

TRIHALOMETHANES IN GROUNDWATER SYSTEMS*

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ABSTRACT

Aqueous chlorine reacts with certain precursors in water to form trihalomethanes which are suspected carcinogens-mutagens. In the past, much attention has been given to the formation of THM's in surface waters, but little attention has been given to groundwater systems. In this study, groundwater supplies in six small towns in Maryland were studied. Samples of both raw and finished water were collected and analyzed for THM's and for THM formation potential at ambient pH and at pH9. In raw water samples, the only THM detected was chloroform, and the highest concentration was 2.5 $\mu\text{g}/\text{l}$. In finished water samples, chloroform concentrations were somewhat higher and no other species were detected, except for one supply where the chloroform concentration was 24.8 $\mu\text{g}/\text{l}$ and total THM's were 103.5 $\mu\text{g}/\text{l}$, the difference being brominated compounds. Significant amounts of brominated compounds were found in only one other supply, but total THM's were relatively low. The results of THM formation potential generally followed the same pattern, and showed a slight increase in formation potential at higher pH. The results indicate that more attention needs to be given to monitoring groundwater supplies in small towns.

Trihalomethane (THM) formation in water is associated with the interaction of aqueous chlorine and certain precursors. The formation of THM continues until the precursors or chlorine is exhausted. THMs formation is not instantaneous and the concentration in drinking water continues to increase as the water moves

* This research was partly supported by U. S. EPA Grant R-805689-02.

through the distribution system. Hence it is important to measure the trihalomethane formation potential (THMFP) which represents the maximum THM concentration that may be present in drinking water at the tap.

In the past much attention has been given to the formation of THM in surface waters; little attention was given to groundwater systems. Many small communities in the State of Maryland have groundwater supplies. Several reports indicate the presence of trihalomethane precursors and/or THMs in groundwater [1-3]. However, mainly chloroform has been detected in well waters. A study conducted on Florida groundwater from wells eighteen to thirty meters deep showed a THMFP ranging from 650 $\mu\text{g}/\ell$ to 950 $\mu\text{g}/\ell$. In Texas, a study conducted by Glaze, et al. revealed low THM levels in ten groundwater treatment plants [3]; the results of one indicated that there was indeed a trihalomethane problem in that particular supply system. The results showed THM concentration of 482 $\mu\text{g}/\ell$. The water was chlorinated at 2 mg/ ℓ for 24 hours at 26°C.

It is estimated that about 100 million people are served by groundwater and a majority of that population is served by small utilities. Currently water utilities serving less than 10,000 people are not required to monitor THM.

Groundwater supplies are generally not suspected of THM contamination. However, they may contain compounds with acetyl groups present in industrial discharges, and naturally occurring humic acid like materials. These precursors react with aqueous chlorine to form THM. Hence the groundwater supplies of small towns in the State of Maryland ranging from 104 to 4000 people were investigated for THMFP.

EXPERIMENTAL

The formation of trihalomethanes in various groundwater supply systems in the State of Maryland was studied. Samples of both raw and finished waters from various groundwater supply systems were collected in one-gallon bottles and analyzed.

Prior to collecting the samples from the distribution system, sodium thiosulfate solution was placed in the sampling bottles to neutralize the excess chlorine. Residual chlorine was measured at the sampling stations. The samples from the distribution systems were immediately analyzed (for THM) on arrival in the laboratory.

The raw sample from each well was divided into two portions. The THMFP in one portion was measured at the same pH, and the other sample was conducted at an elevated pH of 9.00. The reason for performing THMFP at higher pH was that groundwater often requires softening. Instantaneous TTHM analyses were formed on both the raw and finished waters to determine the initial concentrations. To each raw well water sample chlorine was added to obtain an initial concentration equivalent to that added at the plant. Each

water supply system adds a different dose of chlorine depending on the water quality of the wells. The chlorine solution was prepared by bubbling chlorine gas through Super "Q" water.¹ A known amount of this water was added to the sample to obtain the required chlorine dose.

Since the maximum retention in the distribution systems investigated is not more than twenty-four hours, a reaction time of twenty-four hours was selected for all THMFP experiments. The reaction vessel was kept in a constant temperature bath. The actual temperature of the bath was within ± 0.5 of the set reaction temperature. At various time intervals two samples of approximately 100 ml each were withdrawn from the reaction vessel for analysis. In one sample the pH was measured and excess chlorine was neutralized with sodium thiosulfate solution, and THM measured. The free residual chlorine in the other sample was measured by a specific ion electrode,² which was calibrated with standard DPD method.

THM ANALYSIS

The analysis for THM was performed by the liquid-liquid extraction technique. The ml of the sample were taken in a screw capped test tube to which 1 ml of pentane was added. The tube was capped tightly, and shaken vigorously for one minute. It was allowed to stand until the separation of phases was clearly visible. A sample of the upper organic phase was removed carefully with a disposable pipette and transferred to micro vials before it was sealed. These micro vials were arranged in sequence on the rack for the G.C. analysis. The instrument automatically injects one sample after another, and the results are printed. The area on the graph was integrated for determination of the concentration of the sample in micrograms per liter ($\mu\text{g}/\ell$).

The quantitative measurements for all the samples were carried out with a Hewlett-Packard Model 5830 Gas Chromatograph fitted with a Ni⁶³ electron capture detector. The glass column was $\frac{1}{4}$ " \times 4', packed with 10 percent FFAP on gas-chrom Q. The operating data of the GC is provided below:

- Column — 6.4mm \times 1.22m ($\frac{1}{4}$ " \times 4'), Glass
- Packing — 10 percent FFAP on Gas-Chrom Q
- Carrier Gas — Argon-Methane, 95%/5%
- Carrier Gas Flow Rate — 50ml/min
- Oven Temperature — 90°C
- Injection Temperature — 250°C
- Detector — Ni⁶³ Electron Capture
- Detector Temperature — 300°C

¹ Source, Millipore Corporation.

² Orion.

The liquid-liquid extraction method using pentane has been investigated in detail by many researchers [4-6]. These researchers found that pentane has the advantage of low solubility in water, good distribution coefficients and favorable polarity and volatility for effective separation from the THMs.

This technique has the advantages of being fast (about five minutes per sample), has minimal interferences from other commonly occurring organics in water and requires very little equipment besides an electron-capture GC detector. In low concentrations the results were verified by the Purge and Trap Method also.

RESULTS AND DISCUSSION

Water samples from supplies in Charles, Prince Georges, Montgomery, and Anne Arundel Counties were analyzed. The population of the towns varied from 104 to 4000; the type of treatment also varied. The results (average of several samples) are summarized in Table 1.

Raw water from the various wells was analyzed immediately upon arrival at the laboratory. In most cases the chloroform concentration was very low, less than $1 \mu\text{g}/\ell$, with the exception of the water from well number 2 from Town D where the chloroform concentration was $2.5 \mu\text{g}/\ell$. The remaining three trihalomethanes were not detected in the raw waters (Table 1).

Samples of finished water were obtained from a number of points in the distribution system of each town and analyzed for THM. Some typical results are shown in Table 2. The Town C results were unusual in several important respects. First, total THM in these samples taken varied from $3.4 \mu\text{g}/\ell$ to $103.5 \mu\text{g}/\ell$, the latter being in excess of the drinking water standard. In most systems chloroform was the predominant compound, except for Town C where brominated compounds ranged from 41 to 88 percent of the total. The source of these brominated compounds is not known at the present time.

It may be that since Town C is further down the estuary toward Chesapeake Bay, it is more likely to have saltwater intrusion and sea water has a relatively high concentration of bromine.

Various doses of chlorine ranging from $2 \text{ mg}/\ell$ to $0 \text{ mg}/\ell$, depending on the dose administered at that particular water utility, were added to the raw water and the THM formation was studied for about twenty-four hours. The THM formation potentials, except for Town C, were low. Typical results are shown in Figures 1 and 2 and in Table 3. Table 3 shows that the maximum concentration of THM (with the exception of Town C) was $14.34 \mu\text{g}/\ell$ at the normal pH, and $22.14 \mu\text{g}/\ell$ at the elevated pH of 9.00. Figure 3 shows the THMFP in well No. 1 in Town C. All the other wells in this town follow a similar pattern. The THM concentration at pH 7.5 (normal pH) at the end of the test was $138.49 \mu\text{g}/\ell$, where at pH 9 the THM was $163.77 \mu\text{g}/\ell$. Both of these values are in excess of $100 \mu\text{g}/\ell$ the maximum contaminant level (MCL) promulgated by EPA (Federal Register [7]).

Table 1. Trihalomethanes in Raw Maryland Groundwaters

<i>Name of Water Utility or Plant</i>	<i>Population Served</i>	<i>Water System</i>	<i>CHCl₃ (µg/ℓ)</i>	<i>TTHM (µg/ℓ)</i>
Town A	2800	Bowie Combined Sewer	0.59	0.59
Town B	3100	Well No. 1	0.77	0.77
		Well No. 2	0.71	0.71
		Well No. 3	0.62	0.62
		Well No. 4	0.79	0.79
Town C	1800	Well No. 1	1.09	1.09
		Well No. 2	0.79	0.79
		Well No. 3	0.96	0.96
Town D	2800	Well No. 1	1.02	1.10
		Well No. 2	2.49	2.95
Town E	4000	Well No. 6	0.98	0.98
		Well No. 7	0.86	0.86
Town F	104	Well No. 3 (John Hansen)	0.72	0.72
		Well No. 4 (Berry Road)	0.65	0.65
		Well No. 5 (St. Charles)	0.66	0.82

Table 2. Trihalomethanes in Finished Water

<i>Name of Water Utility or Plant</i>	<i>pH</i>	<i>Free Chlorine mg/ℓ</i>	<i>CHCl₃ µg/ℓ</i>	<i>TTHM µg/ℓ</i>
Town A	8.2	0.7	2.06	2.44
Town B	7.0	1.0	2.40	4.41
Town C	7.6	0.2	24.8	103.5
Town D	7.5	0.9	1.54	2.27
Town E	8.0	0.8	3.00	4.69
Town F	7.3	1.3	2.95	3.36

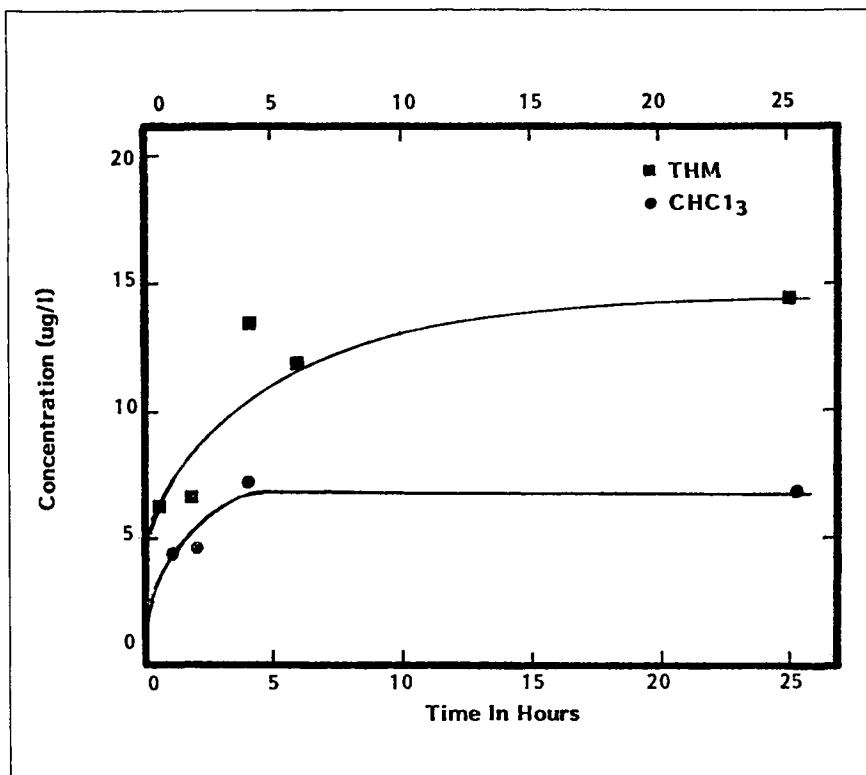


Figure 1. Town B Well No. 1: THM formation as a function of time at sample pH.

In Town C, water, THM concentration in the raw water was low and brominated species were not detected. However, THMFP was the highest observed and consisted mainly of brominated species as shown below. This is in contrast to all other systems, where THM was 90 percent or more chloroform.

• CHCl ₃	=	17.24 $\mu\text{g}/\ell$	13.4 percent
• CHBrCl ₂	=	34.10	24.6 percent
• CHBr ₂ Cl	=	61.13	44.2 percent
• CHBr ₃	=	26.02	18.8 percent

Similar results were obtained for wells numbers 2 and 3 of Town C. The high dibromochloromethane, dichlorobromomethane and bromoform concentrations in this water suggest the presence of bromide salts as well as THM precursors, because chlorination in the presence of bromide has been shown to result in the

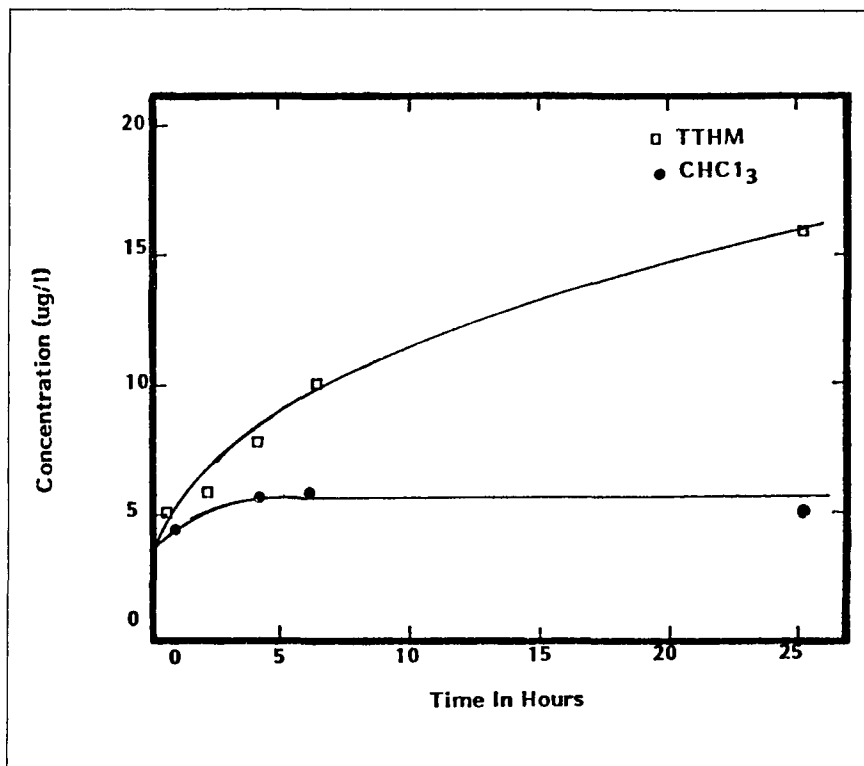


Figure 2. Town B Well No. 1: THM formation at pH = 9.

formation of brominated trihalomethanes. The tests were repeated several times during the year, and seasonal variations were observed.

Another water utility, Town D, is situated in the same geographical location, that is, in the Patuxent-Patapsco Basin thereby obtaining water from the same aquifer. Hence, the water from Town D was also tested (Table 4).

At pH 7.5 for Town D and Town C the THMFP values were $3.4 \mu\text{g}/\ell$ and $138.5 \mu\text{g}/\ell$ respectively.

The effect of pH on THM formation was studied at the normal water pH of the sample and at an elevated pH of 9. In samples from Town B well No. 1, the results indicate that higher concentrations were obtained at the elevated pH. However, the increase was slight (Figures 1 and 2 and Table 3). Also, no significant difference in the results were noticed due to seasonal variation (Tables 3 and 5). The lower concentration was at the sample collected at the "Laundra-Mat," and the highest was at the Post Office. At this time, the

Table 3. Trihalomethane Formation Potential in Chlorinated Groundwaters Supplies in Maryland (Spring 1980)

Name of Water Utility or Plant	Water System	Normal pH – $\mu\text{g}/\ell$		pH 9 – $\mu\text{g}/\ell$	
		CHCl_3	TTHM	CHCl_3	TTHM
Town A	Bowie Combined Raw	4.03	4.03	4.16	4.17
Town B	Well No. 1	6.60	14.34	4.54	15.74
	Well No. 2	2.26	6.12	2.43	8.99
	Well No. 3	7.42	13.79	13.62	22.14
	Well No. 4	4.31	6.77	5.23	9.56
Town C	Well No. 1	17.24	138.49	17.14	163.77
	Well No. 2	15.44	71.51	17.69	96.29
	Well No. 3	15.51	89.66	15.70	112.40
Town D	Well No. 1	2.26	3.39	2.55	4.28
Town E	Well No. 2	5.17	7.14	6.74	10.49
	Well No. 6	2.67	3.34	5.47	7.25
	Well No. 7	3.79	4.90	4.96	6.74
Town F	Well No. 3	6.32	8.25	8.32	10.81
	Well No. 4	9.19	12.50	9.18	12.50
	Well No. 5	3.92	4.99	7.43	11.86

Table 4. Trihalomethanes in Potomac Heights

Before pH Adjustment					After pH Adjustment (pH = 9)				
Time (Hours)	pH	Free Cl (mg/l)	($\mu\text{g}/\ell$)	($\mu\text{g}/\ell$)	Time (Hours)	pH	Free Cl (mg/l)	($\mu\text{g}/\ell$)	($\mu\text{g}/\ell$)
0.5	7.8	2.2	1.54	1.96	0.5	9.1	2.2	1.49	2.06
2.0	7.8	2.1	1.62	2.19	2.0	9.1	2.1	1.87	2.67
4.0	7.8	2.1	1.43	1.99	4.0	9.1	2.1	1.78	2.70
6.0	7.8	2.1	1.75	2.42	6.0	9.1	2.1	1.99	3.02
25.0	0.9	2.0	2.26	3.39	25.0	9.1	2.0	2.55	4.28

Note: Source: Potomac Heights, Charles County; Type: Groundwater; Sample 1D: pH 1, Well No. 1; Field pH: 7.5; Cl Added: 2.5 mg/l.

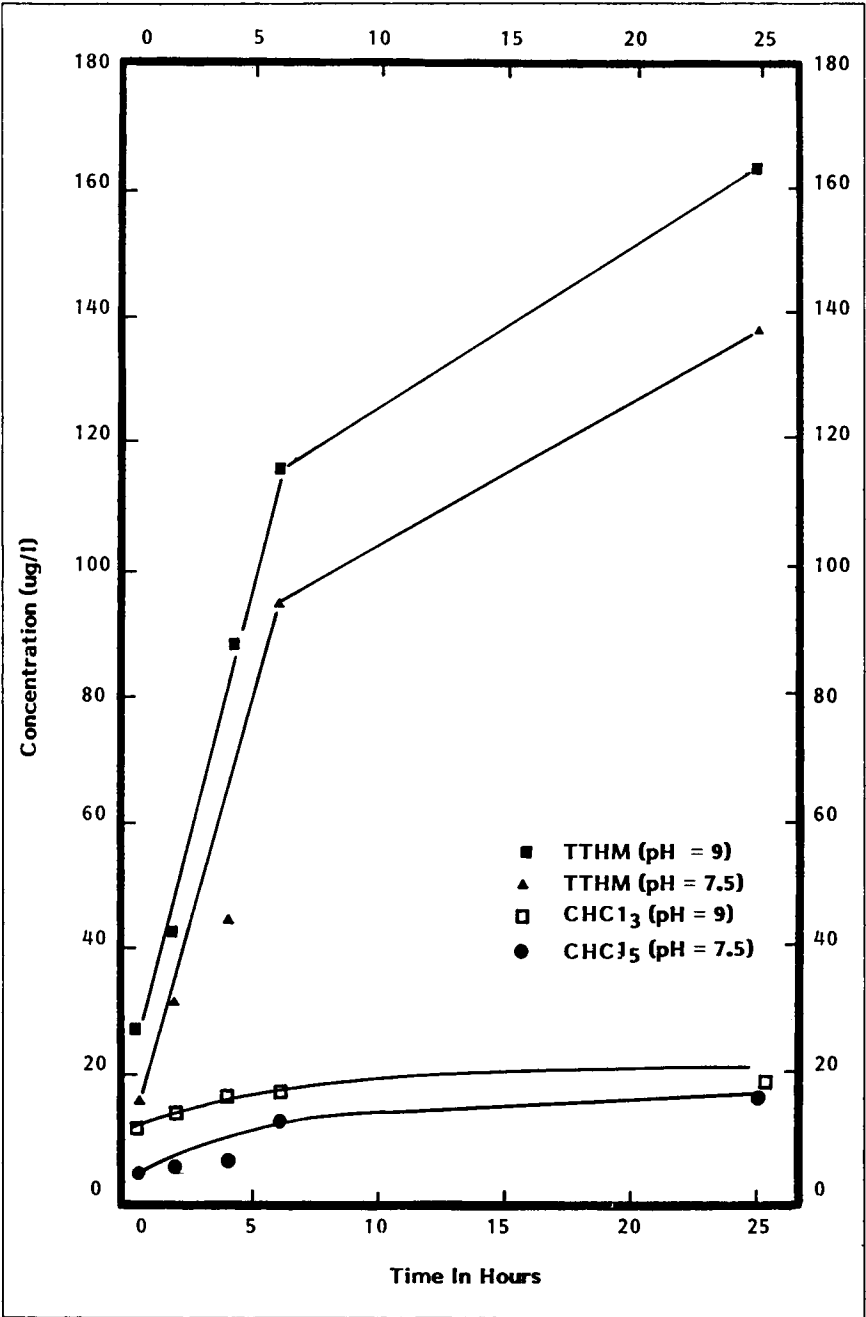


Figure 3. Town C Well No. 1: THM formation as a function of time.

Table 5. Trihalomethane Formation Potential in Chlorinated Groundwater Supplies in Maryland (Winter 1980)

Name of Water Utility or Plant	Water System	At Water pH		pH	
		CHCl ₃ (µg/l)	TTHM (µg/l)	CHCl ₃ (µg/l) pH	TTHM (µg/l) pH
Town A	Bowie Combined Raw	2.5	2.78	6.59	8.74
Town B	Well No. 1	5.43	13.54	8.62	20.13
	Well No. 2	2.91	6.92	3.92	9.96
	Well No. 3	2.22	5.66	2.62	8.95
	Well No. 4	3.73	6.43	4.59	7.97
Town C	Well No. 1	33.37	35.24	41.05	44.07
	Well No. 2	31.11	31.11	47.79	47.79
Town D	Well No. 2	5.60	6.29	8.77	10.32
	Well No. 5	15.60	16.74	6.49	8.8
	Well No. 7	11.51	13.27	16.14	19.19
	Well No. 8	5.68	8.89	9.65	11.14
Town E	Well No. 1	17.47	17.47	23.98	23.98
	Well No. 3	36.66	36.66	38.38	38.38
	Well No. 5	39.20	39.20	46.98	46.98

distribution pattern of Town C is not a closed loop system so there are some dead ends, where the water may be stagnant. This may cause the build-up of precursors. The town has decided to close the loop in the near future.

In most water supplies examined, THM concentration in the finished water was relatively low (less than 8 µg/l) and chloroform was the predominant compound. In the Town C system, total THM concentration as high as 103 µg/l were found, only about 25 percent of which was chloroform. The remainder being brominated species. In the Town B supply, the total THM concentration was low, but brominated species accounted for as much as 45 percent of the total. This study tends to show that certain groundwaters may contain THM precursors therefore it needs routine monitoring in order to safeguard the health of the people. The monitoring is more important for small towns who serve less than 10,000 people. THMFP potential was reduced in the plants where chemical precipitation was used.

REFERENCES

1. R. D. Kloeffer, et al., Characterization of Organic Components in Municipal Water Supply, *Environ. Sc. and Technology*, 6:1036, 1973.
2. P. R. Wood, et al., Treatment of Groundwater with Granular Activated Carbon, *J. AWWA*, 71:674, 1979.
3. W. H. Glaze, et al., A Preliminary Survey of Trihalomethane Levels in Selected East Texas Water Supplies, *J. AWWA*, 71:509, 1979.
4. J. J. Richard and G. A. Junk, Liquid Extraction for the Rapid Determination of Halomethanes in Water, *J. AWWA*, 69:1, p. 62, January 1977.
5. J. P. Mieure, A Rapid and Sensitive Method for Determining Volatile Organohalides in Water, *J. AWWA*, 69:62, 1977.
6. M. M. Varma, et al., Analysis of Trihalomethanes in Aqueous Solution: A Comparative Study, *J. AWWA*, 71:389, 1979.
7. Federal Register, National Interim Primary Drinking Water Regulations: Control of Trihalomethanes in Drinking Water, Final Pub., Federal Register No. 44FR68641, November 29, 1979.

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