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Dechlorination and Trihalomethane Yields

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In the last few years, dechlorination with sulfur (IV) compounds, usually SO_2 or Na_2SO_3, has been increasingly adopted, especially at wastewater treatment plants (Helz and Kosak-Channing, 1984). This technology may offer a means of reducing potential damage to fish and other organisms from the oxidants in chlorinated effluents. Whether dechlorination also offers a practical means of reducing the halocarbon emissions associated with chlorinated effluents is not known.

Wastewater treatment plants, paper mills and electric power plants are major dischargers of chlorinated effluents to rivers, lakes, estuaries and the sea. Chlorinated effluents are sources of both trihalomethanes and macromolecular halocarbons (Carpenter, et al., 1980; Bean, et al., 1982; Fogelqvist, et al., 1982; Bean, et al., 1983; Helz, et al., 1984). At wastewater treatment plants and paper mills, chlorine is used for disinfection and bleaching, respectively. In these applications substantial chlorine contact times are necessary. In contrast, at power plants chlorine is used to control fouling in cooling water while it is passing through conduits and condensers. Contact times of only a few minutes are sufficient because of the short transit time of water through a plant. The purpose of this study is to test whether dechlorination after chlorine contact times of only a few minutes can reduce or eliminate trihalomethane emissions. Macromolecular halocarbons have not been investigated.

MATERIALS AND METHODS

In this study, we have used a unique model condenser research facility operated by Public Service Electric and Gas Co. for the Electric Power Research Institute. At this facility, researchers have freedom to select different fouling control agents and to manipulate doses and treatment schedules. Such freedom is not possible with an actual power plant cooling system. The facility consists of three 90 kw (3 x 10^5 Btu/hr), pilot-scale steam condensers designed to simulate operating characteristics of a main power plant condenser (Sugam, et al., 1984). A small chemical laboratory is associated with the facility.

At the time of this study, the model condenser research facility was located at a site a few kilometers south of Trenton, NJ, and was using Delaware River water for cooling. The Delaware River is one of the major rivers draining the eastern United States. Its long-term mean discharge at Trenton is 330 m^3/s; at the time of our experiments, in June, 1983, its discharge was 360 m^3/s. Some chemical characteristics of the water are given in Table 1.

Table 1. Composition of Delaware River Water During This Study*

	μM	Mg/L
Dissolved Fe	11.1	0.62
Dissolved Mn	2.0	0.11
Ammonium	9.0	0.16
Nitrite	4.02	0.185
Primary Organic Amines+	0.65	--
Total Organic N	45	0.63
Total Organic C	349	4.19

*Analyst: D.A. Dotson, University of Maryland.
+Fluorescamine method; reported as micromoles of glycine per liter necessary to produce the same fluorescence as observed in the sample.

Water samples for trihalomethane determination were collected from the outlet pipes of the model condenser. Glass bottles (125mL) were filled to the top with test water, and sealed with a Teflon-backed septum held in place by a crimped aluminum collar. Duplicate samples were collected, one of which was dechlorinated with 100μL of 1.0 M Na_2SO_3 instantly upon collection. These samples were shipped on ice by overnight express to the University of Maryland and analyzed within a few days of collection.

For the laboratory experiments, water was collected in 2.5 liter glass bottles. These glass bottles were cleaned before use by washing with detergent and water and then by leaching with dilute nitric acid. They were rinsed several times with the river water sample before being filled. After being filled, they were shipped overnight on ice to the University of Maryland and stored in a cold room at 4°C for a few days before use in the experimental work.

Trihalomethanes were determined by a headspace-gas chromatographic method employing a Perkin-Elmer 3920 gas chromatograph fitted with a 6 foot x 0.25 inch, 60/80 mesh chromosorb 101 glass column and a ^{63}Ni electron capture detector. Operating conditions were: oven temperature, 130°C; carrier gas flow rate, 30 mL/min of 95% argon - 5% methane. A primary standard solution, consisting of 100 mg/L of each trihalomethane in 100% ethanol, was diluted with distilled

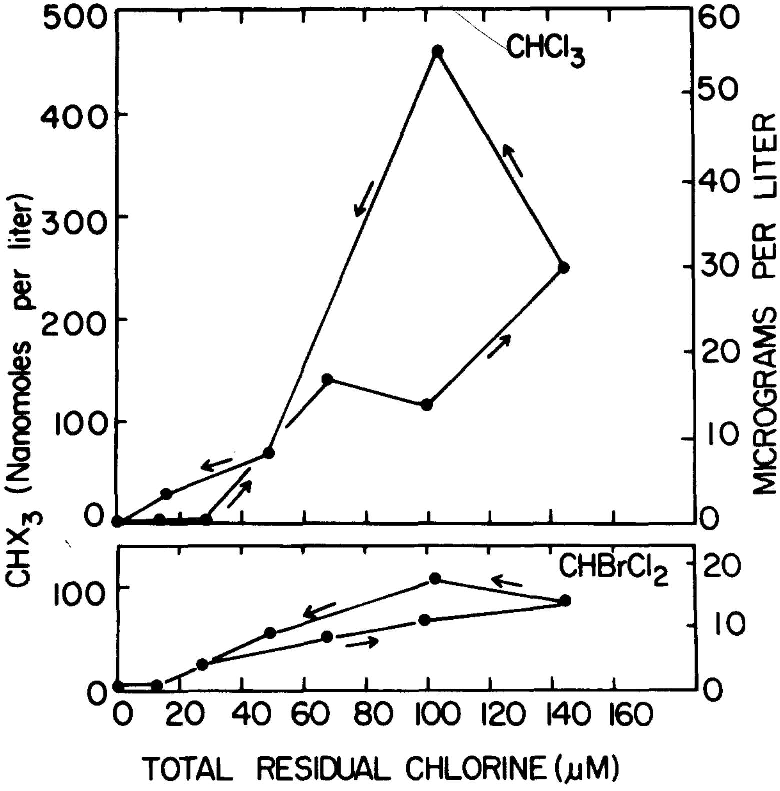

Figure 1: Yield of trihalomethanes as a function of total residual chlorine measured in the discharge from the model condenser. Arrows show the order in which the experiments were performed. Sampling date: June 24, 1983. Residual chlorine values are given in both μM and Mg/L units in Table 2.

water to appropriate concentrations (in the μg/L range) in order to calibrate the instrument. Twenty-five mL of water was removed from the 125 mL sample vials to create a headspace; then the samples were equilibrated at 40°C for an hour prior to injecting 0.5 mL of the vapor phase into the gas chromatograph. In some preliminary work, a hexane extraction, method similar to that of Nicholson et al. (1977), was used instead of the headspace method. Analytical conditions were otherwise similar.

RESULTS AND DISCUSSION

Because negligible trihalomethane yields were observed in some preliminary experiments involving chlorine doses below 15 μM (1 mg/L), the relation between trihalomethane yield and residual chlorine concentration in the cooling water was investigated (Figure 1). This experiment was performed a few days after the model condenser had been scoured clean with brushes and superchlorinated to remove any residual biofilm. The chlorine dose was raised in five steps to a level that gave a residual chlorine concentration at the condenser outlet of 140μM (10 mg/L as Cl_2). It should be noted that the highest residual chlorine concentration in these experiments exceeded by more than an order of magnitude the concentrations that would ordinarily be found in an operating power plant. After each increment in chlorine dose, the system was allowed to stabilize for one-half hour at the new level before samples were taken. After sampling at the highest residual chlorine level, the dose was lowered in four steps to zero. Again, samples were taken after a one-half hour stabilization period at each level. Two samples were collected at each step, one being immediately dechlorinated with enough Na_2SO_3 solution to give a diluted concentration of 800 μM. It is estimated that the contact time between chlorination and dechlorination in these samples was less than 15 seconds. Total residual chlorine was determined immediately in the undechlorinated sample; trihalomethanes were determined two days later.

As seen in Figure 1, the only trihalomethanes observed were $CHCl_3$ and $CHBrCl_2$. When the chlorine dose was sufficient to give a residual of 15 μM (1 mg/L) or less at the condenser outlet, trihalomethanes were undetectable. (Experience with the model condenser suggests that the actual chlorine dose was about 15 μM higher than the residual measured at the condenser outlet.) At higher chlorination rates, the trihalomethane yield increased with dose. However, the highest yields were not observed at the highest dose, but rather later, when the dose and observed residual had been reduced to three fourths of the maximum value. Possibly, the yield of trihalomethanes is a function not solely of the concentration of chlorine in the water, but also of the previous history of the condenser. The highest concentrations used in this experiment may have passivated some chlorine demand in the condenser system, leading to higher subsequent trihalomethane yields. However, we cannot rule out the possibility that an unnoticed shift in the quality of the intake water caused the higher yields later in the experiment.

Table 2 compares the chloroform yields in the dechlorinated and non-dechlorinated samples from this experiment. In the non-dechlorinated samples, chlorine was allowed to decay naturally for two days prior to analysis. Except at the lowest doses, dechlorination markedly reduced the chloroform yield. Typically, the yield is lowered to about 10% of the value observed in the non-dechlorinated samples. At the lowest chlorine concentrations, dechlorination appears to have less effect on chloroform yields. No $CHBrCl_2$ or other trihalomethanes were observed in any of the dechlorinated samples.

In these trihalomethane yield experiments at the model condenser facility, the contact time between chlorination and dechlorination was made as short as possible (<15s) and a rather high sulfite dose was used for dechlorination. An experiment was subsequently conducted to determine how strongly trihalomethane yields depend upon contact time and sulfite dose. A series of sealed septum

Table 2. Effect of Dechlorination on Chloroform Yields in the Model Condenser*

Residual Chlorine		$CHCl_3$ (No Na_2SO_3)		$CHCl_3$ (with Na_2SO_3)	
μM	mg/L	nM	μg/L	nM	μg/L
13	0.92	4.4	0.5	4.7	0.6
28	1.99	5.6	0.7	3.8	0.5
67	4.76	142	16.9	5.	0.6
100	7.10	114	13.6	12	1.4
145	10.30	251	29.9	24	2.9
105	7.46	460	54.7	38	4.5
49	3.48	68	8.1	7.4	0.9
15	1.06	31	3.7	5.0	0.6

*All measurements made in water from the condenser outlet. Dechlorination was with 100μL of 1.0 M Na_2SO_3 per 125mL of sample.

vials containing Delaware River water was chlorinated by injecting enough Cl_2 gas to give a dose of 100 μM in the solution. After an appropriate contact time, various doses of Na_2SO_3 were injected to quench the reactions.

Results are presented in Table 3. Dechlorination is seen to have reduced trihalomethane yields in every case compared to the yield in the non-dechlorinated sample. In general, the yields are smaller with shorter contact times, although there is considerable scatter. Dechlorination appears to be more effective at reducing $CHCl_3$ yields than at reducing $CHBrCl_2$ yields. It is not clear from the data that the Na_2SO_3 dose has much effect on yields. For the shortest contact times, yields of chloroform actually appear to increase with increasing Na_2SO_3 dose, but this unexpected trend is not confirmed in the $CHBrCl_2$ data and may be spurious.

A significant point with regard to the data in both Tables 2 and 3 is that dechlorination is capable of reducing but not eliminating trihalomethane production. For the two-minute contact time experiment in Table 3, chloroform was reduced by 2/3 to 3/4 of the yield in the non-dechlorinated sample and $CHBrCl_2$ was reduced by roughly ½. In the model condenser experiment (Table 2, contact time <15s), chloroform yields were reduced typically by about 9/10 at the higher dose levels. Evidently, the chemical processes that produce trihalomethanes are set in motion extremely rapidly.

Table 3. Effect of Sulfite Dose and Contact Time Between Chlorination and Dechlorination on Trihalomethane Yields*

Contact Time (min)	Na_2SO_3 Dose (μM)			
	none	100	200	1000
	A. $CHCl_3$	(nanomoles per liter)		
2	-	126(8)	134(9)	168(12)
10	-	84(6)	168(12)	193(13)
50	-	327(22)	310(22)	335(23)
⩾120	478(34)	-	-	-
	B. $CHBrCl_2$	(nanomoles per liter)		
2	-	55(9)	43(7)	43(7)
10	-	37(5)	67(10)	43(7)
50	-	73(11)	49(7)	55(9)
⩾120	85(13)	-	-	-

*Water treated with 100μM chlorine as Cl_2 gas. All trihalomethane yields in nanomolar units; to convert to mg/L units, multiply $CHCl_3$ values by 0.119 and $CHBr_3$ values by 0.164. Figures in parentheses represent standard deviation of triplicates. The water used in this experiment was collected from the Delaware River at Mercer on June 30, 1983, three days before the experiment.

The results of this work indicate that the benefits of dechlorination can include reduction in trihalomethanes, as well as oxidant emissions. However, it was necessary to use chlorine doses somewhat higher than normally used at power plants in order to obtain measurable trihalomethane yields at this study site. For such sites, reducing chlorine doses to the minimum concentrations effective for biofouling control might prove to be a more satisfactory means of reducing trihalomethane emissions.

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