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# Trihalomethanes in Chlorinated Cooling Waters of Nuclear Reactors*

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The recently proven carcinogenicity of certain trihalomethanes (THMs) has stimulated much concern about the production of these compounds during the chlorination of water (NATIONAL ACADEMY OF SCIENCE 1978). THM levels in public drinking water have received most of the attention; however, chlorination of water in large cooling systems represents another potential source of significant THM production. The electric power generating industry uses approximately 26,000 tons of chlorine annually to control biofouling (HAMILTON 1978). Factors influencing the formation of THMs in fresh water include: dosage of chlorine (ROOK 1976), chlorination contact time (STEVENS 1976), temperature (YOUNG & STEVENS 1979), and concentration of humic substances (OLIVER & LAWRENCE 1979).

The Savannah River Plant (SRP) near Aiken, SC has three operating nuclear reactors (designated C, K, and P) and uses approximately 100-300 kg/day of chlorine to combat reactor heat exchanger biofouling. SRP cooling water is high in organic carbon and, following chlorination (1 h/day), is occasionally heated to temperatures exceeding 70°C as it passes through the heat exchangers. Thus, conditions conducive to THM formation are present. This study was conducted to examine the production and persistence of THMs resulting from the chlorination and heating of SRP reactor cooling water.

## MATERIALS AND METHODS

Field Experiments. Effluent water samples were collected in April and November 1980 from each of the three SRP reactor areas before and during chlorination of cooling water. Samples were also collected from the Savannah River at locations upstream and downstream from the SRP site. Water temperature and total residual chlorine (TRC) were measured immediately after the collection of each sample. TRC was determined using both an amperometric titrimeter (Fisher Model 393) and a DPD chlorine test kit (Hach Model CN-66). The performance of the two methods at temperature

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ranges of 20-65°C was comparable when tested using known standards. Samples for THM and total organic carbon (TOC) analyses were collected in glass vials. Sodium thiosulfate (ca. 10 mg) was added to the vials used for THM samples prior to collection. All vials were filled to the top with sample, capped, and stored in the dark on ice prior to analysis. Two standard THM solutions (EPA Quality Control Samples) were used to fortify samples in the field at the 10-50 ppb level to determine THM losses via volatilization during handling and storage of samples. THM concentrations were determined using the liquid-liquid extraction technique (BRASS 1980). TOC was measured using a Beckman 915-B carbon analyzer.

**Laboratory Experiments.** Water was collected during the November sampling from the P-Area reactor outfall prior to chlorination for use in laboratory experiments. After collection, the water was stored in the dark at 4°C. Eight 75 mL aliquots of the water sample were placed in water baths set at 25, 45, and 65°C. After the samples had equilibrated, they were fortified with enough NaOCl to initially give a 5.0 mg/L $Cl_2$ solution. After contact periods of 5, 30, 90, and 300 min, duplicate samples were removed from each water bath. In the samples used for analysis of THMs, residual chlorine was quenched by adding sodium thiosulfate. Analyses of THM, TRC, and TOC were performed as described above.

An additional laboratory experiment using the same temperatures and contact times was performed to estimate how much free chlorine was likely to volatilize from the cooling water samples. Double distilled chlorine-demand-free water samples were fortified with NaOCl to give a 5.0 mg/L $Cl_2$ solution. Approximately 28% of the chlorine was lost via volatilization. Even though the volatilization of the chlorine was faster at the higher temperatures, the total loss after the 300 min time period was the same for all sample temperatures. This indicated that up to 28% of the added chlorine would be removed from the system via volatizing as free chlorine. The remaining chlorine could be consumed by chlorine demand or volatization of THMs after the chlorine reacted with organics in the water.

## RESULTS AND DISCUSSION

The concentrations of total THM in all water samples collected in and around the SRP site were less than 59 µg/L (Table 1). There was no appreciable increase in the concentrations of THM in the Savannah River downstream of the SRP site. The analyses of the EPA standard THM samples indicated that no significant losses of THM occurred in the samples during shipment and storage.

Although the THM levels in all cases were below EPA drinking water guidelines (100 µg/L), laboratory experiments were performed in an effort to explain the increased THM concentration downstream from P-Area reactor effluent and also to determine the process(es) which contributed to the eventual decrease of THM levels reflected by the low values reported for the Savannah River. The organic carbon content of the P-Area cooling water used in these experiments was 7.6 mg/L.

Table 1. Trihalomethane Levels in Water Samples Collected at the Savannah River Plant

| | April 20, 1980 | | November 16, 1980 | |
|---|---|---|---|---|
| | Temp °C | Total THM(μg/L)* | Temp °C | Total THM(μg/L)* |
| Savannah R. Upstream | 22 | 1 | 17 | <1 |
| Savannah R. Downstream | 17 | 2 | 16 | <1 |
| C-Area Reactor Effluent | | | | |
| No Chlorination | 17 | <1 | 12 | <1 |
| During Chlorination | 17 | 15 | 12 | 36 |
| K-Area Reactor Effluent | | | | |
| No Chlorination | 55 | 2 | 59 | <1 |
| During Chlorination | 55 | 12 | 59 | 12 |
| P-Area Reactor Effluent | | | | |
| No Chlorination | 64 | <1 | 59 | 1 |
| During Chlorination | 64 | 41 | 59 | 43 |
| .75 Miles Downstream | 63 | 58 | 59 | 52 |

* Results are the average of duplicate samples.

The relative distribution of the individual THM compounds during the formation and loss of total THM was fairly uniform for all temperatures and contact times (Table 2). Chloroform was the most abundant THM compound in every sample (86-92% of total THM), while dichlorobromomethane was always the second most abundant THM compound (7-13% of total THM). The total residual chlorine levels continuously decreased with time in all samples.

Laboratory chlorination of the 65° water produced higher THM concentrations in shorter contact times than did chlorination of 25° and 45° water (Figure 1). However, the dissipation of THM was also greater at the higher temperature (65°C). The lower temperature samples never yielded THM concentrations as high as the 65° samples, even at the longer contact time periods (300 min).

This study showed that THM levels resulting from the chlorination of reactor cooling water at the SRP are insignificant. Elevating the temperature of chlorinated water enhanced THM production; however, heating also caused more rapid dissipation of THM compounds.

Table 2. Formation of Trihalomethanes in Laboratory Fortification Experiments with Chlorine and Reactor Cooling Water*

| Sample | Temp °C | CT† | TRC†† mg/L | Trihalomethanes g/L | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $CHCl_3$ | $CHClBr_2$ | $CCl_2Br_2$ | $CHBr_3$ | Total |
| 1 | 25 | 5 | 3.2 | 22.5 | 2.2 | 0.5 | <0.1 | 25.2 |
| 2 | 25 | 30 | 3.0 | 31.2 | 4.1 | 0.6 | <0.1 | 35.2 |
| 3 | 25 | 90 | 2.8 | 37.2 | 5.1 | 0.9 | <0.1 | 43.9 |
| 4 | 25 | 300 | 2.3 | 42.5 | 5.6 | 0.8 | <0.1 | 48.2 |
| 5 | 45 | 5 | 3.0 | 35.8 | 5.1 | 0.8 | <0.1 | 41.9 |
| 6 | 45 | 30 | 2.0 | 45.3 | 6.5 | 1.1 | <0.1 | 52.7 |
| 7 | 45 | 90 | 2.0 | 46.4 | 6.4 | 0.9 | <0.1 | 53.9 |
| 8 | 45 | 300 | 1.5 | 32.5 | 2.5 | 0.4 | <0.1 | 35.7 |
| 9 | 65 | 5 | 2.8 | 54.2 | 8.0 | 1.3 | <0.1 | 63.4 |
| 10 | 65 | 30 | 1.7 | 71.9 | 10.0 | 1.5 | <0.1 | 83.5 |
| 11 | 65 | 90 | 1.1 | 61.3 | 6.1 | 0.8 | <0.1 | 68.2 |
| 12 | 65 | 300 | 0.3 | 4.8 | 0.5 | 0.1 | <0.1 | 5.4 |

* Mean of duplicate samples.
† Contact time, min.
†† Total residual chlorine.

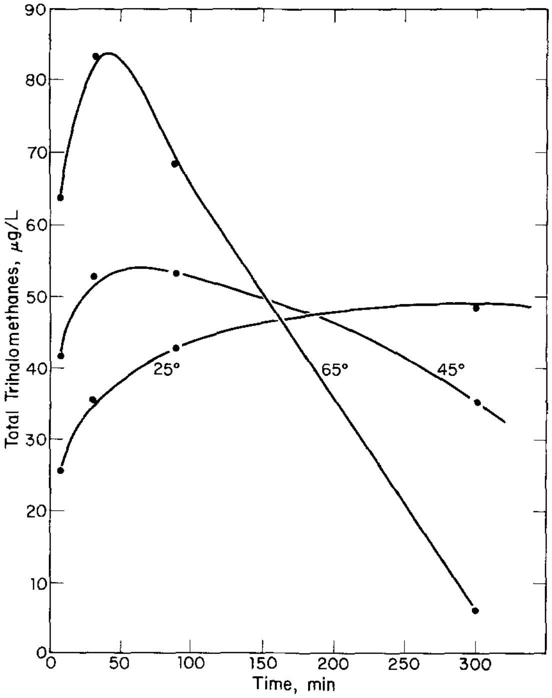

Figure 1. Formation and Loss of Trihalomethanes at Three Different Temperatures

# REFERENCES

BRASS, H. J.: American Lab. July 23 (1980).

HAMILTON, D. H.: Water Chlorination, Environmental Impact and Health Effects, P. 687, Vol 2, R. L. Jolley (ed), Ann Arbor Science, Ann Arbor, MI (1978).

NATIONAL ACADEMY OF SCIENCE: Epidemiological Studies of Cancer Frequency and Certain Organic Constituents of Drinking Water - A Review of Recent Literature Published and Unpublished. Washington, DC (1978).

OLIVER, B. G. and J. LAWRENCE: J AWWA 71, 3, 161 (1979).

ROOK, J. J.: J AWWA 68, 168 (1976).

STEVENS, A. A.: J AWWA 68, 615 (1976).

YOUNG, J. S. and P. C. SINGER: J AWWA 71, 2, 38 (1979).