

A New Water Treatment System for the Removal of Chloroform and Other Volatile Organics from Drinking Water

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Background

Chlorination is by far the most widely practiced method of water purification in the United States. It has been utilized since the turn of the century and has virtually eliminated the transmittal of once common and deadly water-borne diseases. In recent years, however, studies have been made that implicate this method of water treatment as a contributor to the death rate due to certain types of cancer. It has been found that this method of water treatment leads to the production of chloroform, a known carcinogen. Organic chemical contamination of drinking waters is not new. Middleton and Rosen (5) reported organics in drinking water as early as 1956. The concern for organic chemical contamination of drinking water was brought to the public's eye when Robert Harris (4) published a paper entitled, "Is the Water Safe to Drink? Part 1: The Problem." This paper called attention to the data contained in a rather obscure United States Environmental Protection Agency Report (2). These reports prompted further study that finally led to the discovery of 86 specific organic chemicals in the New Orleans drinking water (3). Following the report that some chemical carcinogens had been found in some Louisiana drinking water supplies, several epidemiological studies were conducted (1) (8) (9). These studies concluded that those parishes that derive their drinking water from the Mississippi River have higher cancer rates.

After some of the initial findings the EPA conducted a national survey of 80 water supplies, and found the universal problem of chloroform contamination following purification by chlorination. Other haloforms were formed as well, such as dichlorobromomethane, chlorodibromomethane and bromoform; all formed during the water purification process. The organic chemical usually found in highest concentration was chloroform. The National Cancer Institute completed a study on chloroform and found it to be carcinogenic (7). Using the standard methods for carcinogenic testing, they found a dose response relationship for epithelia tumors of the kidneys and renal pelvis in the rat, and hepatocellular carcinomas in mice. The latency period for the carcinogenic effects decreased as the dose increased. Other studies have also shown this effect; therefore, chloroform presents a potential carcinogenic risk to humans. The National Academy of Science (6) calculated the risk at the upper 95% confidence level. They estimate the risk at 1.5×10^{-5} at an average two liters consumption of water, with $21 \mu\text{g}/\text{l}$ [median concentration in the NORS study (11)] of chloroform for a lifetime. This corresponds to one excess cancer for every 66,666 persons

exposed for a lifetime. The National Academy of Sciences suggested that strict criteria be applied when limits for chloroform in drinking water are established. The EPA proposed that all cities of populations over 75,000 must have haloforms (chloroform and others) in concentrations of less than 100 $\mu\text{g}/\text{l}$. After public comment, the EPA changed their regulation to include all cities of over 10,000 people.

Experimental

Table 1 shows the amount of chloroform and other haloforms that were found in selected Indiana cities (10). It should be noticed that the raw water supply frequently did not contain chloroform and other haloforms, but the finished water contained chloroform in all cases. Thus, the water purification systems are making chloroform. Not only is chloroform produced during the treatment process, but it also continues to build up in concentration as it passes through the distribution system (Figure 1).

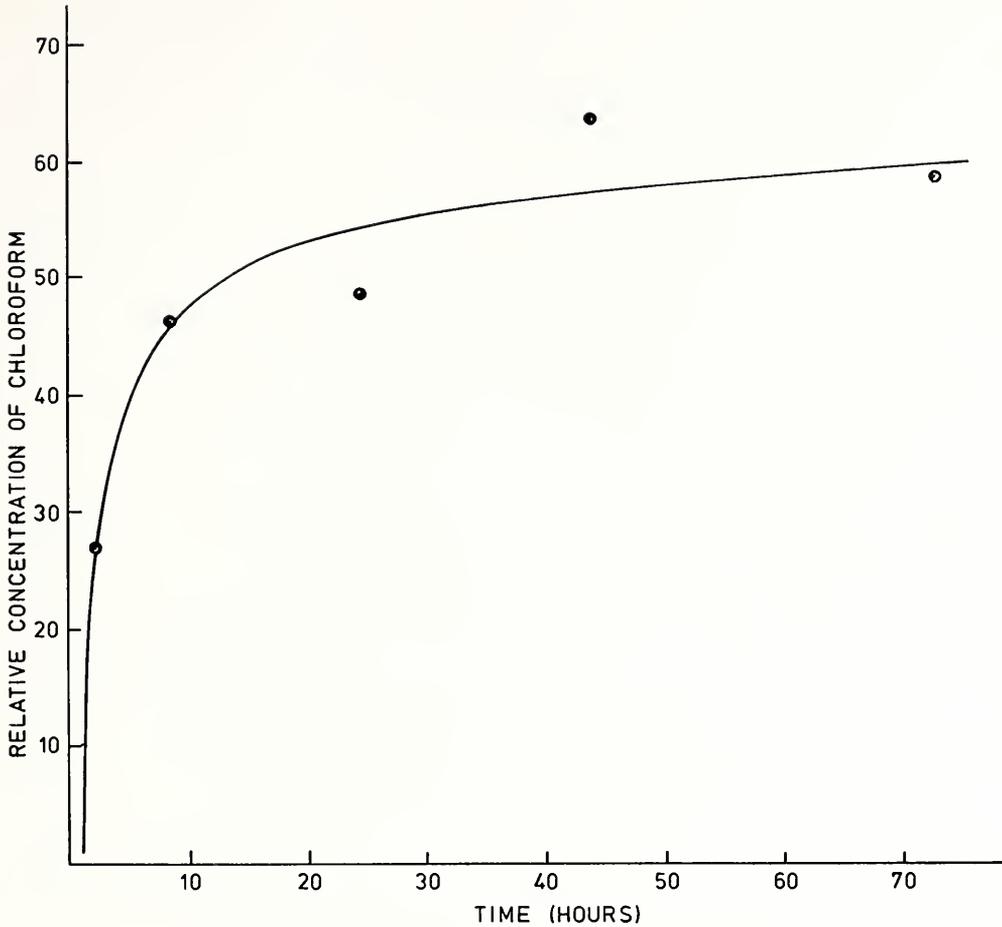
TABLE 1. *Raw and finished water analysis for selected Indiana cities.*

Indiana Cities	CHCl ₃		BrCHCl ₂		Br ₂ CHCl		Br ₃ CH	
	R	F	R	F	R	F	R	F
Bedford	5	84	nf	12	nf	.8	nf	.8
Bloomington	nf	19	nf	5	nf	.5	nf	<.3
Evansville	nf	29	nf	12	nf	1.7	nf	1
Fort Wayne	4	29	nf	.7	nf	.4	nf	1
Gary	nf	7	nf	5	nf	1	nf	<.5
Hammond	nf	4	nf	<.5	nf	<.5	nf	<.5
Indianapolis	nf	19	nf	6	nf	.5	nf	.6
Kokomo	9	30	nf	11	nf	1.4	nf	.3
Lafayette	nf	5	nf	1	nf	.3	nf	.6
Mt. Vernon	nf	18	nf	9	nf	1.2	nf	.9
Muncie	nf	31	nf	17	nf	1	nf	.5

R = Raw Water
F = Finished Water
nf = <1 microgram per liter

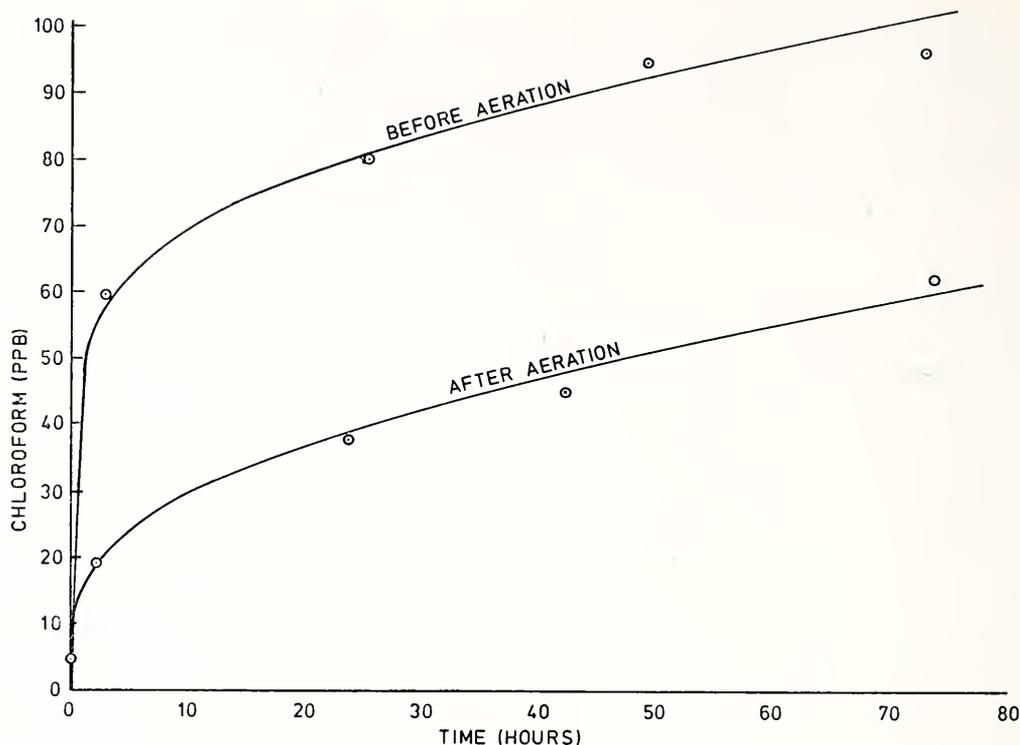
A water sample was collected from a municipal water plant approximately one hour after the chlorine had been added. The sample was stored in a baked-out bottle in order to simulate the time it would spend in distribution system. The water sample was analyzed periodically for chloroform. Marbles were added to replace the volume removed by taking an aliquot. This allowed the bottle to remain liquid-full so that there would be no evaporation loss due to head space. It can be seen by examination of Figure 1 that the chloroform concentration increased with elapsed time. About 50% of the maximum chloroform concentration was attained after 2½ hours, 70% after 5¾ hours, 80% after 10 hours, and 90% after 21 hours. We believe that the chloroform problem is greater than the EPA 80-city survey suggests. The concentrations in the distribution system would in all probability be higher than at the water treatment plant.

If the chloroform is allowed to build up to its maximum concentra-



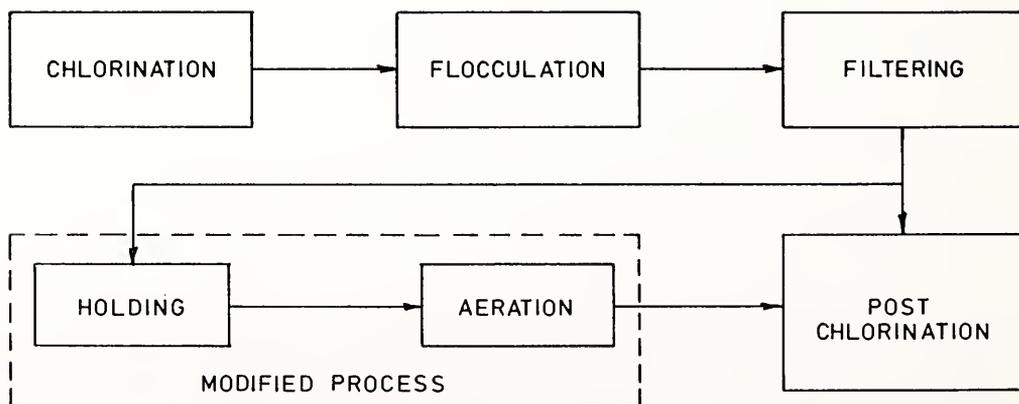
tion and then subjected to "aeration," the chloroform concentration is substantially reduced. A water sample was collected from a municipal water plant and allowed to stand in a baked-out capped bottle for 24 hours. A 1500 ml portion of this sample was analyzed and then nitrogen was passed through it at a rate of 15 ft³/hour for 20 minutes. The "aerated" sample was found to contain 94% less chloroform, 97% less dichlorobromoethane, and 97% less chlorodibromomethane. This method is also very effective in the removal of methylene chloride, carbon tetrachloride, 1,2-dichloroethane, bromoform, and other volatile organics from drinking water.

Since we determined that the increase in chloroform concentration during holding of the municipal water sample terminated due to the depletion of chlorine, we did another determination keeping the chlorine concentration relatively constant during the holding period. It can be seen by examination of Figure 2 that there is a relatively rapid formation of chloroform during the initial hours of holding, and then a decline in rate at later times. This would seem to indicate that there is more than one kind of reactive precursor. If the sample is "aerated" and then rechlorinated, chloroform again begins to form, except at a slower rate (Figure 2).



If a water treatment plant were to be operated under these conditions one could expect to drink about 50% less chloroform than would be produced by a conventional process. By regulating the pH, temperature of the water during chlorination, and holding times, one could achieve a range of reductions in formation of chloroform.

A flow diagram of a proposed municipal water treatment is shown in Figure 3.



Only very minor modifications of existing conventional water treatment plants would be necessary. The only two additional items would be a holding tank and an aeration unit. Both of these items are readily commercially available and the technology is well developed. The holding tank would be designed at a sufficient size so that the requisite number

of hours needed for chloroform formation would pass as the water continually flowed through the reservoir.

There are several other water purification methods presently being investigated by the United States Environmental Protection Agency. They are all aimed at reducing the amount of chloroform and other organic chemicals presently found in our drinking water supplies. Some of these methods employ other disinfectants such as ozone and chlorine dioxide. Both of these methods suffer from the fact that they do not produce a residual protection for bacteria contamination after the water leaves the treatment plant. Both chemicals are effective disinfectants but have short half lives. Carbon filtration after conventional chlorination is also being examined. Preliminary results indicate that even though this method shows promise, it suffers from the fact that the chemical contaminants leech through after a few weeks, and the carbon has to be physically removed and replaced. The spent carbon then must be reactivated, which requires a great deal of energy. Continual replacement with new carbon would probably be too expensive.

Aeration does not suffer from any of the above deficiencies. It would require only minor modification of our present water treatment systems, and would not require any sophisticated equipment or a change in the chemical disinfectant that has been so effective over the past several decades.

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