Distribution and Biomagnification of Hexachlorophene in Urban Drainage Areas

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Hexachlorophene (HCP)* has been a widely used bacteriostatic agent for the last twenty years. Until the recent ban on its use, other than as a preservative in cosmetics and as a prescription antibacterial drug (EDWARDS, 1972), HCP was a ubiquitous ingredient in soaps, creams, lotions, disinfectants, deodorants, and various other products. The use of HCP was curtailed when a subacute toxicity was demonstrated (KIMBROUGH and GAINES, 1971; LOCKHART, 1972), in addition to the long known fact that HCP was toxic in high concentrations (GUCKLHORN, 1969; GUMP, 1969; KIMBROUGH, 1971). Though HCP has been widely studied in terms of its medical usefulness and safety, the environmental effects, or even the presence of HCP in the environment have not beel well studied, despite its structural similarity to chlorinated hydrocarbon pesticides. In response to this lack of information a study was undertaken to determine the presence and distribution of HCP in the waterways of the Upper Haw River Basin near Greensboro, North Carolina. HCP is thought to be a pollutant whose source is the urban environment, and would therefore be found in municipal effluents, as has recently been substantiated by BUHLER et al. (1973).

MATERIALS AND METHODS

The series of sampling sites within the Haw River section of the Cape Fear River basin were chosen in relation to their distance from the two wastewater treatment plants of Greensboro, North Carolina (population approximately 150,000), each producing about 10,000,000 gallons of wastewater per day. Sampling sites are shown in Figure 1. Site 1, downstream from both wastewater treatment plants, was sampled fourteen times over a five month period and an additional sampling in March of 1973, following the FDA ban on HCP. The other sites were sampled intermittently, four times during October and November of 1972. Sites 2, 3, and 4 were located upstream of the sewage treatment plants and are intended to represent urban sources other than sewage treatment plants. The site downstream from the South Buffalo Wastewater

*Hexachlorophene is 2,2'-methylene-bis(3,4,6-trichlorophenol).

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Treatment Plant (5 on Figure 1) was chosen to assess the effects of that plant before the junction with North Buffalo Creek. Sites 6 and 7 were chosen to determine the effects of dilution with distance from the sewage treatment plants.

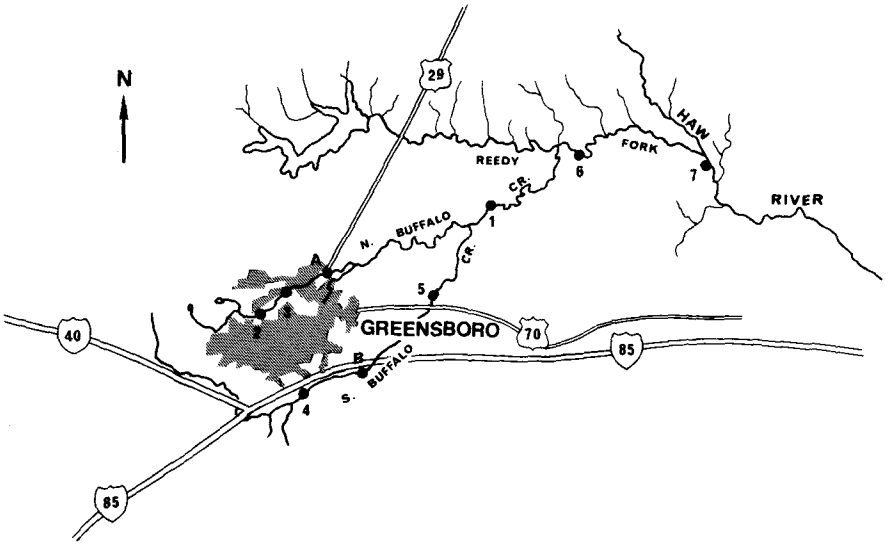

Figure 1. Map of Sampling Area. Symbols 1-7 refer to sample stations, A and B refer to the North- and South Buffalo Creek Wastewater Treatment Plants.

On each sampling occasion at site 1 grab samples of both surface and bottom water, and sediment were collected. An Eckman dredge was employed for sediment samples and a Nalgene jeri-can for water. Organisms were collected from water by straining water through a 28 mesh screen and from sediment by picking by hand. All samples were stored at 5°C in polyethylene containers until extraction and analysis. At other sites only surface water samples were collected. At all sites pH, dissolved oxygen, temperature, and BOD measurements were made according to standard methods (APHA, AWWA, WPCF, 1973).

One hundred milliliter aliquots of water samples were extracted for 4 hours in continuous liquid-liquid extractors using anhydrous ethyl ether as the extracting solvent. This

procedure varies in efficiency with concentration, but in a predictable manner, as shown in Figure 2. It also offers the advantage of being much more reproducible at any given concentration than are separatory funnel extractions. After extraction, the ether was dried by filtering through anhydrous Na_2SO_4, and evaporated to near dryness with a rotary evaporator. The residues were resuspended in 5-10 ml of benzene and stored at 5°C until acetylation and analysis.

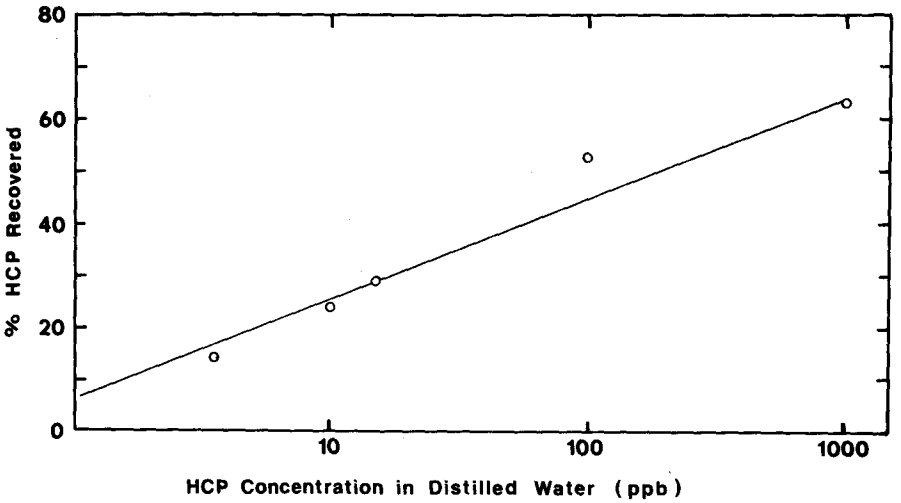

Figure 2. Efficiencies of Water Extraction Procedure (Least squares line of best fit).

Sediment samples were dried in glass petri dishes in a 55°C oven. Fifty gram aliquots of dried sediment were placed in cellulose thimbles and Soxhlet extracted with anhydrous ethyl ether for 4 hours. The organisms were separated from water or sediment, their wet weights determined, and were then extracted three times with benzene in a Thomas tissue grinder. The extracts of both organisms and sediments were handled in the same manner as the water extracts.

Acetylation was carried out according to the procedure of BROWNING et al. (1968) with no significant modifications.

TABLE 1 Distribution of Hexachlorophene in Upper Haw River Basin

Date	Hexachlorophene Concentration (parts per billion)								
	Site 1			Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
	surface water	bottom water	sediment	surface water	surface water	surface water	surface water	surface water	surface water
June 27	44.3	30.0	377.0						
July 9	18.0	22.0	106.8						
July 16	21.2	22.0	81.4						
July 23	31.2	21.6	110.9						
August 2	36.3	a	a						
August 12	37.8	41.4	30.5						
August 23	16.4	21.2	19.5						
September 2	41.5	19.2	25.4						
September 20	37.6	15.2	44.9						
September 30	28.4	a	a						
October 15	28.9	48.3	159.2	7.2	9.6		10.4	7.2	3.2
October 22	20.0	20.8	9.3	10.0	9.2		6.0	14.4	6.8
November 5	21.6	26.8	27.1	19.6	6.8		14.0	5.2	8.0
November 12	34.8	16.4	84.8	4.0	4.4	24.8	4.8	14.8	7.6
March 30, 1973	18.0	b	10.						

a. Heavy rainfall prevented collection of bottom water and sediment. Very high flow rate.
b. No bottom water sample collected.

Immediately following acetylation the samples were injected into the gas chromatograph. Extraction efficiencies were determined for water and sediment by adding known amounts of HCP to distilled water and dried sediment samples and measuring amounts recovered using the procedures discussed above. All data reported below have been corrected for extraction efficiency.

Extracts of water, sediment, and organisms were analyzed on a Perkin-Elmer Model 900 gas chromatograph with a ^{63}Ni electron capture detector. Analytical parameters were as follows. Column packing--5% SE-30 on Chromosorb W-AW in a 1/4" x 6 ft pyrex column. Nitrogen carrier gas at a flow rate of 100 ml/min. Injector temperature was 250°C, column temperature 220°C, manifold temperature 245°C and detector temperature 250°C. The detector was used in the pulsed mode. A digital integrator was used to give relative values for chromatographic peak areas. Each sample was injected repeatedly and the average for each sample was compared to a calibration curve obtained by injecting known concentrations of acetylated, authentic HCP. The concentration-peak area relationship was linear in the range of the calibration curve, 0.1 ng to 2.0 ng HCP. Another column system, 10% DC-200 on Chromosorb W, was used to assure that the peak in the sample which was thought to be HCP corresponded to an acetylated HCP standard in both column systems.

RESULTS AND DISCUSSION

As is evident from the data in Table 1, HCP is present in both the waters and sediments of the upper Haw River basin. At the Buffalo Creek site (1) where extensive sampling was conducted the concentrations ranged from 16.4 ppb to 44.3 ppb in the surface waters, 15.2 ppb to 48.3 ppb in the bottom waters and 9.3 to 377 ppb in the sediments. This is a small stream that has sewage treatment plant effluent as a significant and, at times of low natural flow, a major part (as much as 90%) of its flow. One of the obvious features of the HCP concentrations at site 1 is the variability from one sampling date to the next. HCP levels in the sediment are generally higher than in the water but also vary appreciably. This variation could be due to a number of factors including changes in flow, and changes in input from the two wastewater treatment plants. One of the more significant influences is probably precipitation. Those samples taken following occasions of heavy rainfall seem to show a change in sediment levels, and increases in bottom water concentrations. Buffalo Creek has a hard, sandy bottom on top of which is a layer of loose, unconsolidated material several centimeters thick. The high water flows associated with heavy rainfall appear to suspend this loose material and transport it to downstream areas,for after heavy rainfall only the hard, sandy bottom is present at site 1. The HCP levels at site 1 shown no significant correlation with pH, dissolved oxygen, temperature, or BOD.

At stations upstream of the North Buffalo Creek Wastewater Treatment Plant (sites 2 and 3) or the South Buffalo Creek Wastewater Treatment Plant (site 4) there is still some variability but generally lower concentrations of HCP than site 1. The levels observed at these stations probably reflect the HCP inputs from untreated wastewaters from upstream residential areas or from industries using HCP cleaning solutions. Likewise, the stations downstream from site 1 (sites 6 and 7) show decreasing concentrations with distance, probably the result of dilution with water from the tributaries which near sites 6 and 7 drain agricultural areas.

These distribution data clearly indicates that the two wastewater treatment plants are the major sources of HCP. One previous report also implicates wastewater treatment plants as major inputs of HCP to waterways (BUHLER et al., 1973). Hospitals may contribute significantly to sewerage systems through their use of HCP cleaning solutions. The two largest hospitals in Greensboro both contribute their wastewater to the North Buffalo Creek Treatment Plant which may explain why site 5, downstream of the South Buffalo Creek Treatment Plant and prior to the convergence of North and South Buffalo Creeks shows relatively low levels of HCP compared to what is seen at site 1. These two hospitals used 63-74 gallons of a 3% HCP cleaning solution per month prior to the ban, and 26-34 gallons per month after the ban. This may very well constitute the single largest input of HCP in the area.

Table 2 shows the HCP concentrations in the organisms collected at site 1. Since the stream flow at this point is principally treatment plant effluent there will be a large input to the system of allochthonous carbon. At no time during the sampling were any algae or other organisms characteristic of a grazing food chain observed. In a detritus based system like this it is nearly impossible to establish any trophic relationships. The organisms collected all show HCP concentrations significantly higher than those found in the water or sediment, and with the water scavengers, crayfish and water boatmen, considerable biomagnification appears to be occurring. With the exception of the sludge worms, the food sources for these organisms are probably bacteria, protozoa, and small invertebrates.

The single sampling subsequent to the ban on HCP may indicate that levels in the water and sediment are decreasing, but readily detectable amounts of HCP are still present. Since the hospitals continue to use HCP cleaning solutions and biomagnification can occur, it appears unlikely that a complete elimination of HCP from the ecosystem will be effected.

The HCP levels found in the water and sediment do not suggest a direct hazard to human health nor toxicity to environmentally significant microorganisms. Toxic symptoms can

Table 2

HCP Concentrations in the Major Organisms of Buffalo Creek

Organism	Number of Samples	Average HCP Concentration
Sludge worms (Tubifex tubifex)	4	335 ppb
Water Scavengers (Hydrophilus triangularis)	1	<1500 ppb
Crayfish (immature Cambarinae)	2	1338 ppb
Water Boatmen (Sigara spp.)	2	27,800 ppb

occur at about 20 ppm in tissues (20/mg/kg/day) (LOCKHART, 1972). Inhibition of microorganisms occurs at concentrations near 100 ppm (SILVERNALE et al., 1971). The threat to human health and the key to any environmental deterioration may lie in the biomagnification of HCP from the low concentrations in water observed in this study to potentially toxic levels. It appears that more detailed study of the extent and effects of HCP contamination of the environment is warranted.

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