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A Survey of Trihalomethanes in the Drinking Water System of Murfreesboro, Tennessee

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The reaction between chlorine and organic compounds producing organohalides has probably been occurring ever since chlorine was first used as a disinfectant. The volatile organohalides eluded detection until recently because they were lost during routine gas chromatographic procedures. The presence of organohalides in finished drinking waters was first detected by ROOK (1974), whose investigation at the Rotterdam water utility (using new analytical procedures) revealed significant levels of haloforms present after chlorination. BELLAR et al. (1974) reported a few months later that organohalides were present in some U. S. drinking waters. The passage of the Safe Drinking Water Act (PL93-523) by Congress induced a series of studies which included the National Organics Reconnaissance Survey for Halogenated Organics (NORS) (SYMONS et al. 1975). The NORS reported chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$) and bromoform ($CHBr_3$) as being ubiquitous (in varying amounts) in all 80 cities studied.

During 1978 MINEAR et al. of the University of Tennessee conducted a survey of trihalomethanes in Tennessee. The study by MINEAR, which included 29 cities, revealed that the total trihalomethane levels in Murfreesboro were consistently among the highest in the state. The purpose of the present study was to establish consistent and accurate trihalomethane levels to which Murfreesboro residents are being exposed and to evaluate seasonal changes and patterns of THM concentrations as related to distribution of water.

METHODS AND MATERIALS

Murfreesboro is a city of approximately 35,000 located in Rutherford County, Tennessee, 30 mi southeast of Nashville. Two separate water treatment plants serve Murfreesboro, each with distinct water sources. Six sample sites were chosen to represent an adequate cross-section of the city. Sample sites A and D represent the two water plants, and B, E, C and F represent two intermediate and two distant points (respectively) in the distribution system (Fig. 1).

The sampling program encompassed ten months beginning November 17, 1979 and ending August 15, 1980. Each week (except during November), two samples were taken from each site. One sample from each site was analyzed immediately and represented

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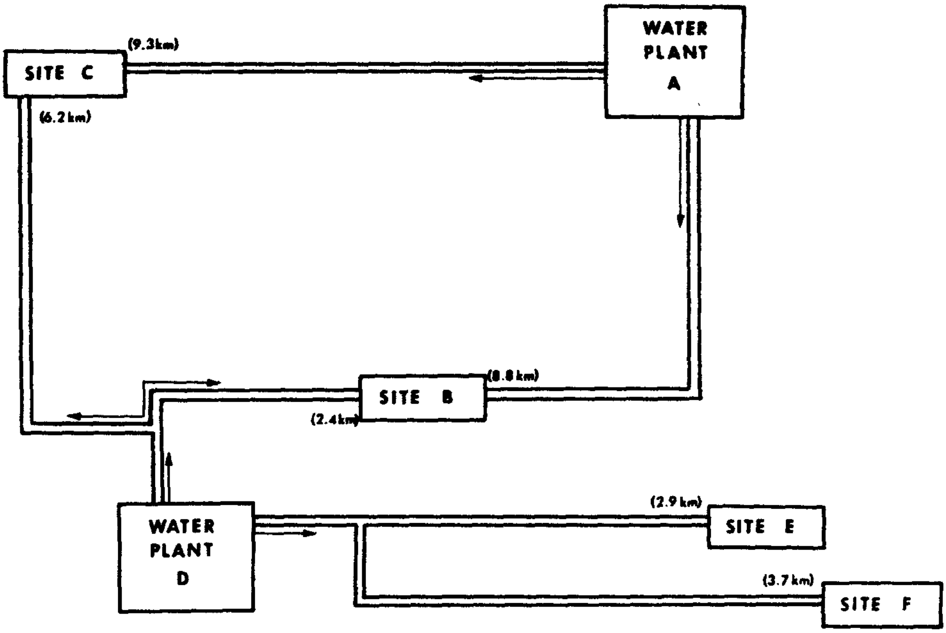

Fig. 1. Water collection sites within Murfreesboro, TN.

the trihalomethane levels at the time of discharge (at each water plant) and at the time of consumption (at the residential sites). Analysis of the remaining samples was conducted after seven days, and was indicative of the levels of potential trihalomethane formation. Samples were collected directly from the individual sites using 120-ml septum bottles. To prevent loss of trihalomethanes, bottles were crimped and sealed using a teflon coated rubber septum and an aluminum septum retainer.

Samples were prepared for analysis using the method of HENDERSON et al. (1976), which is a liquid-liquid extraction using pentane. A 5 ul aliquot of pentane was injected into a Varian 3700 gas chromatograph using the following conditions:

GC--Varian 3700
Packing material--0.2% carbowax 1500 on 80/100
Column--6 ft. x 1/8 in.
Program--3 min @ 60^0 + 8^0C/min to 160^0
Flow rate--30 ml/min N_2
Attenuation--64 or 128 (depending on sample concentration)
Detector--electron capture detector

Retention times for each of the trihalomethanes were determined by injecting each individual compound into the gas chromatograph and noting the resulting peak times. Standards for each of the trihalomethanes were run prior to each analysis. According to TRUSSELL et al. (1978), the sample/solvent ratio has a significant effect on the average extraction efficiency. The authors gave the ratio of 25 as being most efficient (approximately 80%). Spiked samples were run at various concentrations in order to determine the approximate extraction efficiency of this procedure. Peaks from the analysis were converted to concentrations by means of peak height (or area) vs. concentration of standards (corrected for volume). The data were adjusted for loss during analysis using the extraction efficiency results. A Varian CDS 111 was used in some cases to compute the area of standard and sample trihalomethane peaks. The final values were interpreted and analyzed statistically.

RESULTS

Chloroform concentrations of samples collected in the winter averaged the lowest of the three seasons monitored. Spring levels were slightly higher, and summer values were well above the maximum contamination levels of 100 ppb established by the Environmental Protection Agency (Table 1). Bromodichloromethane concentrations followed a similar pattern, while chlorodibromomethane showed only minute seasonal variation. The potential levels of chloroform were lowest during the spring, whereas winter and summer values were comparatively high. Bromodichloromethane and chlorodibromomethane potential levels varied only slightly throughout the sampling period, with summer values averaging the highest. Fold increases (potential levels/collection time levels) between collection time levels and potential levels were highest in the winter while summer values were the lowest. The trihalomethane levels for each individual site also varied seasonally. Water plant A and site C had the highest chloroform levels while water plant D released water with the lowest levels. Sites B and C received water from both water plants A and D, but sites E and F received water solely from plant D (Fig. 1). Interpretation of water distribution maps showed that, although water at site B was mixed, it was primarily from water plant D. Site C, on the other hand, received a larger proportion of its water from water plant A. The brominated species of trihalomethanes were highest at water plant D and those sites receiving water entirely (sites E and F) or primarily (site B) from that water plant. The chloroform levels at sites D, E and F reflect a possible distribution time effect as there is a progressive increase from water plant D to site E (2.9 km from D) and finally to site F (3.7 km from D). Sites B and C also reflect similar patterns, although their values were consistently higher due to the mixing of water from water plant A (which released water with notably higher chloroform levels than water plant D). The brominated trihalomethanes did not vary significantly.

A comparison of total trihalomethane values to potential levels according to site and season reveals that highest concentrations were primarily during the summer sample period (Figs. 2,3). The lowest

Table 1. Seasonal collection-time, potential trihalomethane levels and fold increases for individual water collection sites, Murfreesboro, TN. The winter sample period extended from December through mid-March. The spring period was from mid-March through mid-May, and the summer period extended from mid-May to mid-August. Levels given are in parts per billion ± standard error.

		Chloroform			Bromodichloromethane			Chlorodibromomethane		
Sample Site	Water Source[a]	Collection level	Potential level	Fold incr.	Collection level	Potential level	Fold incr.	Collection level	Potential level	Fold incr.
					WINTER					
A	A	86 ± 14	176 ± 26	2.0	5.0 ± 0.5	8.5 ± 0.9	1.7	1.7 ± 0.2	3.3 ± 0.6	1.9
B	A + D	87 ± 15	152 ± 19	1.7	7.0 ± 0.6	11.7 ± 1.3	1.7	4.1 ± 0.6	5.8 ± 0.9	1.4
C	A + D	97 ± 16	159 ± 16	1.6	5.2 ± 0.5	8.5 ± 0.8	1.6	2.1 ± 0.2	3.3 ± 0.5	1.6
D	D	48 ± 5	115 ± 9	2.4	6.6 ± 0.8	12.0 ± 1.5	1.8	4.8 ± 0.6	7.9 ± 1.1	1.6
E	D	60 ± 6	139 ± 11	2.3	7.6 ± 0.5	12.0 ± 1.4	1.6	5.2 ± 0.6	7.0 ± 1.1	1.3
F	D	62 ± 6	156 ± 22	2.5	7.8 ± 0.5	12.4 ± 1.3	1.6	5.3 ± 0.7	7.3 ± 1.2	1.4
					SPRING					
A	A	119 ± 48	161 ± 47	1.4	5.8 ± 0.3	8.3 ± 0.4	1.4	1.6 ± 0.1	1.8 ± 0.1	1.1
B	A + D	76 ± 14	125 ± 14	1.6	8.6 ± 0.7	12.0 ± 0.3	1.4	2.8 ± 0.2	3.5 ± 0.2	1.3
C	A + D	100 ± 26	137 ± 25	1.4	5.6 ± 0.3	8.1 ± 0.3	1.4	1.4 ± 0.2	2.0 ± 0.2	1.4
D	D	69 ± 9	106 ± 13	1.5	8.7 ± 0.8	12.4 ± 0.3	1.4	3.1 ± 0.2	4.2 ± 0.3	1.4
E	D	73 ± 12	118 ± 15	1.6	8.2 ± 0.6	11.1 ± 0.5	1.4	3.2 ± 0.3	3.6 ± 0.4	1.1
F	D	75 ± 13	128 ± 16	1.7	9.0 ± 0.5	12.3 ± 0.5	1.4	3.0 ± 0.3	3.8 ± 0.4	1.3
					SUMMER					
A	A	155 ± 17	209 ± 20	1.4	10.6 ± 0.5	12.0 ± 0.4	1.1	1.8 ± 0.1	2.4 ± 0.1	1.3
B	A + D	115 ± 13	153 ± 13	1.3	11.9 ± 0.4	12.9 ± 0.3	1.1	3.7 ± 0.2	4.8 ± 0.3	1.3
C	A + D	157 ± 18	203 ± 20	1.3	10.7 ± 0.7	12.0 ± 0.6	1.1	2.0 ± 0.2	2.6 ± 0.1	1.3
D	D	94 ± 10	133 ± 9	1.4	11.6 ± 0.4	13.2 ± 0.2	1.1	3.8 ± 0.3	5.6 ± 0.3	1.5
E	D	99 ± 11	148 ± 12	1.5	11.5 ± 0.5	12.5 ± 0.4	1.1	4.2 ± 0.4	5.5 ± 0.2	1.3
F	D	109 ± 12	157 ± 14	1.4	11.9 ± 0.4	13.4 ± 0.2	1.1	4.0 ± 0.3	5.1 ± 0.3	1.3
					TOTALS					
A	A	118 ± 16	182 ± 18	1.5	7.1 ± 0.5	9.6 ± 0.5	1.4	1.7 ± 0.1	2.6 ± 0.3	1.5
B	A + D	93 ± 8	144 ± 9	1.5	9.0 ± 0.5	12.2 ± 0.5	1.4	3.6 ± 0.3	4.9 ± 0.4	1.4
C	A + D	117 ± 12	166 ± 12	1.4	7.1 ± 0.6	9.5 ± 0.5	1.3	1.9 ± 0.1	2.7 ± 0.2	1.4
D	D	69 ± 6	118 ± 6	1.7	9.0 ± 0.5	12.5 ± 0.6	1.4	3.9 ± 0.3	6.1 ± 0.5	1.6
E	D	76 ± 7	136 ± 7	1.8	9.0 ± 0.5	12.0 ± 0.6	1.3	4.3 ± 0.3	5.6 ± 0.5	1.3
F	D	81 ± 7	148 ± 11	1.8	9.5 ± 0.4	12.6 ± 0.5	1.3	4.2 ± 0.3	5.6 ± 0.6	1.3

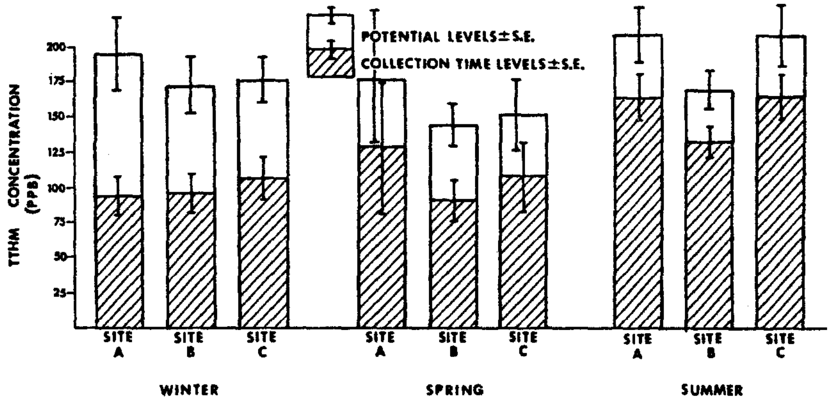

Fig. 2. Seasonal total trihalomethane levels and potential concentrations in water collected at sites A, B, and C, Murfreesboro, TN.

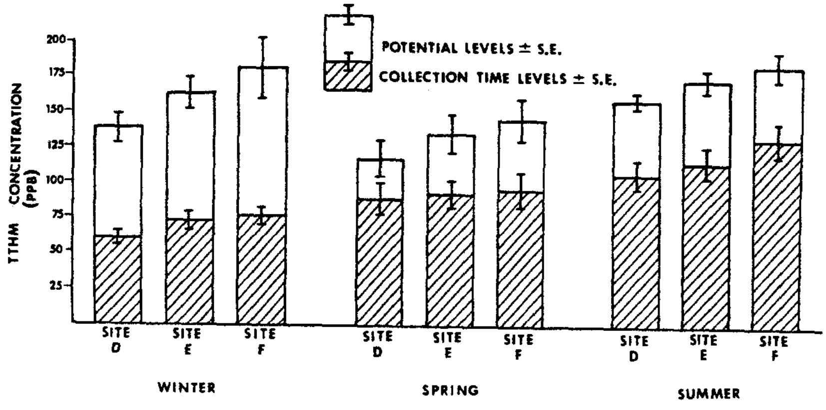

Fig. 3. Seasonal trihalomethane levels and potential concentrations in water collected at sites D, E, and F, Murfreesboro, TN.

levels for the sites were mostly during the winter. Distribution effects are more clearly seen as the total trihalomethane concentrations vary according to site and source. The final mean values for the entire sample period show three sites averaging above the maximum allowable contamination level of 100 ppb. The sites fed entirely by water plant D averaged slightly below the allowable limits (Fig. 4).

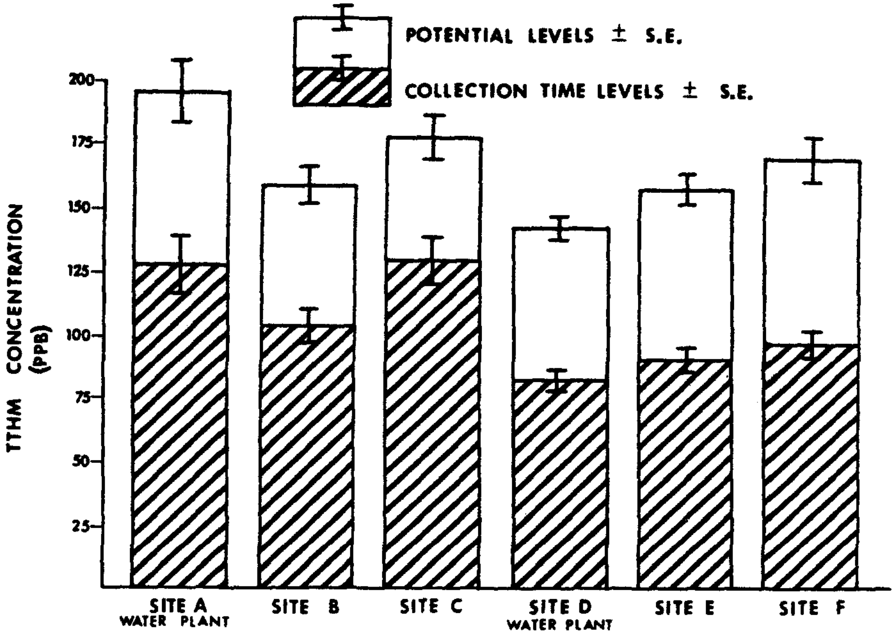

Fig. 4. Mean total trihalomethane levels for all water collection sites monitored from December 1979 through August 1980 (Murfreesboro, TN).

DISCUSSION

Total trihalomethanes in Murfreesboro were found to vary from site to site and from season to season. Seasonal changes can be explained by the fact that water temperatures fluctuate seasonally, and warmer temperatures (i.e., summer) cause the trihalomethane reaction rate to increase. Seasonal variation in potential levels was evident, but the lowest values were in the spring rather than winter. It was assumed that a lower spring potential was due to either the lack of degrading organics in the spring or the dilution of organics by spring rains (or both). Winter potentials were probably high due to massive degradation of organics. Summer potentials were most likely high due to the low amount of rainfall and subsequent concentration of organics in the waters. The decline in fold increase levels from winter to summer was expected because as water temperatures rose, the fold increase levels lowered when trihalomethane formation approached its potential at a faster rate.

The variation from site to site was attributed mainly to the source water plant and distance of each site from that water plant. The treatment at both water plants was identical, thus the water source was apparently responsible for the differences in values. Water plant A, which produced water with the highest levels of chloroform, obtained its raw water from the Stones River. Water plant D, on the other hand, treated groundwater. Raw water temperatures did not fluctuate radically with the groundwater source, and organic precursors were probably not as abundant. The brominated species of trihalomethanes were, however, higher at water plant D and the sites that received water from D. This was probably due to natural bromine, which is usually more prevalent in groundwaters than surface waters.

The "uncharacteristically high levels" of trihalomethanes which appeared in April were apparently due to a change in the point of application of chlorine by water officials. After several weeks, the point of chlorination was returned to its original position and the trihalomethane values responded accordingly.

The effect of distribution time was more evident with chloroform than with the brominated trihalomethanes. All of the sites showed increases in trihalomethanes as distance from the source water plant lengthened. Importantly, all of the residential sites monitored in this study received at least a portion of their water from water plant D, which was the lowest producer of trihalomethanes. However, part of Murfreesboro receives water entirely from water plant A, and the areas receiving this water would most likely produce the highest values. In addition, water plant A sells water to surrounding areas in Rutherford County which would be more drastically affected by distribution time (due to the greater distances) than any of the Murfreesboro residents.

Clearly, the problem centers around water plant A. Several solutions are possible, but economic conditions render some of them impractical at this time. Alternate disinfectants such as ozone or chlorine dioxide could be used. Ozone, although effective, does not produce a disinfectant residual and would have to be used in conjunction with chlorine. By-products from the reaction of ozone with organics are not known, so the end result could be worse than with chlorine. Chlorine dioxide does produce a residual, but again, the by-products of adverse reactions are not known (LOVE et al. 1976). The next option is controlling organic precursors. This can be done with advanced coagulation techniques (KAVANAUGH 1978) or with better organic filtration (as with granular activated carbon). The modified coagulation techniques are inexpensive and call for only slight increases in operating costs. However, these techniques may not have enough influence on trihalomethane levels to comply with the 100 ppb trihalomethane maximum concentration levels. Filtration with granular activated carbon (GAC) has been shown to be the most effective of all treatments. It eliminates most organic precursors, any trihalomethanes that are already present, and even most dangerous pesticides that might find their way into the water. However, cost of the GAC is high, and filters must be changed frequently in order to be fully functional (SYMONS 1976). The last alternative is to change the point of application of the disinfectant (STEVENS & SYMONS 1976). This seems to be the most practical option for water plant A, where the point of chlorine application could be changed from raw water to post-coagulation or filtration (when organic precursors are at their lowest concentrations).

The effects of temperature and distribution time found in this study support other studies which have tested similar trends. The most important fact is, however, that water produced by plant A is in violation of Environmental Protection Agency (EPA) standards, and changes must be made at that plant in order to comply with EPA regulations. Water Department officials were already aware of such violations as a result of the study conducted by MINEAR et al. (1978). However, the only steps taken were toward monitoring trihalomethanes. No action was taken to actually alleviate the problem.

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