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Pentachlorophenol Aquatic Fate and Effects

May 18, 2007

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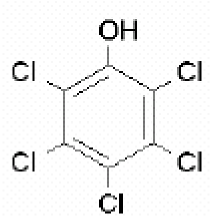
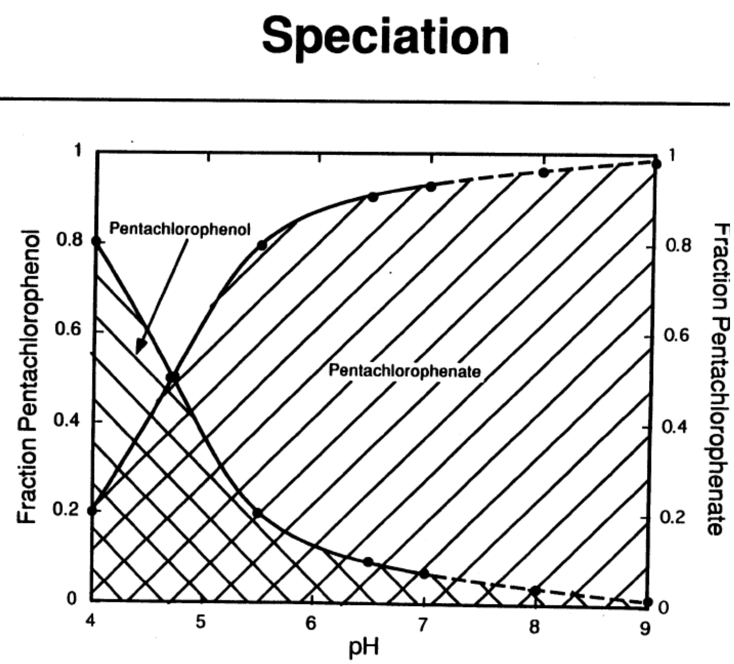
Background

- Pressure and thermal wood treatment with pentachlorophenol (penta) are the only registered uses in the United States
- Penta treated wood does not become brittle and retains its strength
- Material of choice in timber bridge construction over small rivers and streams

Physical Properties

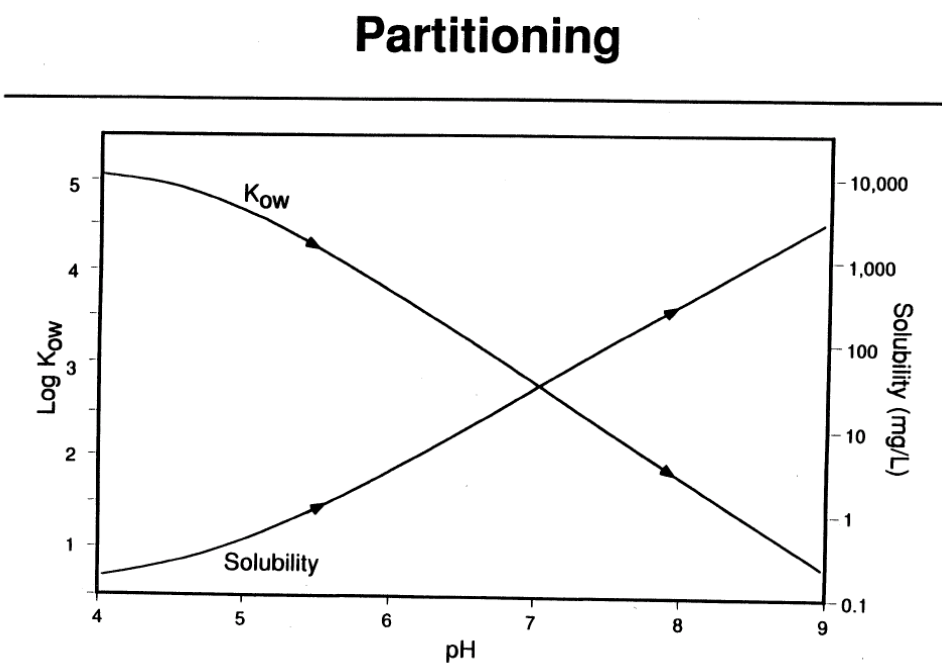
Structure	
Formula	C_6Cl_5OH
Mol wt	266.34
Melting point	191°C
Boiling point	310°C (decomposes)
Density	1.98 g/cm^3 at 22°C
Vapor pressure	0.00415 Pa (1.1x10^{-4} Torr at 25°C)
Dissociation Constant K_a	1.6x10^{-14}
Log K_{ow}	5.1 (pH 4) 3.3 (pH 7) 1.9 (pH 8)
Water solubility	10 mg/L at pH 6 20 mg/L at pH 8
Organic solvent solubility	Readily dissolves in most solvents

Speciation and Partitioning



SOURCE: *RIVM. Integrated Criteria Document: Chlorophenols (1991)*

pH dependent speciation



SOURCE: *RIVM. Integrated Criteria Document: Chlorophenols (1991)*

Influence of pH on solubility and log K_{ow}

Photodegradation

- Photodegradation – major degradation pathway for dissolved penta in water
- Photodegradation of pentachlorophenol is very rapid and eventually results in the destruction of the aromatic ring
- Studies with natural or UV light have shown half-lives from hours to days depending on conditions

Biodegradation

- Penta half-lives in fresh-water streams have been reported to be between 40 and 120 hours
- A large number of bacteria strains (>50) have been shown to degrade penta
  - *Pseudomonas sp.* naturally present in contaminated surface water could reduce concentrations of pentachlorophenol from 1.0 mg/l to <0.002 mg/l in 32 days
  - Generally an acclimation period (e.g. 10-20 days) is needed

Biodegradation/Photodegradation

Author	Half-life, days	Conditions
Boyle *et al.* (1980)	18.6	Aerobic in the laboratory
Boyle *et al.* (1980)	79.8	Anaerobic in the laboratory (dark – biodegradation only)
Crossland and Wolff (1985)	2.0 to 4.7	Outdoor mesocosms
Liu *et al.* (1981)	0.36	Aerobic in the laboratory
Liu *et al.* (1981)	190.0	Anaerobic in laboratory, dark
Wong and Crosby (1981)	2.0	pH 7.3 (natural sun-light)
Yu and Ward (1994)	~1.5	Mixed bacterial cultures

Effect of pH on Photodegradation Rate

- As pH increases, photolysis rates increase

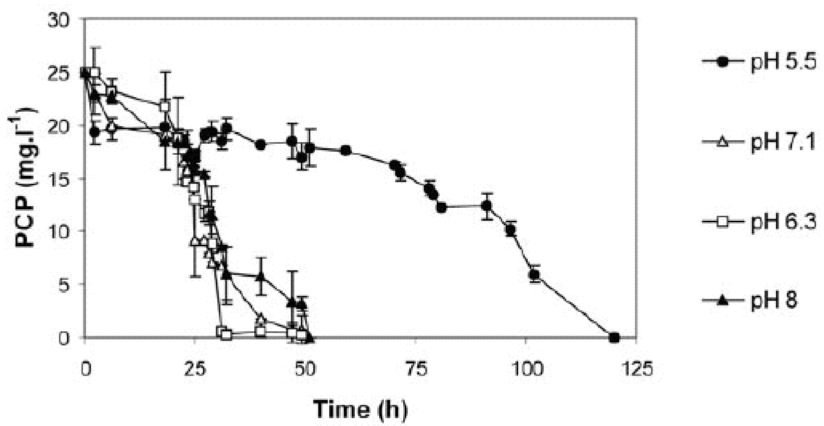
Author	pH	Half-Life, hours
Wong and Crosby (1981) simulated sunlight[1]	3.3	100
Wong and Crosby (1981) natural sunlight	7.3	72
Wong and Crosby (1981) simulated sunlight	7.3	10

[1] UV portion of sunlight, λ_{max} = 320 nm

Effect of pH on Biodegradation Rate

- Biodegradation rates are also pH dependent with studies carried out in the dark giving longer half-lives at lower pHs

Author	pH	Half-life, hours
Wolski et al. (2006)	5.5	90
Wolski et al. (2006)	6.3 – 8.0	36



Effect of Temperature on Degradation Rate

- As is generally the case with organic chemicals, degradation rates increase with increasing temperature (i.e. $t_{1/2}$ is shorter at higher temperatures)

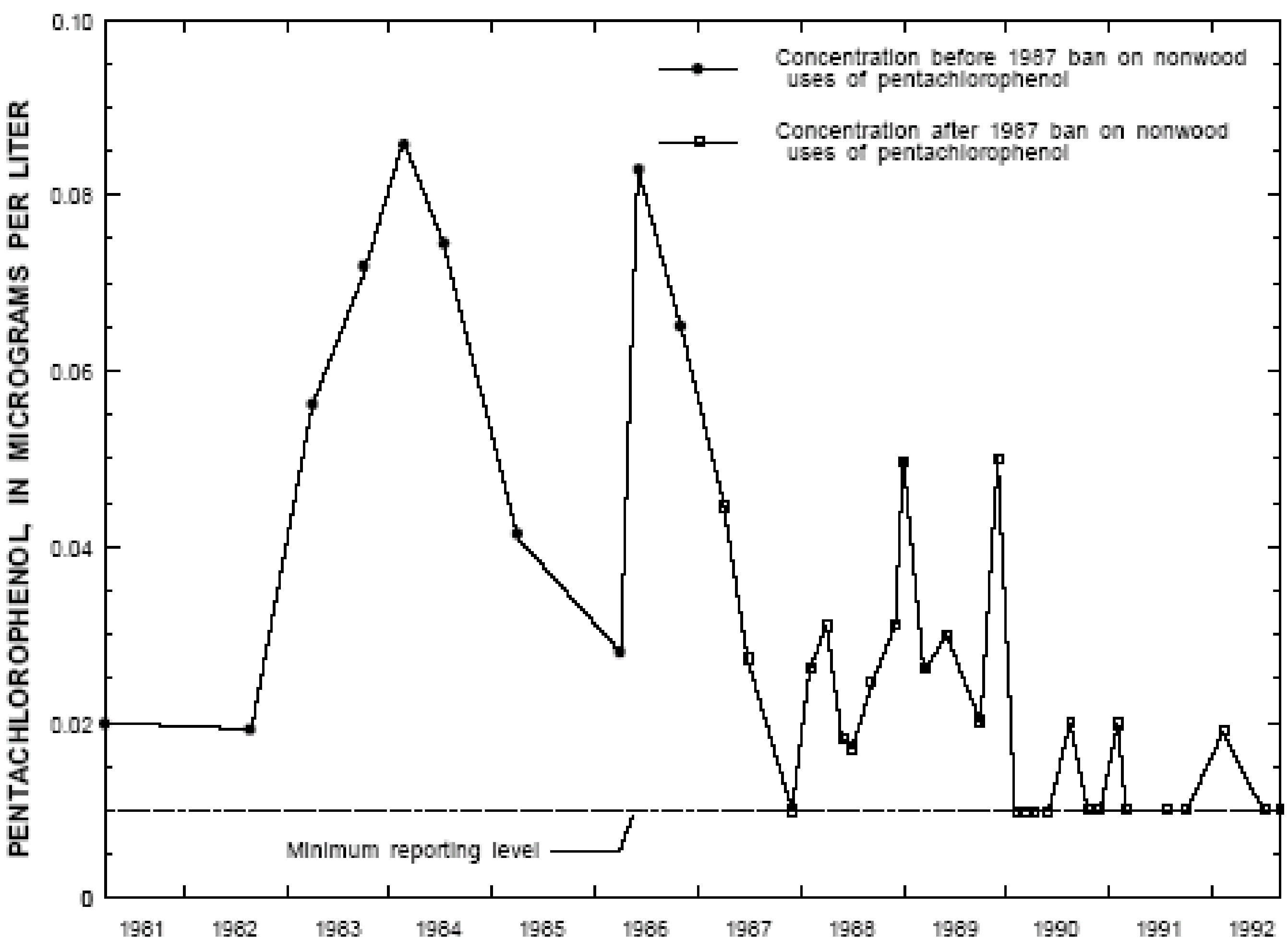
Author	**Temperature (°C)**	**Half-life (days)**
Topp *et al.* (1988)	20	<12
Topp *et al.* (1988)	4	>80
Trevors (1982)	0	No degradation

Monitoring Data – Washington State

	Frequency %	Median µg/L	Max, µg/L
Thornton Creek			
2003	78	0.015	0.083
2004	42	0.016	0.078
2005	21	0.0081	0.03
Marion Drain			
2003	5	0.01	0.01
2004	0	ND	ND
2005	0	ND	ND
Sulfur Creek Wasteway			
2003	10	0.0063[1]	0.0078
2004	3	0.0054[1]	0.0054[1]
2005	0	ND	ND
Spring Creek			
2003	5	0.0014[1]	0.0014[1]
2004	6	0.0041[1]	0.0051[1]
2005	0	ND	ND

[1] note that reported values below the MDL of 0.007 ug/L are estimates

Monitoring Data - Illinois



Fate in Sediment

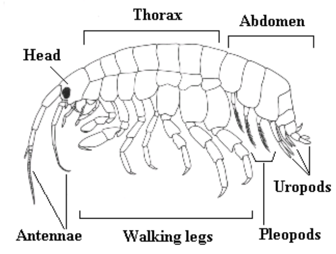
- Aerobic degradation
  - ➢ Studies have shown that at levels as high as 300 µg/kg in sediment, microbial populations can acclimate and degrade penta
- Anaerobic degradation
  - ➢ Various researchers have shown that microbial populations also acclimate under anaerobic conditions
  - ➢ Degradation rates are slower, but degradation does occur

Conclusions on Fate

- Degradation in water will occur mainly through photodegradation
- Degradation is relatively rapid and in natural systems has been shown to proceed to CO_2, HCl, and small organic fragments
- A variety of micro-organisms are able to degrade pentachlorophenol in sediments
  - After an adaptation period microbial communities can tolerate rapidly metabolize relatively high concentrations of penta
- Increased degradation occurs at moderate temperatures (between 10^{o}C and 35^{o}C) and at environmentally relevant pH (between 6 and 8)
- The many available studies provide a complete environmental fate database so that risks can be assessed.

Acute Toxicity

- Most freshwater species 96-h LC_{50} 100 – 2,000 µg penta/L
- Rainbow trout 96 hr LC_{50} 15 – 160 µg/L
- Bluegill sunfish 96 hr LC_{50} 52 – 60 µg/L
- Fathead minnow 96 hr LC_{50} 205 – 600 µg/L
- Daphnia 48 hour EC_{50} 82 – 450 µg/L
- LC_{50} values for amphipods 92 – 3,120 µg/L for exposures ranging from 24 hours to 30 days



Acute Toxicity – Rainbow Trout

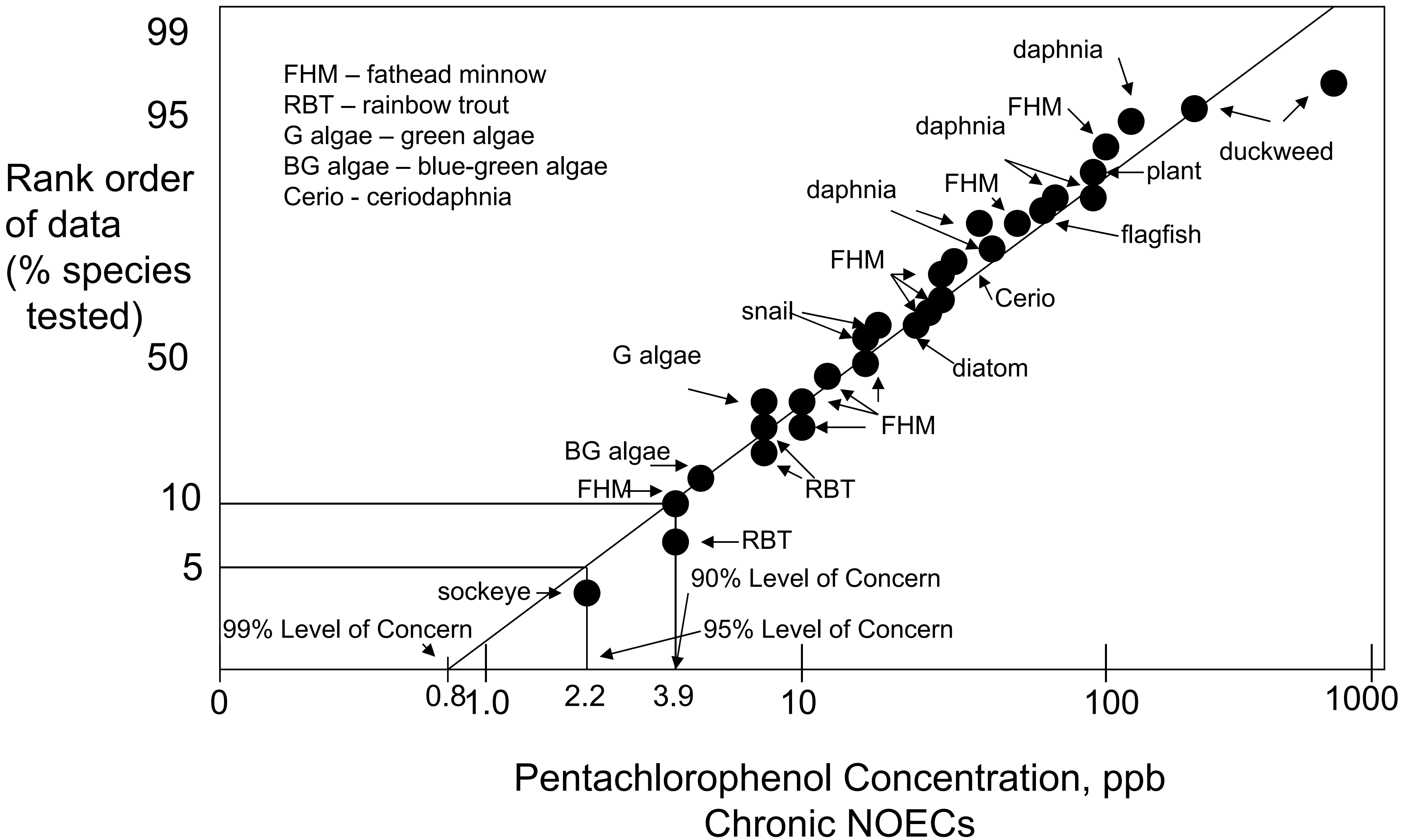
Change in formulation has reduced toxicity

Author	LC_{50} (µg penta/L)	Study Year
USEPA (2005)	15 and 75	1980 and 2001
Eisler (2000)	34 to 121	1980 - 1987
Dwyer et. al. (2005)	160	2003

Chronic Toxicity

- Wide range of chronic endpoints from reproduction and growth to delayed metamorphosis
- EPA water quality criteria indicate that these values are generally protective at the NOEL
  - Criteria give concentrations well below the LOEL in all cases
- Sensitivity of rainbow trout, fathead minnows, and sheepshead minnows to several federally listed endangered fish indicate that the current factor of 0.5 used to determine safe exposure levels for endangered species is protective

Chronic Toxicity



Effects of pH and temperature on toxicity

- Toxicity is inversely related to pH
- EC_{50} values increased from 384 µg/L at 25^{o}C and pH = 4 to 2,052 µg penta/L at the same temperature and pH = 8.0
- Toxicity generally increases with increasing temperature
- The effect of pH is stronger than the effect of temperature

Biotransformation

Species	**Half-life**	**Reference**
Daphnia magna	24 hrs	Kukkonen and Oikari (1988)
Midge	15 hours	Lydy *et al.* (1994)
Hyalella azteca	3.6 hrs	Nuutinen, et. al (2003)
Rainbow Trout	6.2 hrs (blood); 23.7 hrs (fat)	Glickman *et al.* (1977)

- Penta is rapidly metabolized in all species tested
- Metabolites are also rapidly eliminated
  - A combined half-life of 9.1 hours was measured for both penta and its metabolites in *Hyalella azteca*

Bioaccumulation/Bioconcentration

- Uptake of penta is a function of pH
  - At pH 4 it is fully protonated resulting in higher bioconcentration potential
  - At pH 9.0 it is completely ionized with lower bioconcentration potential and significantly reduced toxicity
- Laboratory and monitoring studies demonstrate that penta does not significantly bioaccumulate
- Penta clearance in all tested organisms is fast enough to minimize any potential for biomagnification in food chains

Bioconcentration

Route of Exposure	**Test Species**	**BCF**
Water	freshwater mussels *Anadonta anatina*	145 to 342
Water	freshwater mussels *Anadonta anatina*	100
Water	Depressed River Mussel *Pseudanodonta complanata*	73
Water	Scud *Hyalella azteca*	132
Water	Salmon eggs	25.2 – 38.7, 37.7 and 103.4 – 188.5 for eggshell, yolk sac and embryo
Water	Duckweed *Lemna polyrhiza*	79 and 62
Water & sediment	midge *Chironomus riparius*	458
Water & sediment	Midge larvae	229 – water 7.3 sediment
Sediment	Blackworm *Lumbriculus variegatus*	424
Oral - PCP in meal worms	Sub-adult African clawed frogs	no significant bioaccumulation

EPA Aquatic Criteria

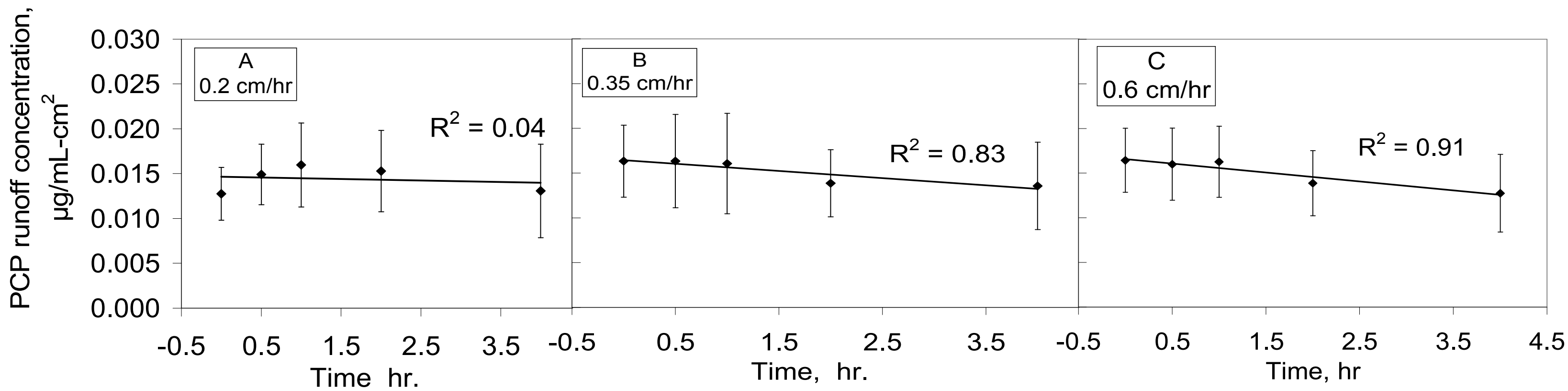
Freshwater		Saltwater	
acute (µg/L)	chronic (µg/L)	acute (µg/L)	chronic (µg/L)
19	15	13	7.9

- Freshwater aquatic life values for pentachlorophenol are expressed as a function of pH, and are calculated as follows: CMC = exp(1.005(pH)-4.869); CCC = exp(1.005(pH)-5.134). Values displayed in table correspond to a pH of 7.8
- WA monitoring data show maximum of 0.08 ug/L with detection frequency and concentrations in decreasing trend

Conclusions on Effects

- Many studies are available to show the acute and chronic effects of pentachlorophenol on aquatic species
- Effects of pentachlorophenol are dependent on environmental conditions, including the pH of the aquatic system
- The vast majority of the acute risk values are as much as one to two orders of magnitude higher than the LC50 for the most sensitive species
  - more recent studies have resulted in an order of magnitude less toxicity than those studies conducted previously because of formulation changes
- The ability of the organisms to metabolize pentachlorophenol and the lack of significant bioconcentration also reduce the potential risk

Exposure – Rainwater Runoff



- Average PCP levels in runoff from 8 PCP treated Douglas-fir boards subjected to 0.20, 0.35 or 0.60 cm/hr of simulated rainfall at 15 °C for 4 hr
- Amounts were consistent regardless of temperature or rainfall levels
- Average loss rate was 0.015 µg/ml-cm^2

Simonson et. al. in press

Dilution in Receiving Water

- Runoff will be diluted both by
  - The receiving water
  - The non-runoff rainfall that goes into the receiving water (not considered in this model)
- Brooks modeled the dilution of the rainwater runoff in a receiving water body using a box model
  - Width of the box = length of the span over water
  - Assume worst case dilution = laminar flow
- Based on studies of dilution of rainwater in receiving water, a mixing depth of 20 cm is used in the model

Concentration in Receiving Water

- Dissolved Penta(RW) (µg Penta/L) = $(TSA*RR*17.0*10^{-0.020*Time\ (hours)\ -\ 0.0104*RR\ (cm/hr)}/(360*20*Vss*CW)$
  - Where TSA = treated surface area
  - RR = rainfall rate
  - Vss = average current speed
  - CW = channel width

Estimated Water Concentrations – Skull Canyon Example

- The model predicts a water column concentration of 0.06 µg penta/L on the downcurrent dripline during the first rainfall event
  - Runoff is predicted to be mixed into the upper 20 cm of the water column at that point
  - All of the rainwater runoff from the bridge's long span is assumed to be delivered into the narrower channel defined by the 20 year low flow of the North Fork John Day River
  - The predicted value is 1.7% of the US EPA chronic WQC
  - Penta concentrations re predicted to decline as total rainfall accumulates.
- Note that predicted water column concentrations increase with increasing rainfall.
  - A 2.5 cm/hour rainfall would increase the predicted water column concentration to 1.54 µg penta/L or 44% of the standard
  - Rainfall rates that high would quickly increase local river flow and the use of the 20 year low flow for this analysis likely result in significant overestimates of the concentration

Sediment Concentrations

- The amount of sedimented pentachlorophenol is a function of receiving water pH and how anaerobic the sediment is
- The highest accumulations are predicted to occur in high pH anaerobic sediments

Sediment Monitoring: Cougar Smith Bridge - Washington

- Cougar Smith bridge was built with penta treated lumber in 1996 and sediment sampled in 1998
- Penta was detected in one sediment sample located 0.45 m (1.5 ft) downstream from the downstream perimeter of the bridge at a level of 9.0 µg/kg
- The sediment concentration at the 1.8 m (6.0 ft) downstream station was estimated at 6.6 µg/kg, which was less than the calculated detection limit
- Penta was not detected in other samples at this bridge
- All measures of biological response at distances downstream from the bridge were either equal to or exceeded those found at the upstream control

Sediment Monitoring: Upper Dairy Creek Bridge - Oregon

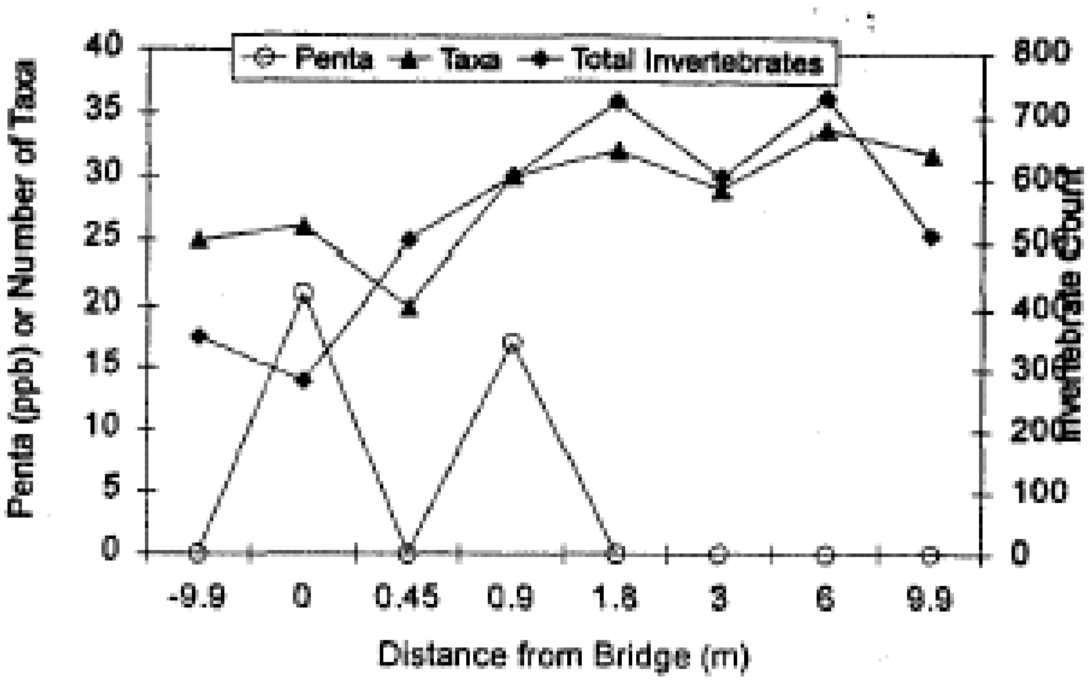


Figure 18.—*Pentachlorophenol levels in sediments compared to number of invertebrate taxa and total number of invertebrates adjacent to a pentachlorophenol-treated bridge.*

No adverse affects were noted when a bioassay was conducted on sediments collected from under the bridge

Sediment Benchmarks

- Washington State has developed an apparent effects threshold (AET) penta standard for marine sediments at 360 µg/kg.
- The New York State Department of Environmental Conservation has established a freshwater sediment criterion for penta of 100 µg penta/g sedimented organic carbon for acute toxicity and 40 µg penta/g sedimented organic carbon to prevent chronic toxicity.
    - a sediment with 1% organic carbon, the corresponding chronic criterion value is 400 µg penta/kg dry sediment (40 mg/g TOC × 0.01 TOC = 0.4 mg/kg), or 800 µg/kg at 2% TOC, 1,200 µg/kg at 3% TOC, etc.

Conclusions on Fate, Effects and Exposure

- Pentachlorophenol will degrade in the environment, limiting aquatic exposures
- Aquatic organisms can metabolize penta and there is not significant bioaccumulation
- EPA water quality criteria are protective for acute and chronic exposures
- Concentrations in water and sediment as a result of run-off from treated structures will be less than EPA water quality criteria and published sediment criteria

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