Pentachlorophenol Distribution in a Fresh Water Ecosystem

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On or about December 15, 1974, an undetermined amount of wood treating wastes, containing pentachlorophenol (PCP) overflowed a pole-treating company wastewater holding pond and contaminated a small creek leading to a 30 acre man-made lake near Hattiesburg, Mississippi. The resulting fish kill was described as extensive to total (Mississippi Air and Water Pollution Control Commission, (1975). This investigation was undertaken to study the ability of the fresh water ecosystem to assimilate the acute influx of PCP by observing changes in the PCP concentration in the water, suspended particulates, sediments, leaf litter from the stream bank, and organisms.

The toxicity and fate of PCP have been studied intensively under laboratory conditions (GOODNIGHT, 1942; BEVENUE and BECKMAN, 1967; HAMADMAD, 1967; HOLMBERT et. al., 1972; CROSBY, 1972 a,b; KIRSCH and ETZEL, 1973; PLIMMER, 1973; AKITAKE and KOBAYASHI, 1974; KOBAYASHI and AKITAKE, 1975; ARSENAULT, 1976; CARDWELL et. al., 1976; PRUITT et. al, 1976). Pentachlorophenol is a highly toxic pesticide that has many industrial and agricultural applications. Its toxicity to fish (TLm) has been reported to be in the range of 0.2 to 0.6 parts per million (ppm) GOODNIGHT, 1942; CARDWELL et. al., 1976; PRUITT et. al., 1976). Human illness and death have occurred from improper handling of PCP-treated lumber and sawdust and from exposure to spray formulations (BEVENUE and BECKMAN, 1967; ARSENAULT, 1976).

Although laboratory studies provide necessary insight to natural phenomena, additional studies on the fate of PCP in the natural environment are needed. Of special concern is the contamination and biological magnification of PCP and degradation products in aquatic organisms resulting from chronic exposure. Fish have been found to concentrate PCP over 1000 times that in the water, thus creating a potential hazard for animals eating the fish (MOORE, 1973; RUDLING, 1970; SHAFIK, 1973; STARK, 1969; ZITKO et. al., 1974). Contamination of drinking water supplies drawn from PCP-polluted rivers also have been reported (BUHLER et. al., 1973; CHRISWELL et. al., 1975. The

Bulletin of Environmental Contamination & Toxicology,
Vol. 18, No. 2 © 1977 by Springer-Verlag New York Inc.

problem is magnified by the persistence of PCP and degradation products, many of which also are toxic (CROSBY, 1972 a,b).

An understanding of the mode of transport and sites of accumulation is essential to determine PCP distribution in an aquatic environment. Since chlorinated hydrocarbons readily absorb to suspended particulate matter (PIERCE, et. al., 1974; WILSON, et. al., 1970), particulate matter may effectively scavenge PCP from the water providing an efficient mechanism for transporting large concentrations of the pollutant through the water column and concentrating it in sediments and in detritus-feeding organisms. Sediments, considered to be a sink for pesticides (OLOFFS et. al., 1973), provide a source for contamination of micro- and macroorganisms, thus introducing pesticides into the food web.

Materials and Methods

Six sample sites were chosen throughout the stream and lake in such manner as to assess the horizontal and vertical distribution of PCP. Water samples were collected in 4-liter glass jugs with aluminum lined caps. Particulate matter was obtained by filtering water samples through medium porosity Reeves Angel glass-fiber filter pads (glass-fiber was used to minimize PCP absorption). Sediments were collected with an Eckman Dredge by combining three grabs to provide about 1 kg total sample. Leaf litter was obtained from along the stream bank which had been soaked with PCP-in-oil as a result of the spill. Fish were collected by seine along the lake shore.

The samples were extracted and analyzed by filtering 2-liters of water from each site, acidifying to pH 2 and extracting into benzene in a separatory funnel. Pentachlorophenol associated with particulate matter was extracted by ultrasonication of the particulate matter on filter pads in benzene. Sediments were air-dried and 200 g samples were extracted with ultrasonication in benzene, followed by acidification with 0.1 N HCl and re-extraction in benzene. Fish samples were analyzed by blending 25 g of air-dried, chopped fish with 25 g anhydrous Na_2SO_4 in 100 ml benzene, filtering and repeating the extraction. Leaf litter was analyzed in a manner similar to fish, without Na_2SO_4.

Methylation of the phenol for analysis was accomplished by bringing the organic solution to about 5 ml volume and passing diazomethane through the solution generated according to the procedure of SCHLENK and GELLERMAN (1960). After about 5 minutes reaction time, the samples were brought to the appropriate volume for gas chromatographic (GC) analysis.

The samples were analyzed with a Varian Model 2740 gas chromatograph with electron capture, Sc^3H detectors. Two 1/8" x 6' stainless steel columns were used, a non polar 3% SP-2100 on 80/100 Supelcoport and a polar 10% SP-1000 on 80/100 Chromosorb WAW. Injector temperature was 175°C, column temperature 200°C, and detector 250°C. The carrier gas was N_2 at a flow rate of 25 ml/min. The presence of PCP was verified by subjecting representative samples to GC-mass spectrometric analysis.

Reagent blank analyses were performed according to each extraction procedure. Background PCP concentrations were determined by analyzing samples collected from a "clean" pond chosen as a control site. The control site was a 5 acre man-made pond to which no pesticides had been added and which did not receive drainage from agricultural land. The efficiency of the extraction procedures was determined by the addition of known amounts of PCP to clean samples and subjecting the "spiked" samples to the extraction and analysis procedure.

Results and Discussion

A low background concentration of PCP was observed in the control pond samples: 0.5 ppb in water and suspended particulates, 5 ppb in sediments and 50 ppb in fish and leaf litter. Therefore, PCP-contaminated environmental samples were recorded as concentrations exceeded that of the control. The extraction procedures were found to provide the following percent recoveries (± standard deviation): water, 90 ± 15; fish, 62 ± 4; sediment, 90 ± 38. Replicate analyses were performed on representative environmental samples and the variance was found to be within the experimental error of the above standard recoveries. The PCP concentrations reported for environmental samples (Table 1) were not corrected for percent recovery of the extraction procedure.

TABLE 1.

PCP CONCENTRATION IN WATER AND SEDIMENTS

Sample Date		Sample Site					
		1	2	3	4	5	6
2/27/75	Water[a]	9	11	6	9	19	8
	Sediment[b]	800	<5	22	26	119	2
4/24/75	Water	11	6	8	8	9	15
	Sediment	1,160	36	21	98	180	34
6/28/75	Water	13	8	2	3	2	82
	Sediment	1,300	5	5	583	860	92
8/5/75	Water	-	-	3	2	3	1
	Sediment	-	-	10	205	207	42
10/11/75	Water	10	5	<1	<1	<1	<1
	Sediment	927	471	48	91	56	24
12/6/75	Water	76	25	1	2	2	-
	Sediment	163	900	11	97	97	-
2/7/76	Water	29	-	15	10	10	26
	Sediment	100	-	313	10	84	81
5/3/76	Water	18	-	2	-	2	2
	Sediment	96	-	20	-	21	7

a. Reported as ug PCP/liter water
b. Reported as ug PCP/kg air-dried sediment

The concentrations of PCP observed in the stream and lake (Table 1) indicate that the fresh water ecosystem was incapable of assimilating the acute influx of PCP (i.e. degradation, dispersion or evaporation to background levels) within seventeen months after the spill.

Lethal concentrations of PCP reached the lake immediately after the spill as evidenced by the extensive fish kill. Within two months after the spill, however, water samples were found to contain low PCP concentrations (6 to 19 ppb) and the concentration remained near this level throughout the study. The concentration of PCP associated with suspended particulate matter remained near background levels (0.5 ug/liter of water filtered).

These results indicate a short residence time for PCP in the water column as supported by a rapid repopulation of fish in the lake by the time of the first sampling (February, 1975). The low level PCP concentrations found in the water throughout the study were probably due to the continuous influx from contaminated water shed areas. This is supported by anomolously high PCP concentrations observed in February, 1976, which followed a two month period of high rainfall. Surface water samples were analyzed periodically, but did not show a marked increase in PCP content over bulk water as had been expected, even in the presence of a visible oil sheen.

Sediments contained much larger amounts of PCP (up to 1,200 ppb) than were found in the water column. Samples of stream sediments near the spill source contained over ten times that found in other sediments in February, April and June, 1975. By December, 1975, the PCP content of stream sediments showed a drastic reduction probably due to resuspension and redistribution of PCP-containing sediments. The concentrations in lake sediments remained relatively constant throughout the study. Rapid PCP degradation was not apparent in the sediments, perhaps due to the association of PCP with naturally-occurring organic matter which may inhibit microbial and photodegradation as suggested by Crosby (1972a) and Hamadmad (1967).

Leaf litter collected from the stream bank contained high concentrations of PCP throughout the study (Table 2). In a separate study (Pierce, et. al., 1976) it was shown that PCP-contaminated leaf litter released ten percent of the PCP to water after a 24-hour equilibrium period. These results indicate that PCP associated with leaf litter and vegetation along the bank of a stream may be released over a long period of time, serving as a source for chronic PCP contamination of the aquatic environment.

Fish were found to contain concentrations of PCP up to six months following the spill (Table 2). Within ten months, the concentration in small fish dropped to near background levels. Unfortunately, the collection of fish by seining along the shore resulted in capturing small individuals that feed near the first consumer level. Therefore, these fish reflect the low PCP concentration in the water column and do not provide information regarding biological magnification via the benthic food chain.

TABLE 2.

PCP CONTENT IN FISH AND LEAF LITTER SAMPLES

	ng PCP/g Dry-weight sample (ppb)[a]	
Sample	Fish	Leaf Litter
2/27/75	2,500 ± 200	6,400 ± 250
4/24/75	1,380 ± 20	2,550 ± 650
6/23/75	130 ± 70	5,200 ± 300
10/11/75	Trace	5,800 ± 1,200
12/6/75	651 ± 650	3,470
2/10/76	87 ± 22	1,680 ± 12
5/3/76	Trace	6,000 ± 1,000

a. Average of replicate samples ± one-half the range.

Summary

The results of this investigation have shown that PCP persisted in leaf litter and sediments for at least seventeen months following contamination. This persistence provides a potential for continuous contamination of the water column and biological magnification via detritus- and benthic-feeding organisms. An investigation of these factors is presently underway.

Acknowledgements

This project was supported by the U.S. Environmental Protection Agency Grant No. R-803-82-0010. The authors are grateful to Dr. Paul Toom and Dr. Gary Blomquist of the Biochemistry Division, Department of Chemistry, USM for assisting with the gas chromatographic analyses. Special acknowledgement is given to Dr. Lee Wolfe, of the EPA Southeastern Environmental Research Laboratory, Athens, Ga., for his assistance with the project and for obtaining the gc-mass spectrometic analyses.

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