74 $\mu\text{g penta/L}$ caused a 50% reduction in the growth of yearling sockeye salmon in a 56-day test. This may seem inconsistent with the chronic EPA value. However, it is important to remember that the EPA criterion is for a maximum four day exposure – not for a 56 day exposure.

These criteria are not rules and they do not have regulatory impact. However, a number of states have used EPA (1986) as the basis for setting regulatory standards for potentially toxic compounds, including pentachlorophenol: Washington State (WAC 173-201), Texas (30 TAC 307.6), Utah (UAC R317-2-14), Florida (FAC 62-302.530), Indiana (327 IAC 2-1-6) and Oregon (OAR, 340 41).

Different criteria have been proposed or adopted by other jurisdictions. The most prominent of these were reviewed by Environ (1996). The data for continuously distributed criteria provided in Environ (1996) were subjected to non-linear regression analysis. The results are presented in Table (5) and Figure (1).

The Draft 1995 CCME/BC criteria and the 1995 Ontario guidelines do not adequately reflect the effect of pH on the toxicity of pentachlorophenol. These criteria are either under protective at low pH or over protective at high pH. The 1994 Aquatic Dialogue Group Level of Concern Approach (see Environ, 1996 for a review) produces two sets of criteria. The lower levels are sufficient to protect 99% of the species and the upper values are sufficient to protect 95% of the species. These are continuous criteria and therefore it is inappropriate to compare their recommendations with those of the one hour and 96 hour EPA criteria.

In response to recommendations made by a US EPA task force in 1992, the Aquatic Risk Assessment and Mitigation Dialogue Group (ADG) was sponsored by the EPA and the North American Chemicals Association in 1993. The ADG included representatives of EPA, agrochemical companies, academia, and environmental and agricultural interest groups. The Society of Environmental Toxicology and Chemistry (SETAC) acted as a facilitator for meetings of the group and published a final report with recommendations (SETAC, 1994). The ADG recommended an “integrated probabilistic risk assessment approach that included both the probability of exposure and effects.” Environ (1996) applied the ADG methodology to derive pentachlorophenol chronic toxicity guidelines sufficient to protect 90%, 95% and 99% of species. The results are included in Table (6) and Figure (3) for the protection of 95% and 99% of species.

Table 6. Comparison of various jurisdictional criteria for pentachlorophenol. The EPA and Great Lakes chronic criteria are for four day exposures. Others listed below are continuous criteria. All values are in $\mu\text{g/L}$.

highest penta dose resulted in inhibition and delays in development of normal growth of embryos of this amphibian. However, the study found no clear mutagenic effects. CCME (1997) concluded that while chlorophenols may have reproductive and fetotoxic effects, they do not appear to be teratogenic or mutagenic.

Summary. For the purposes of this risk assessment, we will use the US EPA chronic criteria as a benchmark against which to compare levels of pentachlorophenol migrating into the water column during the first four days. The 1994 Aquatic Dialogue Group Level of Concern necessary to protect 99% of species will be used as a second benchmark against which to assess long term water column concentrations of pentachlorophenol within a few centimeters of the immersed wood on days ≥ 5.0 following immersion of the treated wood.

Pentachlorophenol contamination of drinking water supplies. Table 7 lists limits for pentachlorophenol in drinking water established by a number of jurisdictions. It appears that most jurisdictions have invoked a maximum continuous pentachlorophenol concentration of 1.0 $\mu\text{g/L}$ in drinking water. This value will be used in assessing the appropriateness of pentachlorophenol structures proposed for construction in association with drinking water supplies.

Table 7. Regulatory limits for pentachlorophenol concentrations in drinking water and/or ground water.

Authority	Maximum permissible Level ($\mu\text{g penta/L}$)
U.S. EPA (MCL = Maximum Contaminant Level)	1.0
Australia and New Zealand	10.0
Florida (FAC 17-302.530)	EPA chronic standard of 1.0 $\mu\text{g/L}$ - not to exceed an annual average of 0.28
Indiana (327 IAC 8-2-5)	1.0
Oregon (OAR Chapter 340, Division 41, DEQ)	1.0
Wyoming (WCWR 020-080-018 Appendix A.	1.0

Sediment quality benchmarks. Washington State (Washington Administrative Code, Chapter 173-204-320) has developed an Apparent Effects Threshold (AET) based pentachlorophenol standard for marine sediments at 360 $\mu\text{g/kg}$. The AET is the lowest concentration of a chemical above which adverse effects are always observed in Puget Sound Sediments. Adverse effects are determined from laboratory bioassays on a variety of test animals and on the paired analysis of infaunal communities and sediment chemistry. These standards are considered sufficient to protect most marine organisms.

The New York State Department of Environmental Conservation (NYSDEC, 1993) has established a freshwater sediment criterion for pentachlorophenol of 100 $\mu\text{g penta/g}$ sedimented

organic carbon for acute toxicity and 40 µg penta/g sedimented organic carbon to prevent chronic toxicity. These criteria are based on an equilibrium partitioning model and state water quality criteria for pentachlorophenol. They are intended for use in screening contaminated sediments. The NYSDEC criteria are expressed as a concentration in sediment by prescribing an organic carbon content. For example, in a sediment with one percent organic carbon, the corresponding chronic criterion value is 400 µg penta/kg dry sediment ($40 \mu\text{g/g TOC} \times 0.01 \text{ TOC} = 0.4 \mu\text{g/kg}$), or 800 µg/kg at two percent TOC and 1,200 µg/kg at three percent TOC, etc.

The Washington State marine standard of 360 µg penta/kg dry sediment weight will be used as benchmark in assessing marine environmental risks associated with the use of pentachlorophenol treated wood and the NYSDEC criteria will be used for freshwater sediments. The risk assessment program will automatically compute the sediment pentachlorophenol criteria based on a user input for Total Organic Carbon.

**Loss of pentachlorophenol from southern yellow pine piling treated
To 0.5 pounds of penta per square foot (in the treated zone)
and immersed in freshwater and saltwater at a variety of pH values.**

Introduction. Pentachlorophenol loss rates used in this assessment were developed data from the 1994 study, “Pentachlorophenol – Leaching From Utility Poles Exposed to the Aquatic Environment” prepared by Springborn Laboratories for the Pentachlorophenol Task Force as part of the data call-in for re-registration of pentachlorophenol by the U.S. Environmental Protection Agency (Springborne, 1994). The study was produced and compiled in accordance with all pertinent EPA Good Laboratory Practice regulations (40 CFR, Part 160).

The utility poles chosen for testing were selected from a kiln-dried stock of southern pine. Two utility pole sections, approximately 11 feet long and 10 inches in diameter were treated to 0.50 pounds of pentachlorophenol per cubic foot in the treated zone using the Lowry Process. An additional 11-foot untreated utility pole section was selected from the same kiln lot as a control. The three poles were cut into 30 segment, each of which was approximately 11 inches long and 10 inches in diameter.

The pole segments were leached in tanks containing unbuffered reagent water, reagent water buffered at pH 5, 7, and 9, seawater and 0.1N HCl solutions. Triplicate tanks of each solution contained a treated pole segment, with an additional tank for each solution containing an untreated control. The pH was measured in each tank daily and adjustment made with either acid or base to maintain the pH within ± 0.1 units. Leachate temperature varied between 18.3 and 22.0 °C during the experiment with a mean and standard deviation of 20 ± 0.2 °C. The air exposed cut end of the pole sections was sealed with epoxy and Tenax® traps installed in the sealed tanks to capture any volatalized penta. The Tenax® traps did not reveal any evidence of the volatilization of pentachlorophenol during the study.

The immersed, cut, end of the poles were not sealed. Haloui *et al.* (1995) determined the diffusivity of pentachlorophenol along three orthogonal axes in treated wood. They found that the longitudinal diffusivity (parallel to the grain structure) was seven times higher than either the radial or tangential diffusivity. This has implications for leaching studies because if the end of the pole is exposed to water, as it was in this case, it can represent a significant fraction of the total leaching

surface area. Pentachlorophenol released from the cut end of a pole or piling that is driven into sediments ca. three meters will not be available to the water column. Therefore, in estimating the preservative lost to the water, only the surface grain should be considered. A pole diameter of 25.4 cm would result in a cut end surface of 506.7 cm². If the poles length was 27.8 cm (11 inches), then the horizontal grain surface area exposed to the water would be 2,218.2 cm². If preservative is lost seven times faster at the cut end, then the loss rates determined in this study should be reduced to 47 percent of the observed rate $\{(506.7 + 2218.2) \text{ Observed Rate of Loss} / (7 \times 506.7 + 2218.2)\}$. = Longitudinal Surface Loss Rate = 0.47 x Observed Loss Rate}.

There is a second problem associated with conducting static leaching tests of highly degradable organic compounds such as pentachlorophenol. The study did not state that the tanks were held in the dark. However, no information was given describing the lighting conditions (intensity or wavelength) under which the glass aquariums were held. The literature describing the degradation of pentachlorophenol clearly demonstrates that in normal sunlight, pentachlorophenol half-lives may be on the order of several days. Certainly less than the 30 days over which this experiment was conducted. Therefore, some photolysis of the pentachlorophenol should be anticipated during the experiment. Secondly, both fungi and bacteria have demonstrated an ability to degrade pentachlorophenol (see McAllister *et al.* 1996 for a review). Springborne (1994) noted the presence of fungi in the pH 5 and 7 treatments after approximately one week of immersion. Bacterial growths were reported in all tanks in this study. It is likely that these growths were metabolizing pentachlorophenol following the first week of immersion.

The antagonistic effects associated with increased loss rates from exposed end grain and decreased loss rates associated with the metabolism of pentachlorophenol by microbes and degradation by light are not quantifiable in this experiment and no correction is attempted. However, it should be noted that the increases due to not sealing the end-grain would be observed immediately as would decreases associated with photodegradation. The decreases in calculated loss rate associated with microbial catabolism would not be observed for perhaps 5 to 10 days. As will be seen in the following paragraphs, this risk assessment focuses on the first five days of immersion because that is the period in which maximum penta concentrations are anticipated in the water column. Therefore, it appears that the assessment may be somewhat conservative in that higher loss rates associated with the exposed end grain are not being balanced by microbial degradation in the near-term.

The leachate was analyzed following 1, 3, 7, 14, 21 and 30 days of immersion using High Performance Liquid Chromatography (HPLC). As previously noted, the study followed US EPA Good Laboratory protocols. It should be noted that between 99.9 and 108 percent of the pentachlorophenol added to spiked samples was recovered in this study.

The data provided by Springborne (1996) was used to develop loss rates per square centimeter per day and that data submitted to the Statistica™ Non-Linear Estimation algorithm for analysis. The sampling times were converted to the mean day during the sample period rather than the day on which samples were collected. The resulting predictive equation is provided below. The regression explained 73% of the variation in the database and each of the final coefficients were significant at $\alpha = 0.05$.

$$\text{Equation (2) Penta Loss} = 10.9 \times \exp^{-0.255 \times \text{Day} + 0.355 \times \text{pH} + 0.01 \times \text{Salinity}} \mu\text{g/cm}^2\text{-day}$$

This expression will be used to estimate the loss of pentachlorophenol from poles treated to 0.5 pounds per cubic foot in the treated zone.

Dioxins in pentachlorophenol

Pentachlorophenol does not contain 2,3,7,8 Tetrachloro-dibenzo-dioxin (2,3,7,8 TCDD). The U.S. EPA (49 FR 5831) has established water quality criteria for this compound of <0.01 µg/L maximum and 0.00001 µg/L continuous concentrations.

Pentachlorophenol does contain less toxic hepta- and hexa-dioxins (HxCDD) for which no water quality standards were available. It is possible, using the Toxic Equivalency Factors (with respect to TCDD) for these compounds and summing over their concentration in commercial pentachlorophenol, to express the sum in terms of a TEQ. The Toxic Equivalency for pentachlorophenol is 2.84 mg/L (Mr. Gene Meyers, Vulcan Chemical, personal communication). This risk assessment assumes that the hepta- and hexa-dioxins found in pentachlorophenol are lost to aquatic environments in proportion to their relative proportion in the preservative (2.84 mg dioxin/L of preservative). The resulting value will be compared with the U.S. EPA standards for 2,3,7,8 TCDD in assessing risk.

A Spreadsheet Model Predicting Treated Wood Contributions of Pentachlorophenol to the Water Column and Sediments

Introduction. Based on the preceding review and the analysis presented in this section, a model has been developed to predict water column and sediment levels of pentachlorophenol associated with creosote treated wood. The model is intended as a tool for engineers to be used in the conceptual stages of design, and as a regulatory tool providing site and project specific assessments of the environmental risks associated with pentachlorophenol treated wood in aquatic environments.

The model is reasonably complete and includes 13 easily measured input parameters. However, it does have certain limitations. It is general in nature and does not include provisions for complex, turbulent or chaotic current or mechanically induced distributions of sedimented pentachlorophenol. Adequate studies and data were not available for all input parameters such as retention, temperature and piling age. Future studies may require modification of the algorithms used to describe the most important parameters.

Pentachlorophenol migration data is not available for treated wood processed using newly designed Best Management Practices (BMPs). The data used to develop migration rates is from non-BMP produced poles. Best Management Practices were designed to minimize preservative loss. Therefore, migration rates calculated in this model may exaggerate potential environmental effects. The model can be easily changed to reflect new data when it becomes available.

This model does not include pentachlorophenol accumulation in sediments associated with the mechanical loss of treated wood fibers from structures. Impregnated wood can be heavier than water and may sink to the bottom. For economic, as well as environmental reasons, treated wood should be protected from excessive abrasion such as that found in association with float pins, ferry dolphins and wingwalls. In addition, this model makes predictions for immersed wood, it does not include algorithms describing preservative lost from overhead structures such as bridges and piers. Aquatic Environmental Sciences and Oregon State University are currently conducting a series of laboratory studies in an attempt to determine preservative loss from overhead structures as a function of solar insolation, retention, sawn wood grain structure, temperature, rainfall, etc. These data should be available for pentachlorophenol in 1999. This model has not yet been tested. However, ongoing studies of pentachlorophenol bridges in the United States are being conducted by Aquatic Environmental Sciences for the U.S. Forest Service.

In every case, the author has intended to be conservative (from the environment's point of view) in developing assumptions and evaluating the parameters upon which predictions are based. That is to say, if there is an error in this model, the error should cause an overestimation of the accumulation of pentachlorophenol in aquatic sediments and in the water column.

Methodology for assessing the risks associated with dissolved pentachlorophenol.

Pentachlorophenol that remains dissolved in the water column is likely to be carried downstream and diluted significantly before being sedimented. For purposes of estimating water column concentrations of pentachlorophenol, this model will assume that the pentachlorophenol is dissolved in a volume of water equal to the cross-sectional area of the immersed pole or piling. This is considered conservative because it ignores horizontal mixing that may increase the dilution volume significantly as water passes downstream. When poles are located parallel with the current such that the water passing one pole also interacts with the next pole downstream, we will assume that turbulence increases the mixing volume by an amount equal to the cross-sectional area of a 30 degree cone as illustrated in Figure (4). The highest concentration of dissolved pentachlorophenol is assumed to occur at the surface of the downstream most pole. In assessing water column concentrations of pentachlorophenol, this model will assume that all pentachlorophenol released from the pole is dissolved in the water column.

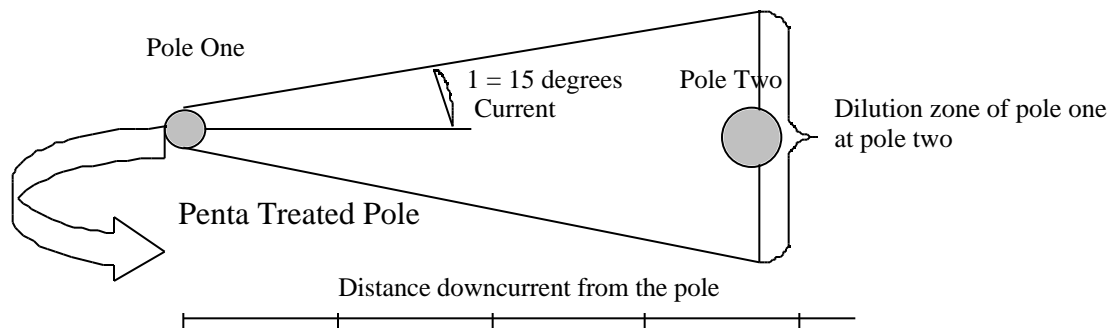


Figure 4. Geometry defining dilution zone associated with a pentachlorophenol treated pole immersed in water. The third dimension is the depth to which the pole is immersed.

This risk assessment will include an assessment of early time (≤ 4.0 days) risk using the U.S. EPA chronic pentachlorophenol standard. A second assessment will be made for day 5.0 against the 1994 Aquatic Dialog Group standard considered sufficient to protect 99% of species (see Figure 2).

Methodology for assessing the risks associated with sedimented pentachlorophenol. Based on the previous review, it appears that dissociated penta is most likely to bind to the clay fraction in aquatic environments. Following the worst case methodology adopted for these risk assessments, it will be assumed that all of the pentachlorophenol released from an immersed pole immediately adsorbs to clay particles. The distribution of sedimented pentachlorophenol will then be determined by tracking the fate of the clay in a non-turbulent column of water. Admittedly, this is not a very realistic scenario. However, it does appear to represent a worst case.

Following sedimentation, it is assumed that the pentachlorophenol degrades with a half-life defined by pH and redox. The model assumes that receiving sediments are naïve and that a period of 15 days of microbial adaptation is required before penta degradation begins. All of the sedimented pentachlorophenol is assumed to remain at the original point of sedimentation and no allowance is made for resuspension during high water or other factors that would reduced the nearfield concentrations.

This model is based on the deposition of clay adsorbed pentachlorophenol. The vertical (settling) velocity of clay particles can be obtained through the application of Stokes Law (Shepard, 1963). This law is expressed in Equation (3).

Equation (3) Stokes law for the settling velocities of small particles:

$$\omega = \frac{g D^2(\rho_s - \rho_w)}{18 \mu}$$

Where: g = gravitational constant (980 cm/sec²)

D = particle diameter (≤ 0.00039 cm)

ρ_s = particle density (1.8 to 2.6 gm/cm³)

ρ_w = density of water (0.998 @ 20 °C)

μ = Coefficient of molecular viscosity (10⁻² g/(cm-sec) for freshwater at 20 °C)

Worst case assumptions would require the largest clay particles ($D = 0.00039$ cm) at the highest density (2.6 g/cm³). Under these conditions, Stokes law predicts a settling velocity of 0.0013 cm/sec and this value will be used to predict the distribution of adsorbed pentachlorophenol to sediments.

Anticipated environmental levels of pentachlorophenol resulting from the use of 0.50 pcf treated wood in freshwater environments dominated by steady state currents.

This model can be used to assess the environmental risks associated with the use of pentachlorophenol treated wood used in freshwaters not influenced by oscillating currents such as upland streams and lakes and rivers at elevations above those where water levels are influenced by the tides. The following assumptions have been made in constructing the model.

- i. that the volume of the receiving water is large (> 400 square meters per piling) in comparison with the total amount of preservative being considered.
- ii. that released pentachlorophenol adsorbs to the heavy clay fraction of the suspended particulate load with a vertical settling velocity of 0.0013 cm/sec.
- ii. Pentachlorophenol concentrations in the water column are determined in the immediate vicinity of the piling. No allowances are made for diffusion.
- iii. that pentachlorophenol accumulates in sediments and is degraded with a half-life that is dependent on water column pH and reduction-oxidation potential measured in millivolts. This assumption ignores bedload movements in streams and or burial by new sediments.
- iv. that there is no additional sedimentation around the piling. The addition of new sediment would reduce the concentration of accumulated pentachlorophenol.
- v. Bioturbation typically homogenizes the upper three to ten centimeters of the sediment column. This biological activity redistributes surface deposited contaminants throughout the bioturbed sediment column – reducing the concentration. The assumption will be made that pentachlorophenol is distributed only in the upper 2.0 cm of the sediment column.

With these assumptions as background, the following derivations are provided to give the reader some insight into the model. That insight is valuable in interpreting the results. The models have been designed to provide a worst case analysis. Predicted preservative levels in the water column are the maxima observed within a centimeter of the piling. At all other distances, the concentration of pentachlorophenol levels will be significantly reduced.

Water column concentrations of pentachlorophenol lost from piling in fresh or brackish water environments dominated by steady state currents. A conservative model for pentachlorophenol concentrations in lotic systems assumes that preservative lost from a piling are diluted in a column of water defined by the current speed and the diameter of the pile. The following equation defines such a dilution volume after converting velocities from centimeters per second to centimeters per day to correspond with the algorithm used to define preservative migration rates.

$$\text{Equation (4) Dilution volume} = 2R_p V_{ss} 86,400$$

Where: R_p = the radius of the piling (cm)
 V_{ss} = the current speed (cm/sec)
86,400 = number of seconds in one day

The dilution zone is not a function of the depth of water because we assume that currents are equal at all depths. Therefore, the preservative lost from an incremental piling height is diluted in an incrementally high volume of water defined by the piling diameter and steady state current speed. Combining this dilution volume with the predicted preservative migration rate developed in Equation (1) gives a conservative prediction of the water column concentration of pentachlorophenol lost from a single pole. This initial risk assessment is for the maximum predicted penta concentration, which occurs during the first day (Day = 0.5) and therefore Equation (5) is appropriate.

$$\text{Equation (5) Penta}_{\text{water}} = (0.000396 \times \exp^{-0.255 \times \text{Day} + 0.355 \times \text{pH} + 0.01 \times \text{Salinity}}) / V_{\text{ss}} \text{ (}\mu\text{g/L)}$$

Deposition rates of pentachlorophenol to sediments in freshwater environments.

The models presented in Brooks (1995a, 1995b and 1995c) were optimized for poorly circulated marine environments where harmonically driven tidal currents interact with weak steady state currents. The dilution algorithms for these models are modified in the following paragraphs to provide more accurate predictions in lotic systems. This dilution model assumes that water is passing a piling with constant velocity. Turbulence associated with the piling creates the geometry described in Figure (5).

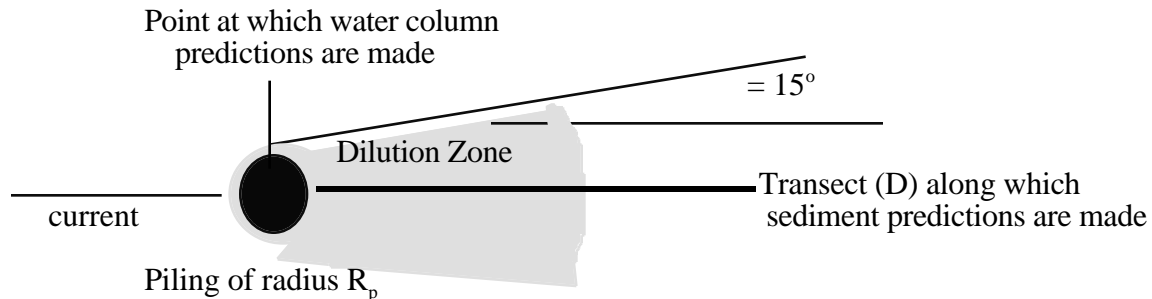


Figure 5. Dilution zone geometry used to predict preservative concentrations in sediments associated with the use of 0.5 pcf pentachlorophenol preserved southern yellow pine.

In this model we let $dA = 2R_p dD + 2D dD$, where

dA = the incremental area

R_p = radius of the piling

dD = the incremental distance along transect D

= the angle representing turbulent mixing = $15^\circ = 0.2618$ radians

Simplifying, we obtain $dA = 2(R_p + 0.2618D)dD$. Note that $D = h(V_{\text{ss}}/V_v)$ and therefore $dD = (V_{\text{ss}}/V_v)dh$, where V_{ss} is the steady state current speed and V_v is the vertical velocity of clay to which pentachlorophenol is assumed to be adsorbed. Both are expressed in cm/sec. The expression then becomes:

$$DA/dh = 2(R_p + 0.2618D)V_{\text{ss}}/V_v$$

This is combined with the appropriate expression describing the preservative loss per square centimeter per day (m), giving an expression for the sediment deposition of preservative components.

$$\text{Deposition} = M/dA = R_p m / [(R_p + 0.2618D)(V_{\text{ss}}/V_v)dh]$$

This expression can be further simplified by substituting $h = DV_v/V_{ss}$ to obtain the final form of the algorithm describing sediment deposition of pentachlorophenol in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{day}^{-1}$.

$$\text{Deposition } (\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{day}^{-1})/dh = R_p m V_v / [(R_p + 0.2618D)V_{ss}]$$

The sediment deposition rate of pentachlorophenol is predicted by substituting the dilution algorithm with the preservative loss rates (m) developed earlier.

Equation (6) Pentachlorophenol deposition = $34.24R_p V_v \exp^{-0.255 \text{ Day} + 0.355 \text{ pH} + 0.01 \text{ Salinity}}$

$$/[(R_p + 0.2618D)V_{ss}] \quad (\mu\text{g}/\text{cm}^2\cdot\text{day})$$

It should be noted that the immersed length of the piling is not a parameter in this relationship. The reason is that the current speed (V_{ss}) and clay-penta complex settling velocity (V_v) are assumed to be constant. Furthermore, it is assumed that there is no turbulent mixing and that the sediment surface is a flat plane. Therefore, a one-centimeter height of immersed piling contributes preservative to an area defined by the relationship:

$$\text{Depositional distance} = V_{ss} dh / V_v$$

Where: V_{ss} is the steady state current speed;
 dh is the incremental height on the piling;
 V_v is the settling velocity of the clay particle = 0.0013 cm/sec.

Accumulation of pentachlorophenol in freshwater sediments.

Following immersion of treated wood, pentachlorophenol is expected to accumulate in the sediments undegraded for a period of approximately 15 days. Following this initial period of accumulation, bacteria, fungi and other microbes will degrade pentachlorophenol with a half-life predicted by Equation (1), which described the degradation of sedimented pentachlorophenol as a function of pH and redox potential.

$$\text{Equation (1) Sedimented Penta Half-life} = 18.19448 * \text{pH} - 0.29284 * \text{Redox (mV)}$$

The concentration of pentachlorophenol at any time t equal to $C_t = C_o \exp^{-nt}$. At the half-life of pentachlorophenol (h), the concentration is $C_{(t=h)/2} = C_o \exp^{-nh}$. Solving this for n provides an expression describing the degradation that has occurred at any time t following sedimentation of the pentachlorophenol:

$$\text{Sediment Penta Concentration}_{(time = t)} = C_o \exp^{(-0.693147t/h)}$$

Substituting Equation (1) for the half-life (h) gives Equation (7) which expresses the sediment concentration as a function of time, pH and redox.

$$\text{Equation (7) Sedimented Penta}_{(time = t)} = C_o \exp^{(-0.69t/(18.19 \times \text{pH} - 0.29 \times \text{Redox}))}$$

Long term trends in sediment levels of pentachlorophenol. The original series invoked to examine this problem is provided in Equation (8). At any given time (t_n) in the future, the pentachlorophenol lost from the piling on day zero will have been degraded for a period of (n) days and the pentachlorophenol lost on day (n) will not be degraded at all. No analytical solution to this series has been developed and a numerical solution is not amenable to a user-friendly spreadsheet.

$$\text{Equation (8). Penta Conc}_{(t=n)} = M_{(t=0)}*D_{(t=n)} + M_{(t=1)}*D_{(t=n-1)} + M_{(t=2)}*D_{(t-2)} + \dots + M_{(t=n)}*D_{(t-n=0)}$$

where $M_{(t)}$ = the pentachlorophenol deposition rate at time = t (Equation 6).

$D_{(t-n)}$ = the pentachlorophenol remaining in the sediments following a period of n days of degradation.

Based on the reviewed literature and assuming that the receiving sediment microflora are naïve with respect to their ability to degrade pentachlorophenol, this model assumes that there is no degradation for a period of 15 days. Following this period of acclimation, sedimented pentachlorophenol is assumed to degrade with a daily degradation rate of 0.6931/half-life in days. The series in Equation (8) can then be simplified and made amenable to an Excel™ spreadsheet by invoking the following series for the first 15 days equals:

$$= 0.6931/\text{half-life} \times \quad t=1 \text{ to } t=15 \quad 34.24R_p \exp^{-0.255 t + 0.355 \text{ pH} + 0.01 \text{ Salinity}}$$

Following the first fifteen days ($t > 15$), the concentration of penta at the start of the day is reduced by the daily degradation coefficient and increased by the amount of new material released from the piling on the current day. The result is the following algorithm, which describes the total amount of pentachlorophenol distributed in the sediments on any day ($t = d$).

$$\text{Equation (9) Sedimented Penta on day (d)} = 34.24R_p \exp^{-0.255*d + 0.355 \text{ pH} + 0.01 \text{ Salinity}} \\ + [0.6931/(18.2*\text{pH} - 0.29*\text{Redox})] \\ \times \text{Penta remaining on day (d - 1).}$$

The series described in Equation (9) was expanded in a Microsoft Excel™ spreadsheet to produce Figure (6). With aerobic sediments (redox = +300 mV) and a high pH, more pentachlorophenol is released from the pole and accumulates in the sediments during the first 15 days. This material is rapidly degraded (half-life = 22.9 days) at the high pH and redox potential and the total sedimented penta is less than ten percent of the maximum 15 day concentration at the end of 100 days. Less penta is released from the pole at a low pH of 6.5. However, the half-life under these conditions is much longer (206 days) and sedimented pentachlorophenol is degraded more slowly. The maximum concentration of 17,420 μg is reached on Day 17.

Seventy-seven percent of this maximum was still sedimented at the end of 100 days. The values in Figure (6) are for each square centimeter. They must be multiplied by the pole radius to determine the total associated with a one centimeter high incremental height of immersed pole.

